Chlorine (Cl) IDEAL GAS $M_r = 35.453$ Chlorine (Cl) $Cl_1(g)$

$IP(Cl, g) = 104591.0 \pm 0.3\ cm^{-1}$
$S°(298.15\ K) = 165.189 \pm 0.004\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 119.621 \pm 0.006\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 121.302 \pm 0.008\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2P^o_{3/2}$	0.0	4
$^2P^o_{1/2}$	882.36	2

Enthalpy of Formation

The adopted value for the enthalpy of formation of Cl(g) is calculated from the dissociation energy of gaseous chlorine, D^o_0 (natural abundance) = 19999.10 ± 1.0 cm^{-1} (239.242 ± 0.012 $kJ{\cdot}mol^{-1}$). This value was calculated from the dissociation energy of $^{35}Cl_2(g)$, D^o_0 = 19997.28 ± 0.10 cm^{-1}, obtained from the extensive spectroscopic measurements of Douglas and Hoy.[1] CODATA[2] used a slightly different value (D^o_0 = 19997.25 ± 0.3 cm^{-1} for $^{35}Cl_2$), as obtained by LeRoy and Bernstein[3] from the measurements of Douglas *et al.*,[4] Brewer and Winn,[5] Huber and Herzberg,[6] and Gurvich *et al.*[7] have adopted one or the other of these two cited values. Wagman *et al.*[16] adopted a dissociation energy which is 63 cm^{-1} greater than our adopted value. Detailed discussions on the spectroscopic information are given by LeRoy,[8] Coxon[9] and Douglas and Hoy.[1]

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weight is taken from Moore.[10, 11] Only two levels are included in the calculation. All other levels (observed and predicted) lie above 71954 cm^{-1}. Our calculations indicate that any reasonable method of filling in the missing levels and cutting off the summation in the partition function[12] has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels. Therefore, we list only the ground state and the first excited state. Extension to higher temperatures may require consideration of the higher excited states and utilization of different fill and cutoff procedures.

The thermodynamic functions at 298.15 K are in agreement with recent CODATA recommendations[2] except for two minor differences. First, the entropy differs by 0.1094 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ because this table uses a standard-state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, entropy differences of the order of 0.001–0.004 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for the monatomic halogens arise due to the use of slightly different values for R; this tables uses R = 8.31441 $J{\cdot}K^{-1}{\cdot}mol^{-1}$. Considering these minor changes, this table agrees within the estimated uncertainty with those by Hultgren *et al.*,[13] Gurvich *et al.*,[7] and Wagman *et al.*[16] The estimated uncertainty is due to uncertainties in the relative atomic mass and fundamental constants which are based on the 1981 scale[14] and the 1973 values,[15] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	C^o_p	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.272	119.621	119.621	INFINITE
100	20.788	142.175	184.104	−4.193	120.244	115.476	−60.319
200	21.079	156.636	167.161	−2.105	120.813	110.482	−28.855
250	21.450	161.378	165.547	−1.042	121.066	107.869	−22.538
298.15	21.838	165.189	165.189	0.	121.302	105.306	−18.449
300	21.852	165.325	165.190	0.040	121.311	105.207	−18.318
350	22.202	168.720	165.457	1.142	121.553	102.504	−15.298
400	22.467	171.703	166.055	2.259	121.795	99.766	−13.028
450	22.644	174.361	166.833	3.387	122.035	96.998	−11.259
500	22.744	176.752	167.708	4.522	122.272	94.203	−9.841
600	22.781	180.905	169.571	6.800	122.734	88.546	−7.709
700	22.692	184.411	171.448	9.074	123.172	82.813	−6.180
800	22.549	187.432	173.261	11.337	123.585	77.019	−5.029
900	22.389	190.079	174.986	13.584	123.972	71.174	−4.131
1000	22.233	192.430	176.615	15.815	124.334	65.288	−3.410
1100	22.089	194.542	178.150	18.031	124.675	59.367	−2.819
1200	21.959	196.458	179.597	20.233	124.997	53.416	−2.325
1300	21.843	198.211	180.963	22.423	125.300	47.438	−1.906
1400	21.742	199.826	182.253	24.602	125.589	41.438	−1.546
1500	21.652	201.323	183.475	26.772	125.863	35.417	−1.233
1600	21.573	202.718	184.635	28.933	126.124	29.379	−0.959
1700	21.504	204.024	185.737	31.087	126.374	23.325	−0.717
1800	21.443	205.251	186.788	33.234	126.612	17.256	−0.501
1900	21.389	206.409	187.790	35.375	126.840	11.175	−0.307
2000	21.341	207.505	188.749	37.512	127.058	5.081	−0.133
2100	21.298	208.545	189.667	39.644	127.265	−1.023	0.025
2200	21.260	209.535	190.548	41.772	127.463	−7.136	0.169
2300	21.226	210.479	191.394	43.896	127.650	−13.259	0.301
2400	21.195	211.382	192.208	46.017	127.827	−19.389	0.422
2500	21.167	212.246	192.992	48.135	127.992	−25.526	0.533
2600	21.142	213.076	193.749	50.250	128.147	−31.670	0.636
2700	21.119	213.874	194.480	52.364	128.290	−37.820	0.732
2800	21.099	214.641	195.186	54.474	128.421	−43.974	0.820
2900	21.080	215.381	195.870	56.583	128.541	−50.133	0.903
3000	21.063	216.096	196.532	58.690	128.649	−56.297	0.980
3100	21.047	216.786	197.174	60.796	128.746	−62.463	1.052
3200	21.032	217.454	197.798	62.900	128.832	−68.633	1.120
3300	21.019	218.101	198.403	65.002	128.908	−74.804	1.184
3400	21.007	218.728	198.992	67.104	128.974	−80.979	1.244
3500	20.995	219.337	199.564	69.204	129.031	−87.155	1.301
3600	20.985	219.928	200.122	71.303	129.081	−93.332	1.354
3700	20.975	220.503	200.665	73.401	129.124	−99.511	1.405
3800	20.966	221.062	201.195	75.498	129.161	−105.691	1.453
3900	20.958	221.607	201.711	77.594	129.195	−111.871	1.498
4000	20.950	222.137	202.215	79.690	129.226	−118.053	1.542
4100	20.943	222.655	202.707	81.784	129.255	−124.235	1.583
4200	20.936	223.159	203.188	83.878	129.284	−130.418	1.622
4300	20.929	223.652	203.658	85.971	129.314	−136.602	1.659
4400	20.923	224.133	204.118	88.064	129.347	−142.786	1.695
4500	20.918	224.603	204.568	90.156	129.384	−148.972	1.729
4600	20.912	225.063	205.009	92.247	129.426	−155.158	1.762
4700	20.907	225.512	205.440	94.338	129.474	−161.345	1.793
4800	20.903	225.952	205.863	96.429	129.530	−167.533	1.823
4900	20.898	226.383	206.278	98.519	129.594	−173.723	1.852
5000	20.894	226.806	206.684	100.609	129.667	−179.914	1.880
5100	20.890	227.219	207.082	102.698	129.750	−186.106	1.906
5200	20.886	227.625	207.474	104.787	129.844	−192.300	1.932
5300	20.883	228.023	207.858	106.875	129.950	−198.496	1.956
5400	20.879	228.413	208.235	108.963	130.068	−204.694	1.980
5500	20.876	228.796	208.605	111.051	130.199	−210.895	2.003
5600	20.873	229.172	208.969	113.138	130.343	−217.098	2.025
5700	20.870	229.542	209.327	115.226	130.501	−223.304	2.046
5800	20.867	229.905	209.678	117.312	130.673	−229.512	2.067
5900	20.865	230.261	210.024	119.399	130.859	−235.724	2.087
6000	20.862	230.612	210.364	121.485	131.059	−241.939	2.106

PREVIOUS: June 1972 (1 atm) CURRENT: June 1982 (1 bar)

Chlorine (Cl) $Cl_1(g)$

Chlorine, Ion (Cl$^+$) **IDEAL GAS** $M_r = 35.45245$ **Chlorine, Ion (Cl$^+$)** **Cl$_1^+$(g)**

IP(Cl$^+$, g) = 192070 ± 10 cm^{-1}
$S°$(298.15 K) = 167.556 ± 0.005 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 1370.807 ± 0.01 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [1378.801] kJ·mol^{-1}

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^3P_2$	0.0	5
$^3P_1$	696.1	3
$^3P_0$	996.4	1
$^1D_2$	11653.5	5
$^1S_0$	27877.8	1

Enthalpy of Formation

$\Delta_f H°$(Cl$^+$, g, 0 K) is calculated from $\Delta_f H°$(Cl, g, 0 K)[1] using the spectroscopic value of IP(Cl) = 104591.0 ± 0.3 cm^{-1}(1251.187 ± 0.004 kJ·mol^{-1}) from Moore.[2] The ionization limit is converted from cm^{-1} to kJ·mol^{-1} using the factor, 1 cm^{-1} = 0.01196266 kJ·mol^{-1}, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization potential and appearance potential data.

$\Delta_f H°$(Cl$^+$, g, 298.15 K) is calculated from $\Delta_f H°$(Cl, g, 0 K) by using IP(Cl) with JANAF[1] enthalpies, $H°$(0 K)–$H°$(298.15 K), for Cl(g), Cl$^+$(g), and e$^-$(ref). $\Delta_f H°$(Cl $\rightarrow$ Cl$^+$ + e$^-$, 298.15 K) differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the lowest four excited states, the next lowest level is approximately 93366 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and four excited states, with the energy of these states taken from recent study by Moore.[2] The reported uncertainty is $S°$(298.15 K) is due to uncertainties in the relative ionic mass, the fundamental constants, and the position of the four lowest excited states. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.386	1370.807		
100	20.809	144.033	187.107	−4.307			
200	21.681	158.648	169.618	−2.194			
250	22.383	163.562	167.931	−1.092			
298.15	22.958	167.556	167.556	0.	1378.801	1355.845	−237.538
300	22.977	167.698	167.556	0.042	1378.850	1355.702	−236.049
350	23.388	171.273	167.838	1.202	1380.190	1351.738	−201.736
400	23.621	174.413	168.467	2.378	1381.530	1347.582	−175.976
450	23.713	177.202	169.286	3.562	1382.865	1343.258	−155.921
500	23.706	179.700	170.205	4.748	1384.192	1338.787	−139.862
600	23.519	184.008	172.158	7.111	1386.817	1329.458	−115.740
700	23.239	187.613	174.115	9.449	1389.398	1319.694	−98.477
800	22.949	190.697	176.000	11.758	1391.936	1309.562	−85.506
900	22.681	193.385	177.785	14.039	1394.436	1299.115	−75.399
1000	22.446	195.762	179.467	16.295	1396.902	1288.391	−67.299
1100	22.244	197.891	181.046	18.530	1399.340	1277.422	−60.660
1200	22.073	199.819	182.532	20.745	1401.753	1266.232	−55.118
1300	21.928	201.580	183.930	22.945	1404.146	1254.841	−50.420
1400	21.806	203.201	185.250	25.132	1406.520	1243.267	−46.387
1500	21.704	204.702	186.497	27.307	1408.878	1231.523	−42.885
1600	21.620	206.100	187.679	29.473	1411.223	1219.623	−39.817
1700	21.552	207.408	188.801	31.631	1413.556	1207.577	−37.104
1800	21.498	208.639	189.870	33.784	1415.878	1195.393	−34.689
1900	21.458	209.800	190.888	35.932	1418.191	1183.081	−32.525
2000	21.430	210.900	191.862	38.076	1420.495	1170.647	−30.574
2100	21.414	211.945	192.793	40.218	1422.792	1158.098	−28.806
2200	21.409	212.941	193.687	42.359	1425.081	1145.440	−27.196
2300	21.413	213.893	194.545	44.500	1427.363	1132.678	−25.724
2400	21.426	214.804	195.370	46.642	1429.639	1119.817	−24.372
2500	21.447	215.679	196.165	48.786	1431.909	1106.861	−23.127
2600	21.475	216.521	196.932	50.932	1434.173	1093.814	−21.975
2700	21.510	217.332	197.672	53.081	1436.431	1080.681	−20.907
2800	21.551	218.115	198.389	55.234	1438.683	1067.464	−19.914
2900	21.596	218.872	199.082	57.391	1440.930	1054.166	−18.988
3000	21.645	219.605	199.754	59.553	1443.171	1040.791	−18.122
3100	21.698	220.316	200.406	61.720	1445.409	1027.342	−17.311
3200	21.753	221.005	201.039	63.893	1447.642	1013.820	−16.549
3300	21.811	221.676	201.654	66.071	1449.872	1000.229	−15.832
3400	21.869	222.327	202.252	68.255	1452.099	986.569	−15.157
3500	21.929	222.962	202.835	70.445	1454.325	972.845	−14.519
3600	21.989	223.581	203.403	72.641	1456.550	959.057	−13.916
3700	22.049	224.184	203.956	74.843	1458.775	945.207	−13.344
3800	22.109	224.773	204.497	77.051	1461.002	931.297	−12.802
3900	22.168	225.348	205.024	79.265	1463.232	917.328	−12.286
4000	22.227	225.910	205.539	81.484	1465.466	903.303	−11.796
4100	22.284	226.460	206.043	83.710	1467.705	889.221	−11.329
4200	22.339	226.997	206.535	85.941	1469.950	875.084	−10.883
4300	22.393	227.524	207.017	88.178	1472.202	860.894	−10.458
4400	22.445	228.039	207.489	90.420	1474.463	846.652	−10.051
4500	22.496	228.544	207.951	92.667	1476.733	832.358	−9.662
4600	22.544	229.039	208.404	94.919	1479.014	818.013	−9.289
4700	22.591	229.524	208.849	97.175	1481.307	803.619	−8.931
4800	22.635	230.000	209.284	99.437	1483.612	789.175	−8.588
4900	22.677	230.467	209.712	101.702	1485.930	774.684	−8.258
5000	22.717	230.926	210.132	103.972	1488.262	760.145	−7.941
5100	22.755	231.376	210.544	106.246	1490.608	745.560	−7.636
5200	22.791	231.818	210.949	108.523	1492.970	730.928	−7.342
5300	22.825	232.253	211.347	110.804	1495.346	716.250	−7.059
5400	22.857	232.680	211.738	113.088	1497.739	701.528	−6.786
5500	22.887	233.100	212.122	115.375	1500.148	686.761	−6.522
5600	22.915	233.512	212.501	117.665	1502.573	671.951	−6.268
5700	22.941	233.918	212.873	119.958	1505.015	657.096	−6.022
5800	22.965	234.317	213.239	122.254	1507.474	642.199	−5.784
5900	22.987	234.710	213.600	124.551	1509.950	627.260	−5.553
6000	23.008	235.097	213.955	126.851	1512.442	612.277	−5.330

PREVIOUS: June 1965 (1 atm)   CURRENT: June 1982 (1 bar)

Chlorine, Ion (Cl$^+$) **Cl$_1^+$(g)**

Chlorine, Ion (Cl^-) IDEAL GAS $M_r = 35.45355$ Chlorine, Ion (Cl^-) $Cl_1^-(g)$

EA(Cl, g) = 3.617 ± 0.003 eV
$S°(298.15\ K) = 153.356 \pm 0.005\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -229.36 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-233.954]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

$\Delta_f H°(Cl^-, g, 0\ K)$ is calculated from $\Delta_f H°(Cl, g, 0\ K)$[1] using the adopted electron affinity of EA(Cl) = 3.617 ± 0.003 eV (348.985 ± 0.289 $kJ \cdot mol^{-1}$). This value, recommended by Hotop and Lineberger,[10] is based on laser optogalvanic spectroscopic and plasma emission studies.[5,6] Additional information on $Cl^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2,10] Rosenstock *et al.*[3] and Massey.[4]

$\Delta_f H°(Cl^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Cl, g, 0\ K)$ by using EA(Cl) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for $Cl^-(g)$, Cl(g), and e^-(ref). $\Delta_r H(Cl^- \rightarrow Cl + e^-, 298.15\ K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3] $\Delta_f H°(298.15\ K)$ should be changed by + 6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for $Cl^-(g)$ is given by Hotop and Lineberger,[2,10] Rosenstock *et al.*[3] and Massey.[4] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

The entropy at all temperatures (0–6000 K) agrees within 0.001 $J \cdot K^{-1} \cdot mol^{-1}$ with the values of Gurvich *et al.*[8] except for one minor difference. The entropy differs by 0.1094 $J \cdot K^{-1} \cdot mol^{-1}$ because this table uses a standard–state pressure of 1 bar, whereas the tabulation of Gurvich *et al.*[8] is based on 1 atm. The estimated uncertainty is due to uncertainties in the relative ionic mass and the fundamental constants which are based on the 1981 scale[9] and the 1973 values,[7] respectively.

References

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−6.197	−229.364		
100	20.786	130.649	171.836	−4.119			
200	20.786	145.057	155.257	−2.040			
250	20.786	149.695	153.698	−1.001			
298.15	20.786	153.356	153.356	0.	−233.954	−240.167	42.076
300	20.786	153.485	153.356	0.038	−233.986	−240.205	41.823
350	20.786	156.689	153.610	1.078	−234.845	−241.174	35.993
400	20.786	159.464	154.172	2.117	−235.721	−242.019	31.604
450	20.786	161.913	154.899	3.156	−236.609	−242.753	28.178
500	20.786	164.103	155.711	4.196	−237.506	−243.388	25.427
600	20.786	167.892	157.435	6.274	−239.322	−244.394	21.276
700	20.786	171.097	159.164	8.353	−241.158	−245.094	18.289
800	20.786	173.872	160.833	10.431	−243.008	−245.530	16.031
900	20.786	176.320	162.420	12.510	−244.868	−245.734	14.262
1000	20.786	178.510	163.922	14.589	−246.736	−245.730	12.836
1100	20.786	180.492	165.340	16.667	−248.612	−245.539	11.660
1200	20.786	182.300	166.679	18.746	−250.492	−245.177	10.672
1300	20.786	183.964	167.945	20.824	−252.379	−244.657	9.830
1400	20.786	185.504	169.145	22.903	−254.270	−243.992	9.103
1500	20.786	186.938	170.284	24.982	−256.165	−243.192	8.469
1600	20.786	188.280	171.367	27.060	−258.065	−242.265	7.909
1700	20.786	189.540	172.400	29.139	−259.969	−241.220	7.412
1800	20.786	190.728	173.385	31.217	−261.878	−240.062	6.966
1900	20.786	191.852	174.328	33.296	−263.792	−238.797	6.565
2000	20.786	192.918	175.231	35.375	−265.710	−237.432	6.201
2100	20.786	193.932	176.097	37.453	−267.635	−235.971	5.869
2200	20.786	194.899	176.930	39.532	−269.565	−234.418	5.566
2300	20.786	195.823	177.732	41.610	−271.502	−232.777	5.287
2400	20.786	196.708	178.504	43.689	−273.446	−231.052	5.029
2500	20.786	197.557	179.249	45.768	−275.399	−229.245	4.790
2600	20.786	198.372	179.969	47.846	−277.360	−227.360	4.568
2700	20.786	199.156	180.666	49.925	−279.330	−225.400	4.361
2800	20.786	199.912	181.339	52.004	−281.309	−223.366	4.167
2900	20.786	200.642	181.993	54.082	−283.298	−221.262	3.985
3000	20.786	201.346	182.626	56.161	−285.297	−219.089	3.815
3100	20.786	202.028	183.241	58.239	−287.306	−216.849	3.654
3200	20.786	202.688	183.838	60.318	−289.324	−214.544	3.502
3300	20.786	203.327	184.419	62.397	−291.351	−212.176	3.358
3400	20.786	203.948	184.985	64.475	−293.386	−209.746	3.222
3500	20.786	204.550	185.535	66.554	−295.429	−207.256	3.093
3600	20.786	205.136	186.071	68.632	−297.478	−204.708	2.970
3700	20.786	205.706	186.594	70.711	−299.533	−202.103	2.853
3800	20.786	206.260	187.105	72.790	−301.593	−199.442	2.742
3900	20.786	206.800	187.603	74.868	−303.655	−196.727	2.635
4000	20.786	207.326	188.089	76.947	−305.720	−193.959	2.533
4100	20.786	207.839	188.565	79.025	−307.785	−191.139	2.435
4200	20.786	208.340	189.030	81.104	−309.850	−188.269	2.341
4300	20.786	208.829	189.485	83.183	−311.913	−185.350	2.252
4400	20.786	209.307	189.930	85.261	−313.973	−182.383	2.165
4500	20.786	209.774	190.365	87.340	−316.028	−179.369	2.082
4600	20.786	210.231	190.792	89.418	−318.077	−176.309	2.002
4700	20.786	210.678	191.211	91.497	−320.120	−173.206	1.925
4800	20.786	211.116	191.621	93.576	−322.155	−170.058	1.851
4900	20.786	211.544	192.023	95.654	−324.181	−166.868	1.779
5000	20.786	211.964	192.418	97.733	−326.198	−163.638	1.710
5100	20.786	212.376	192.805	99.811	−328.204	−160.366	1.642
5200	20.786	212.780	193.185	101.890	−330.198	−157.056	1.578
5300	20.786	213.175	193.559	103.969	−332.181	−153.707	1.515
5400	20.786	213.564	193.926	106.047	−334.151	−150.322	1.454
5500	20.786	213.945	194.286	108.126	−336.108	−146.899	1.395
5600	20.786	214.320	194.641	110.204	−338.051	−143.441	1.338
5700	20.786	214.688	194.989	112.283	−339.981	−139.949	1.282
5800	20.786	215.049	195.332	114.362	−341.896	−136.423	1.229
5900	20.786	215.405	195.669	116.440	−343.796	−132.864	1.176
6000	20.786	215.754	196.001	118.519	−345.682	−129.273	1.125

PREVIOUS. June 1965 (1 atm) CURRENT: June 1982 (1 bar)

Cobalt Chloride (CoCl) IDEAL GAS $M_r = 94.3862$

$S°(298.15\ \mathrm{K}) = 245.68 \pm 6.3\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$

$\Delta_f H°(0\ \mathrm{K}) = 192.8 \pm 12.6\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta_f H°(298.15\ \mathrm{K}) = 192.9 \pm 12.6\ \mathrm{kJ \cdot mol^{-1}}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
$^3\Sigma$	0	[3]	19868.1	[3]	21335.1	[3]	22182.5	[3]
	[11000]	[3]	19945.8	[3]	21640.4	[3]	22402.7	[3]
	17484.1	[3]	20969.1	[3]	22014.8	[3]	22966.2	[3]
	19826.3	[3]	21263.9	[3]	22072.3	[3]	[25000]	[3]

$\omega_e = 421.2\ \mathrm{cm^{-1}}$ $\omega_e x_e = 0.74\ \mathrm{cm^{-1}}$ $B_e = [0.17434]\ \mathrm{cm^{-1}}$ $\alpha_e = [0.000459]\ \mathrm{cm^{-1}}$ $r_e = [2.09]$ Å $\sigma = 1$

Enthalpy of Formation

Kulkarni and Dadape[1] have studied the reaction of $CoCl_2(g)$ with Co(cr) by a transpiration method. They used highly purified argon as the carrier gas and condensed the gaseous products on a mullite cold finger. Chemical and x–ray analyses of the condensate showed the presence of metallic cobalt. The transport of the Co metal was ascribed to the disproportionation of CoCl(g) according to the reaction $2\ CoCl(g) = Co(cr) + CoCl_2(g)$. Partial pressures for CoCl(g) and $CoCl_2(g)$ were reported for the temperature range 1395–1673 K. No consideration was given to possible dimerization of the dichloride. JANAF data[2] for $CoCl_2(g)$ and $Co_2Cl_4(g)$ are used to correct their $CoCl_2$ pressures for dimerization. The corrected pressures are 0.5% less than those of Kulkarni and Dadape[1] at 1395 K, and only 0.1% less at 1673 K. Hildenbrand[3] has also studied the disproportionation reaction of CoCl(g) by mass spectrometry. The monochloride was produced in the effusion cell[4] by vaporizing AgCl in the presence of metallic cobalt. The Ag^+ and $AgCl^+$ signals were also measured and used to derive equilibrium data for the process $Ag(g + CoCl(g) = AgCl(g) + Co(g)$.

Source	Reaction	Point	T/K	$\Delta_r H°(298.15\ \mathrm{K})$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ \mathrm{K})$ kcal·mol^{-1}	$\Delta_{at} H°(298.15\ \mathrm{K})$ kcal·mol^{-1}
Kulkarni and Dadape[1]	A	9	1395–1673	83.3	79.65 ± 1.8	−2.4 ± 3.5	28.6 ± 2.0	101.9
Hildenbrand[3]	B	7	1461–1605	20.0	14.19 ± 0.53	−3.8 ± 1.5	46.6 ± 1.5	83.9
Hildenbrand[3]	C	7	1461–1605	6.21	9.87 ± 0.35	2.4 ± 1.1	45.6 ± 1.5[a]	84.9

Reactions: (A) $CoCl_2(g) + Co(cr) = 2\ CoCl(g)$ (B) $CoCl_2(g) + Co(g) = 2\ CoCl(g)$ (C) $Ag(g) + CoCl(g) = AgCl(g) + Co(g)$

[a] $\Delta_f H°(298.15\ \mathrm{K})$(3rd law) combined with $D_0°(\mathrm{AgCl, g, 298.15\ K}) = 75.0 \pm 0.5\ \mathrm{kcal \cdot mol^{-1}}$.[4]

The two sets of measurements of Hildenbrand[3] lead to consistent values for $\Delta_f H°$, while the results of Kulkarni and Dadape[1] suggest a value roughly 20 kcal·mol^{-1} lower. In the same paper, Kulkarni and Dadape[1] reported vapor pressures for $CoCl_2(l)$ which were also determined by their flow technique. These vapor pressures have been shown to be incompatible with JANAF data (see $CoCl_2(g)$ table). Furthermore, their value for the bond dissociation energy ($D_0°(298.15\ \mathrm{K}) = 101.9\ \mathrm{kcal \cdot mol^{-1}}$) of CoCl appears to be too high by comparison with similar data for other transition metal monochlorides. Values[5] of $D_0°$ for the monochlorides of Cr, Mn, Ni, and Cu show a random variation of from 83.0 to 88.6 kcal·mol^{-1}, suggesting a value for CoCl near 85 kcal·mol^{-1}. The results of Hildenbrand[3] are in agreement with these predictions. It is further noted that Hildenbrand[4] has used a similar technique to study the monochlorides of Ca, Sr, and Ba. The results of these studies are quite consistent with JANAF heat of formation data.[2] Thus, it appears that the method used by Hildenbrand[3, 4] is reliable, and we adopt an average value, $\Delta_f H°(298.15\ \mathrm{K}) = 46.1\ \mathrm{kcal \cdot mol^{-1}}$), of his two results. The uncertainty is estimated to be ±3.0 kcal·mol^{-1}. The adopted values for the ground state vibrational constants are judged to be of insufficient accuracy to warrant a Birge–Sponer calculation for $D_0°$(Co–Cl).

Heat Capacity and Entropy

The bond length is estimated as somewhat less than that for $CoCl_2$.[2] B_e is calculated from the value for r_e. The value for α_e is obtained from the other constants assuming a Morse potential function.

Several band systems have been observed in the electronic spectrum[6–9] of CoCl. Vibrational constants for the upper and lower states of the various systems have been summarized by Rosen.[5] However, since it is not certain which of the observed electronic transitions involve the ground state, no assignments were made. Also, confusion exists as to whether some of the systems belong to triplet–triplet transitions,[7–9] an electronic triplet,[8] or whether they are all separate systems.[9] We adopt the vibrational constants for the ground state suggested by Herzberg.[10] Comparison of these values with those listed by Rosen[5] for the lower states of other systems for CoCl indicate that the adopted ω_e value may be uncertain by as much as ±5 cm^{-1}. Krishnamurty[8] has shown that the ground state electronic configuration for CoCl is either $^5\Sigma$ or $^3\Sigma$. We prefer a triplet ground state, since the electronic configuration for Co^{+1} is ^3F.[11] Other transition metal monochlorides[5] and the corresponding unipositive metal ions[11] have the same ground state multiplicities. If the ground state is a quintet, then the value of $S°(298.15\ \mathrm{K})$ is increased by 1 cal·K^{-1}·mol^{-1}. The adopted electronic levels in the range 17,000–23,000 cm^{-1} are taken from the compilation of Rosen.[5] Each level is assumed to be a separate system and is assigned a quantum weight of 3. Two triplet levels are also included at 11,000 and 25,000 cm^{-1}, since Rao and Rao[9] are believed to have observed two components of a triplet–triplet transition near 14,000 cm^{-1}. By analogy with similar data for other transition metal monochlorides,[5] the lower triplet level is not expected to lie below 10,000 cm^{-1}. The adopted upper levels and assumed quantum weights contribute 0.31 cal·K^{-1}·mol^{-1} to the entropy of CoCl at 4000 K.

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Cobalt Chloride (CoCl) $Cl_1Co_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.447	192.797	192.797	INFINITE
100	29.838	210.257	275.505	−6.525	193.742	182.934	−95.555
200	33.228	232.008	248.842	−3.367	193.471	172.183	−44.970
250	34.377	239.554	246.253	−1.675	193.198	166.892	−34.870
298.15	35.139	245.679	245.679	0.	192.882	161.853	−28.356
300	35.163	245.896	245.679	0.065	192.870	161.661	−28.148
350	35.708	251.360	246.110	1.838	192.520	156.487	−23.354
400	36.097	256.155	247.072	3.633	192.135	151.365	−19.766
450	36.383	260.424	248.323	5.446	191.711	146.293	−16.981
500	36.599	264.269	249.728	7.270	191.249	141.271	−14.759
600	36.899	270.970	252.726	10.946	190.215	131.371	−11.437
700	37.097	276.674	255.750	14.647	189.043	121.654	−9.078
800	37.237	281.637	258.682	18.364	187.310	112.177	−7.324
900	37.342	286.030	261.482	22.093	185.835	102.872	−5.971
1000	37.426	289.969	264.137	25.832	184.133	93.743	−4.897
1100	37.495	293.539	266.650	29.578	182.168	84.796	−4.027
1200	37.556	296.804	269.029	33.330	179.904	76.042	−3.310
1300	37.611	299.812	271.283	37.089	177.193	67.493	−2.712
1400	37.664	302.602	273.421	40.853	173.908	59.175	−2.208
1500	37.718	305.202	275.454	44.622	171.635	51.061	−1.778
1600	37.775	307.638	277.390	48.396	169.616	43.090	−1.407
1700	37.837	309.930	279.238	52.177	167.697	35.241	−1.083
1800	37.906	312.094	281.003	55.964	149.513	27.798	−0.807
1900	37.984	314.146	282.694	59.758	147.344	21.095	−0.580
2000	38.073	316.097	284.316	63.561	145.178	14.507	−0.379
2100	38.175	317.957	285.874	67.373	143.016	8.026	−0.200
2200	38.289	319.735	287.373	71.196	140.858	1.649	−0.039
2300	38.419	321.440	288.817	75.032	138.706	−4.631	0.105
2400	38.566	323.078	290.211	78.881	136.561	−10.817	0.235
2500	38.730	324.656	291.557	82.745	134.423	−16.914	0.353
2600	38.914	326.178	292.860	86.627	132.294	−22.925	0.461
2700	39.119	327.651	294.121	90.529	130.175	−28.855	0.558
2800	39.346	329.077	295.344	94.452	128.069	−34.706	0.647
2900	39.596	330.462	296.532	98.399	125.977	−40.483	0.729
3000	39.872	331.809	297.685	102.372	123.901	−46.187	0.804
3100	40.174	333.121	298.807	106.374	121.844	−51.823	0.873
3200	40.503	334.402	299.900	110.408	−255.004	−55.620	0.908
3300	40.859	335.654	300.964	114.476	−255.587	−49.380	0.782
3400	41.244	336.879	302.003	118.580	−256.142	−43.123	0.662
3500	41.656	338.081	303.016	122.725	−256.669	−36.850	0.550
3600	42.097	339.260	304.007	126.913	−257.164	−30.562	0.443
3700	42.565	340.420	304.975	131.146	−257.625	−24.261	0.343
3800	43.060	341.562	305.923	135.427	−258.048	−17.948	0.247
3900	43.580	342.687	306.851	139.758	−258.433	−11.625	0.156
4000	44.124	343.797	307.761	144.143	−258.775	−5.292	0.069
4100	44.690	344.893	308.653	148.584	−259.073	1.049	−0.013
4200	45.275	345.977	309.529	153.082	−259.326	7.397	−0.092
4300	45.878	347.050	310.389	157.639	−259.530	13.750	−0.167
4400	46.496	348.111	311.235	162.258	−259.684	20.107	−0.239
4500	47.127	349.163	312.066	166.939	−259.787	26.467	−0.307
4600	47.766	350.206	312.884	171.684	−259.838	32.829	−0.373
4700	48.412	351.240	313.689	176.493	−259.835	39.191	−0.436
4800	49.061	352.266	314.482	181.366	−259.780	45.553	−0.496
4900	49.711	353.285	315.263	186.305	−259.671	51.913	−0.553
5000	50.357	354.295	316.034	191.308	−259.509	58.270	−0.609
5100	50.998	355.299	316.794	196.376	−259.294	64.624	−0.662
5200	51.630	356.295	317.544	201.508	−259.028	70.973	−0.713
5300	52.250	357.285	318.284	206.702	−258.712	77.316	−0.762
5400	52.856	358.267	319.016	211.957	−258.347	83.653	−0.809
5500	53.446	359.242	319.738	217.272	−257.937	89.982	−0.855
5600	54.017	360.211	320.452	222.646	−257.482	96.304	−0.898
5700	54.566	361.172	321.158	228.075	−256.987	102.617	−0.940
5800	55.093	362.125	321.856	233.558	−256.453	108.922	−0.981
5900	55.595	363.071	322.547	239.093	−255.839	115.213	−1.020
6000	56.071	364.010	323.230	244.676	−255.226	121.497	−1.058

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

Cesium Chloride (CsCl) CRYSTAL(α–β) $M_r = 168.3584$ Cesium Chloride (CsCl) $Cl_1Cs_1(cr)$

S°(298.15 K) = 101.182 ± 0.021 J·K^{-1}·mol^{-1}
$T_{trs}(\alpha \rightarrow \beta)$ = 743 K
T_{fus} = 918 K

$\Delta_f H^\circ$(0 K) = −442.98 ± 0.8 kJ·mol^{-1}
$\Delta_f H^\circ$(298.15 K) = −442.83 ± 0.8 kJ·mol^{-1}
$\Delta_{trs} H^\circ$ = 3.77 kJ·mol^{-1}
$\Delta_{fus} H^\circ$ = 15.9 kJ·mol^{-1}

Enthalpy Reference Temperature = T_r = 298.15 K						Standard State Pressure = p° = 0.1 MPa	
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K$_f$
0	9.146	3.540	INFINITE	−12.452	−442.979	−442.979	INFINITE
100	44.091	47.798	145.996	−9.820	−443.952	−433.786	226.587
200	50.128	80.726	105.914	−5.038	−443.369	−423.827	110.692
298.15	52.442	101.182	101.182	0.	−442.835	−414.360	72.594
300	52.472	101.506	101.183	0.097	−442.829	−414.183	72.116
400	54.685	116.906	103.267	5.455	−444.485	−404.011	52.758
500	56.902	129.347	107.277	11.035	−443.823	−393.965	41.157
600	59.099	139.916	111.858	16.835	−442.946	−384.072	33.436
700	61.296	149.191	116.541	22.855	−441.858	−374.343	27.934
743.000	62.237	152.873	118.538	25.511	ALPHA <−−> BETA TRANSITION		
743.000	63.388	157.941	118.538	29.276			
800	63.680	162.637	121.515	32.898	−436.758	−365.075	23.837
900	64.174	170.166	126.510	39.290	−435.321	−356.200	20.673
918.000	64.266	171.438	127.379	40.446	−−−− BETA <−−> LIQUID −−−−		
1000	64.685	176.954	131.221	45.733	−500.972	−343.789	17.958
1100	65.187	183.142	135.664	52.227	−498.433	−328.193	15.585
1200	65.689	188.836	139.860	58.771	−495.849	−312.830	13.617
1300	66.191	194.114	143.833	65.365	−493.220	−297.685	11.961
1400	66.693	199.037	147.602	72.009	−490.548	−282.744	10.549
1500	67.195	203.656	151.187	78.703	−487.831	−267.995	9.332
1600	67.697	208.008	154.604	85.447	−485.073	−253.429	8.274
1700	68.241	212.129	157.867	92.245	−482.272	−239.037	7.345
1800	68.743	216.044	160.991	99.094	−479.431	−224.811	6.524
1900	69.245	219.774	163.988	105.993	−476.556	−210.743	5.794
2000	69.747	223.338	166.867	112.943	−473.651	−196.828	5.141

PREVIOUS: CURRENT June 1968

Enthalpy of Formation

The heat of solution ($\Delta_{sln}H^\circ$) of CsCl(cr) in water has been measured by Forcrand,[1,2] Haigh,[3] Samoilov,[4,6] and Rodnikova.[5] Based on their results, Parker[7] derived the corresponding $\Delta_{sln}H^\circ$(aq, ∞, 298.15) values as 4.30, 4.32, 4.08, 4.25, 4.18 and 4.18 kcal·mol^{-1}. Borob'ev *et al.*[8] determined the same quantity and reported $\Delta_{sln}H^\circ$(298.15 K) (CsCl, aq, ∞, H_2O) = 4.20 ± 0.04 kcal·mol^{-1} Using this value, 4.20 kcal·mol^{-1}, and $\Delta_f H^\circ$(298.15 K) = −61.69[9] and −39.952 kcal·mol^{-1} [10] for Cs^+(aq, ∞) and Cl^-(aq, ∞, 298.15), respectively, we evaluate $\Delta_f H^\circ$(CsCl, cr, 298.15 K) = −105.84 ± 0.2 kcal·mol^{-1}, which is adopted.

Heat Capacity and Entropy

Taylor *et al.*[11] measured the low temperature heat capacities, 7.19–299.38 K, with an adiabatic calorimeter; the sample purity was >99.95%. Employing these data we derive the value S°(298.15 K) = 24.183 cal·K^{-1}·mol^{-1} based on S°(7.19 K) = 0.031 cal·K^{-1}·mol^{-1}.

The high temperature enthalpies, 385.2–904.9 K, were measured by Kaylor,[21 12,13] using a Bunsen ice calorimeter and a CsCl sample of 99.8% purity. The heat capacities derived from the reported enthalpy data at temperatures 385.2–740.5 K appear too low (less than the adopted C_p°'s systematically by 0.9 cal·K^{-1}·mol^{-1} to join smoothly with the low temperature data at 298.15 K. The C_p° values derived from the measured enthalpy data in the temperature range 760–920 K increase rapidly from 14.46 to 16.3 cal·K^{-1}·mol^{-1}. In order to rationalize this situation, we adopt the high temperature heat capacities, 298–743 K, for CsCl(α) obtained by linear extrapolation of the low temperature data. The C_p° values for CsCl(B) are adjusted such that the rate of increase in heat capacities is linear and less rapid than the original one, and the total enthalpy remains essentially unchanged. The discrepancy between the high and low temperature C_p° for CsCl(α) may be caused by the incomplete β → α phase conversion involved. In order to resolve this discrepancy, independent enthalpy measurements using a high purity sample with composition well characterized before and after each drop experiment seem necessary.

Transition Data

The temperature of transition (in K) has been reported by many investigators as 718,[14] 752,[15] 745,[16] 742,[21] 742.5,[12] 743,[20] and 733,[17] using different methods and samples of different purity. The value adopted is 743 K.

The heat of transition (in kcal·mol^{-1}) was reported to be 1.8,[14] 1.55,[18] 1.4,[19] 0.80,[21] 0.58,[12] 0.90,[13] and 1.1.[17] A median value 0.90 kcal·mol^{-1} is tentatively adopted.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$\Delta_{sub}H^\circ$(298.15 K) is calculated as the difference between $\Delta_f H^\circ$(298.15 K) for CsCl(g) and CsCl(cr).

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Cesium Chloride (CsCl) LIQUID $M_r = 168.3584$ Cesium Chloride (CsCl) $Cl_1Cs_1(l)$

$S°(298.15\ K) = [101.708]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 918\ K$

$\Delta_f H°(298.15\ K) = [-434.468]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 15.9 \pm 4.2\ kJ{\cdot}mol^{-1}$

Enthaply of Formation

$\Delta_f H°$(CsCl, l, 298.15 K) is calculated from $\Delta_f H°$(CsCl, cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°$(918 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The enthalpies of CsCl(l) at temperatures 923.6–1168.0 K were measured with a Bunsen ice calorimeter by Kaylor *et al.*[1,2] Dworkin[3] derived the heat capacity of CsCl(l) as 18.5 cal·K^{-1}·mol^{-1} from enthalpy data at temperatures 918–980 K. This value is adopted since it is in agreement with the enthalpy values reported by Kaylor *et al.*[1,2] The heat capacity at temperatures above 1168 and below 923.6 K is assumed to be 18.5 cal·K^{-1}·mol^{-1}. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting temperature (in K) of CsCl(cr) has been determined by many investigators as 904 ± 3,[4] 919,[5] 912,[6] 911,[7] 918,[8] 916,[9] and 919.[13] The cause of the discrepancies is probably due to the difference in purity of the samples. The melting temperature adopted is 918 K.

The heat of melting (in kcal·mol^{-1}) was reported to be 4.84,[14] 4.97,[15] 4.58,[10] 4.96,[11] and 4.79,[2] which were obtained calorimetrically. Using a modification of Kelley's method of obtaining heat of melting from freezing point data on binary systems involving CsCl,[16] we derive the value of $\Delta_{fus}H°$ as 3.6–4.0 kcal·mol^{-1}, based on the following systems: CsCl–NaCl,[5] CsCl–CuCl,[6] CsCl–AgCl,[6] CsCl–LiCl[8] and CsCl–$Cs_3(PO_3)_3$.[12] The heat of melting for CsCl(cr) is tentatively adopted as 3.8 kcal·mol^{-1}. The $\Delta_{fus}H°$ values obtained calorimetrically are not used due to the uncertainties of the state of the sample before and after the enthalpy measurements.

Vaporization Data

T_{vap} = 1597.3 K is the temperature at which the calculated total pressures of CsCl(g) and Cs_2Cl_2(g) equal one atmosphere. The vapor composition at T_{vap} is derived as CsCl 80.4% and Cs_2Cl_2 19.6%. The boiling point of CsCl(l) has been determined by several investigators as 1562,[17] 1572[18] and 1576.[19] The heat required to vaporize one mole of liquid to the above vapor mixture at T_{vap} is $\Delta_{vap}H°$.

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	77.404	101.708	101.708	0.	−434.468	−406.150	71.156
300	77.404	102.187	101.710	0.143	−434.416	−405.975	70.686
400	77.404	124.455	104.746	7.884	−433.690	−396.236	51.743
500	77.404	141.727	110.479	15.624	−430.867	−387.199	40.450
600	77.404	155.840	116.899	23.364	−428.050	−378.731	32.971
700	77.404	167.771	123.336	31.105	−425.242	−370.733	27.664
800	77.404	178.107	129.551	38.845	−422.445	−363.137	23.710
900	77.404	187.224	135.462	46.586	−419.659	−355.891	20.655
918.000	77.404	188.757	136.492	47.979	---- BETA <--> LIQUID ----		
1000	77.404	195.379	141.053	54.326	−484.013	−345.255	18.034
1100	77.404	202.757	146.333	62.066	−480.226	−331.563	15.745
1200	77.404	209.492	151.320	69.807	−476.446	−318.215	13.852
1300	77.404	215.688	156.036	77.547	−472.671	−305.182	12.262
1400	77.404	221.424	160.504	85.288	−468.902	−292.439	10.911
1500	77.404	226.764	164.745	93.028	−465.140	−279.966	9.749
1600	77.404	231.760	168.779	100.768	−461.386	−267.744	8.741
1700	77.404	236.452	172.624	108.509	−457.641	−255.756	7.858
1800	77.404	240.877	176.294	116.249	−453.909	−243.988	7.080
1900	77.404	245.062	179.804	123.990	−450.193	−232.427	6.390
2000	77.404	249.032	183.167	131.730	−446.498	−221.062	5.774
2100	77.404	252.808	186.394	139.470	−442.827	−209.880	5.220
2200	77.404	256.409	189.495	147.211	−439.186	−198.873	4.722
2300	77.404	259.850	192.480	154.951	−435.581	−188.030	4.270
2400	77.404	263.144	195.356	162.692	−432.019	−177.344	3.860
2500	77.404	266.304	198.131	170.432	−428.504	−166.805	3.485
2600	77.404	269.340	200.812	178.172	−425.045	−156.405	3.142
2700	77.404	272.261	203.405	185.913	−421.648	−146.138	2.827
2800	77.404	275.076	205.914	193.653	−418.318	−135.995	2.537
2900	77.404	277.792	208.346	201.394	−415.065	−125.970	2.269
3000	77.404	280.416	210.705	209.134	−411.893	−116.055	2.021

PREVIOUS: CURRENT: June 1968

Cesium Chloride (CsCl) $Cl_1Cs_1(l)$

Cesium Chloride (CsCl)

CRYSTAL(α–β)–LIQUID

0 to 743 K crystal, alpha
743 to 918 K crystal, beta
above 918 K liquid

Refer to the individual tables for details.

M_r = 168.3584 Cesium Chloride (CsCl)

$Cl_1Cs_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	9.146	3.540	INFINITE	−12.452	−442.979	−442.979	INFINITE
100	44.091	47.798	145.996	−9.820	−443.952	−433.786	226.587
200	50.128	80.726	105.914	−5.038	−443.369	−423.827	110.692
298.15	52.442	101.182	101.182	0.	−442.835	−414.360	72.594
300	52.472	101.506	101.183	0.097	−442.829	−414.183	72.116
400	54.685	116.906	103.267	5.455	−444.485	−404.011	52.758
500	56.902	129.347	107.277	11.035	−443.823	−393.965	41.157
600	59.099	139.916	111.858	16.835	−442.946	−384.072	33.436
700	61.296	149.191	116.541	22.855	−441.858	−374.343	27.934
743.000	62.237	152.873	118.538	25.511	ALPHA <--> BETA		
743.000	63.388	157.941	118.538	29.276	TRANSITION		
800	63.680	162.637	121.515	32.898	−436.758	−365.075	23.837
900	64.174	170.166	126.510	39.290	−435.321	−356.200	20.673
918.000	64.266	171.438	127.379	40.446	BETA <--> LIQUID		
918.000	77.404	188.757	127.379	56.345	TRANSITION		
1000	77.404	195.379	132.687	62.692	−484.013	−345.255	18.034
1100	77.404	202.757	138.727	70.433	−480.226	−331.563	15.745
1200	77.404	209.492	144.347	78.173	−476.446	−318.215	13.852
1300	77.404	215.688	149.600	85.914	−472.671	−305.182	12.262
1400	77.404	221.424	154.528	93.654	−468.902	−292.439	10.911
1500	77.404	226.764	159.168	101.394	−465.140	−279.966	9.749
1600	77.404	231.760	163.550	109.135	−461.386	−267.744	8.741
1700	77.404	236.452	167.702	116.875	−457.641	−255.756	7.858
1800	77.404	240.877	171.646	124.616	−453.909	−243.988	7.080
1900	77.404	245.062	175.400	132.356	−450.193	−232.427	6.390
2000	77.404	249.032	178.984	140.096	−446.498	−221.062	5.774
2100	77.404	252.808	182.410	147.837	−442.827	−209.880	5.220
2200	77.404	256.409	185.692	155.577	−439.186	−198.873	4.722
2300	77.404	259.850	188.842	163.318	−435.581	−188.030	4.270
2400	77.404	263.144	191.870	171.058	−432.019	−177.344	3.860
2500	77.404	266.304	194.785	178.798	−428.504	−166.805	3.485
2600	77.404	269.340	197.594	186.539	−425.045	−156.405	3.142
2700	77.404	272.261	200.306	194.279	−421.648	−146.138	2.827
2800	77.404	275.076	202.926	202.020	−418.318	−135.995	2.537
2900	77.404	277.792	205.461	209.760	−415.065	−125.970	2.269
3000	77.404	280.416	207.916	217.500	−411.893	−116.055	2.021

PREVIOUS: CURRENT: June 1968

Cesium Chloride (CsCl) IDEAL GAS $M_r = 168.3584$

$S°(298.15\ \mathrm{K}) = 256.070 \pm 0.021\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$

$\Delta_f H°(0\ \mathrm{K}) = -237.98 \pm 4.2\ \mathrm{kJ{\cdot}mol^{-1}}$
$\Delta_f H°(298.15\ \mathrm{K}) = -240.16 \pm 4.2\ \mathrm{kJ{\cdot}mol^{-1}}$

Electronic Level and Quantum Weight

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 213.08\ \mathrm{cm^{-1}}$ $\omega_e x_e = 0.733\ \mathrm{cm^{-1}}$ $\sigma = 1$
$B_e = 0.07134\ \mathrm{cm^{-1}}$ $\alpha_e = 0.000332\ \mathrm{cm^{-1}}$ $r_e = 2.906$ Å

Enthalpy of Formation

The total pressures of CsCl(g) and Cs_2Cl_2(g) over CsCl(cr) and CsCl(l) in the temperature range 605–1577 K have been determined by manometric, transpiration and Knudsen effusion methods by many investigators. Based on the reported results, the partial pressures of CsCl(g) and Cs_2Cl_2(g) are calculated using the derived Gibbs energy functions for CsCl(cr), CsCl(l), CsCl(g) and Cs_2Cl_2(g) and the enthalpies of sublimation and vaporization which are adjusted so that the sum of the calculated partial pressures of CsCl(g) and Cs_2Cl_2(g) approaches the measured total pressures, and the evaluated 2nd and 3rd law $\Delta_f H°$(298.15 K) values are in reasonable agreement. The results obtained are presented in the table below. The value of $\Delta_f H°$(CsCl, g, 298.15 K) adopted is −57.4 ± 1 kcal·mol^{-1}(−240.162 ± 4.2 kJ·mol^{-1}).

Gaydon[10] reported $D_0°$(Cs–Cl) = 4.6 ± 0.2 eV or 106.08 ± 4.61 kcal·mol^{-1}. Using this $D_0°$ value and $\Delta_f H°$(0 K) = 18.683 and 28.52 kcal·mol^{-1} for Cs(g) and Cl(g), we evaluate $\Delta_f H°$(298.15 K) = −59.4 ± 4.6 kcal·mol^{-1} for CsCl(g), which is in fair agreement with the adopted value.

Source	Reaction*	Method	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
1	1	A	793–893	11	46.81 ± 0.35	49.92	3.7 ± 0.4	−55.92
2	1	A	690–891	28	47.80 ± 0.31	47.88	0.1 ± 0.4	−57.96
3	1	B	784–905	10	47.08 ± 0.26	49.17	2.5 ± 0.3	−56.67
4	1	A	605–851	16	45.26 ± 0.38	48.74	4.7 ± 0.5	−57.10
5	2	C	1335–1577	9	49.36 ± 0.50	46.27	−2.1 ± 0.3	−57.57
6	2	C	1259–1568	7	51.61 ± 1.08	46.17	−3.8 ± 0.8	−57.67
7	2	C	1098–1293	9	47.57 ± 0.08	46.52	−0.9 ± 0.1	−57.32
8	2	B	1133–1263	3	48.73 ± 2.09	47.00	−1.4 ± 1.7	−56.84
9	2	C	1165–1387	10	47.46 ± 0.08	46.36	−0.9 ± 0.1	−57.48
10	1	A	1174–1353	10	47.97 ± 0.15	46.54	−1.1 ± 0.1	−57.30

*1 CsCl(cr) = CsCl(g); 2 CsCl(l) = CsCl(g); A = Knudsen effusion; B = transpiration; and C = manometric.

Heat Capacity and Entropy

Clouser and Gordy[11] studied the pure rotational spectra of CsCl(g) in the 0.96–3 mm range of the microwave region with the molecular-beam spectrometer, and derived the values of B_e, α_e, ω_e, $\omega_e x_e$ and r_e, which are adopted and corrected to the average isotopic species.

The Cs–Cl bond distance was measured as 3.06 ± 0.03 Å by the electron diffraction method by Maxwell *et al.*,[12] which is not used. Similar values of B_e and α_e were reported by Honig *et al.*[13] and Rice and Klemperer,[14] determined from microwave and infrared spectra, respectively. Barrow and Caunt[15] gave ω_e = 240 cm^{-1}($CsCl^{35}$) which is singificantly different from the adopted value 214.22 cm^{-1} for $CsCl^{35}$ and the value 209 ± 6 cm^{-1} reported by Rice and Klemperer.[14]

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Cesium Chloride (CsCl) $Cl_1Cs_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.130	−237.985	−237.985	INFINITE
100	33.194	217.326	288.246	−7.092	−238.551	−245.338	128.151
200	36.120	241.467	259.429	−3.593	−239.251	−251.857	65 778
250	36.643	249.588	256.677	−1.772	−239.660	−254.963	53.272
298.15	36.952	256.070	256.070	0.	−240.162	−257.867	45.177
300	36.961	256.299	256.071	0.068	−240.184	−257.977	44.918
350	37.175	262.014	256.522	1.922	−242.885	−260.558	38.886
400	37.330	266.988	257.526	3.785	−243.482	−263.042	34.350
450	37.450	271.392	258.827	5.655	−244.071	−265.451	30.813
500	37.548	275.343	260.284	7.530	−244.655	−267.795	27.976
600	37.702	282.203	263.383	11.292	−245.815	−272.314	23.707
700	37.827	288.025	266.498	15.069	−246.971	−276.640	20 643
800	37.935	293.083	269.512	18.857	−248.126	−280.799	18.334
900	38.034	297.557	272.384	22.656	−249.282	−284.814	16.530
1000	38.126	301.569	275.105	26.464	−317.569	−285.000	14.887
1100	38.215	305.207	277.679	30.281	−317.706	−281.737	13.379
1200	38.301	308.536	280.114	34.107	−317.840	−278.461	12.121
1300	38.386	311.605	282.420	37.941	−317.971	−275.174	11.057
1400	38.468	314.453	284.607	41.784	−318.100	−271.877	10.144
1500	38.550	317.110	286.686	45.635	−318.227	−268.571	9.352
1600	38.631	319.600	288.667	49.494	−318.354	−265.257	8.660
1700	38.712	321.945	290.556	53.361	−318.483	−261.934	8.048
1800	38.792	324.160	292.362	57.236	−318.616	−258.604	7.504
1900	38.872	326.259	294.091	61.119	−318.757	−255.266	7.018
2000	38.951	328.255	295.750	65.010	−318.911	−251.921	6.579
2100	39.030	330.157	297.343	68.909	−319.081	−248.567	6.183
2200	39.109	331.975	298.876	72.816	−319.274	−245.205	5.822
2300	39.188	333.715	300.354	76.731	−319.495	−241.833	5.492
2400	39.266	335.384	301.779	80.654	−319.750	−238.452	5.190
2500	39.345	336.989	303.155	84.585	−320.045	−235.058	4.911
2600	39.423	338.534	304.486	88.523	−320.388	−231.652	4.654
2700	39.502	340.023	305.775	92.469	−320.785	−228.232	4.415
2800	39.580	341.461	307.024	96.423	−321.242	−224.796	4.194
2900	39.658	342.851	308.236	100.385	−321.766	−221.342	3.987
3000	39.736	344.197	309.412	104.355	−322.365	−217.869	3.793
3100	39.814	345.501	310.555	108.333	−323.045	−214.375	3.612
3200	39.892	346.767	311.667	112.318	−323.812	−210.858	3.442
3300	39.970	347.995	312.750	116.311	−324.632	−207.318	3.282
3400	40.048	349.190	313.804	120.312	−325.574	−203.749	3.130
3500	40.126	350.352	314.831	124.321	−326.616	−200.151	2.987
3600	40.204	351.483	315.834	128.337	−327.763	−196.522	2.851
3700	40.282	352.586	316.812	132.361	−329.004	−192.861	2.723
3800	40.360	353.661	317.768	136.394	−330.355	−189.164	2.600
3900	40.438	354.710	318.702	140.433	−331.805	−185.432	2.484
4000	40.516	355.735	319.615	144.481	−333.386	−181.659	2.372
4100	40.593	356.737	320.508	148.537	−335.082	−177.845	2.266
4200	40.671	357.716	321.382	152.600	−336.895	−173.988	2.164
4300	40.749	358.674	322.239	156.671	−338.825	−170 087	2.066
4400	40.827	359.611	323.077	160.750	−340.577	−166.173	1.973
4500	40.905	360.530	323.899	164.836	−342.127	−162.250	1.883
4600	40.982	361.430	324.706	168.931	−344.225	−158.230	1.797
4700	41.060	362.312	325.496	173.033	−346.410	−154.163	1.713
4800	41.138	363.177	326.272	177.143	−348.679	−150.049	1.633
4900	41.216	364.026	327.034	181.260	−351.028	−145.887	1.555
5000	41.293	364.860	327.782	185.386	−353.449	−141.676	1.480
5100	41.371	365.678	328.518	189.519	−355.939	−137.416	1.407
5200	41.449	366.482	329.240	193.660	−357.960	−133.184	1.338
5300	41.526	367.272	329.950	197.809	−360.500	−128.837	1.270
5400	41.604	368.049	330.648	201.965	−362.809	−124.485	1.204
5500	41.682	368.813	331.335	206.130	−365.246	−120.073	1.140
5600	41.760	369.565	332.011	210.302	−367.853	−115.592	1.078
5700	41.837	370.305	332.677	214.481	−370.484	−111.064	1.018
5800	41.915	371.033	333.332	218.669	−373.133	−106.489	0.959
5900	41.993	371.751	333.977	222.864	−375.792	−101.869	0.902
6000	42.070	372.457	334.612	227.068	−378.457	−97.204	0.846

PREVIOUS. June 1968 (1 atm) CURRENT. June 1968 (1 bar)

Copper Chloride (CuCl) CRYSTAL $M_r = 98.999$ Copper Chloride (CuCl) $Cl_1Cu_1(cr)$

$\Delta_fH°(0\ K)$ = Unknown

$S°(298.15\ K) = 87.03 \pm 4.2\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -138.07 \pm 1.7\ kJ\cdot mol^{-1}$

$T_{fus} = 703\ K$ $\Delta_{fus}H° = 10.230 \pm 2.1\ kJ\cdot mol^{-1}$

Enthalpy of Formation

There have been three calorimetric determinations of the enthalpy of formation. Thomsen[1] reported −32.875 kcal·mol^{-1}. Berthelot[2] reported −35.6 kcal·mol^{-1} and Wartenberg and Werth[3] reported −32.1 ± 0.4 kcal·mol^{-1}. In addition, values of the enthalpy of formation have been derived from several sets of equilibrium data. Noyes and Chow[4] from a study of cell potentials derived a $\Delta_rH° = 7.19$ kcal·mol^{-1} for the reaction $Cu(cr) + HCl(\infty,aq) \rightarrow CuCl(cr) + 1/2\ H_2(g)$ which yields $\Delta_fH°$(CuCl, 298.15 K) = −32.76 kcal·mol^{-1}. Several investigators have studied the reaction $2\ CuCl(cr) + H_2(g) \rightarrow 2\ Cu(cr) + 2\ HCl(g)$ and its reverse reaction. These include Bagdasarian[5] who reported equilibrium constants which result in 2nd and 3rd law heats of reaction of 24.3 and 23.2 kcal·mol^{-1}; Kapustinsky[6] who obtained similarly 20.1 and 21.8 kcal·mol^{-1}; Shchukarev and Oranskaya[7] who obtained 25.4 and 21.5 kcal·mol^{-1} for the 2nd and 3rd law heat of reaction. These yield values for $\Delta_fH°$(CuCl, 298.15 K) ranging from −32.1 to −34.8. Watanabe[8] from cell studies reports $\Delta_fH°$(CuCl, 298.15 K) = −34.6 kcal·mol^{-1}. A value of $\Delta_fH°$(298.15 K) can also be obtained from $\Delta_fH°(CuCl_3, g)$ which is fixed independently and known with good precision. Using the 3rd law heat of sublimation of CuCl(cr) to trimer determined by Magee[9] [see trimer table], we obtain $\Delta_fH°$(CuCl, cr, 298.15 K) = −33.01 ± 0.3 kcal·mol^{-1}. A weighted average of −33.0 ± 0.4 kcal·mol^{-1} (−138.072 ± 1.7 kJ·mol^{-1}) was adopted.

Heat Capacity and Entropy

The entropy of CuCl was obtained from the several pieces of equilibrium data reported above and the adopted $\Delta_fH°$(298.15 K). A weighted average of 20.8 ± 1 cal K^{-1}·mol^{-1} was adopted for $S°$(CuCl, cr, 298.15 K). The enthalpy and heat capacity above 298.15 K have been reported by Krestovnikov and Karetnikov.[10] However, these values were not adopted since they do not give reasonable heat capacities, and other data by these workers are not in agreement with established values. Heat capacities equal to those of AgCl, as given by Kelley,[11] were adopted here above 298.15 K.

Fusion Data

The temperature and enthalpy of fusion were those selected by Kelley[12] from phase studies. The enthalpy of fusion was reported by Krestovnikov and Karetnikov[10] as 2.54 kcal·mol^{-1}.

Sublimation Data

The enthalpy of sublimation was calculated from the adopted enthalpies of formation at 298.15 K for the reaction $x\mathrm{CuCl(cr)} \rightarrow \mathrm{(CuCl)}_x\mathrm{(g)}$ where x = 1 or 3. See the individual ideal gas tables for details.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	48.534	87.027	87.027	0.	−138.072	−120.876	21.177
300	48.771	87.328	87.028	0.090	−138.059	−120.769	21.028
400	56.902	102.675	89.065	5.444	−136.933	−115.157	15.038
500	59.831	115.711	93.128	11.291	−135.437	−109.882	11.479
600	61.505	126.773	97.838	17.361	−133.803	−104.924	9.134
700	62.760	136.354	102.671	23.578	−132.097	−100.244	7.480
703.000	62.791	136.623	102.815	23.767	--- CRYSTAL <--> LIQUID ---		
800	63.680	144.795	107.419	29.901	−130.348	−95.813	6.256
900	64.388	152.337	111.999	36.305	−128.580	−91.602	5.316
1000	65.019	159.155	116.379	42.776	−126.812	−87.588	4.575
1100	65.531	165.376	120.554	49.304	−125.064	−83.751	3.977
1200	66.011	171.099	124.531	55.881	−123.363	−80.071	3.485
1300	66.459	176.400	128.320	62.505	−121.753	−76.529	3.075
1400	66.874	181.341	131.932	69.172	−133.393	−72.700	2.712
1500	67.258	185.968	135.382	75.879	−131.866	−68.418	2.383

PREVIOUS: CURRENT: March 1966

Copper Chloride (CuCl) LIQUID M_r = 98.999 Copper Chloride (CuCl) $Cl_1Cu_1(l)$

$S°(298.15\ K) = [93.752]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 703°K$

$\Delta_f H°(298.15\ K) = [-131.178]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 10.230\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(CuCl, l,298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(703\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity was estimated to be constant at 8 $cal \cdot K^{-1} \cdot mol^{-1}$. The entropy was calculated in a manner analogous to that of the heat of formation.

Vaporization Data

The boiling point and heat of vaporization were calculated from the respective liquid, monomer and trimer gas tables. The boiling point, T_{vap} = 1485 K, was taken as the point where the total pressure reached 1 atm. At this point the partial pressures are 0.021 atm of monomer and 0.979 atm of trimer.

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	66.944	93.752	93.752	0.	−131.178	−115.987	20.320
300	66.944	94.166	93.754	0.124	−131.131	−115.893	20.179
400	66.944	113.425	96.379	6.818	−128.665	−111.189	14.520
500	66.944	128.363	101.338	13.513	−126.322	−107.093	11.188
600	66.944	140.569	106.890	20.207	−124.064	−103.461	9.007
700	66.944	150.888	112.457	26.901	−121.879	−100.201	7.477
703.000	66.944	151.174	112.622	27.102	--- CRYSTAL <--> LIQUID ---		
800	66.944	159.827	117.832	33.596	−119.759	−97.249	6.350
900	66.944	167.712	122.945	40.290	−117.701	−94.560	5.488
1000	66.944	174.765	127 781	46.985	−115.709	−92.096	4.811
1100	66.944	181.146	132.347	53.679	−113.795	−89.828	4.266
1200	66.944	186.971	136.659	60.373	−111.976	−87.731	3.819
1300	66.944	192.329	140.738	67.068	−110.296	−85.779	3.447
1400	66.944	197.290	144.603	73.762	−121.908	−83.545	3.117
1500	66.944	201.909	148.271	80.457	−120.394	−80.857	2.816
1600	66.944	206.229	151.760	87.151	−118.884	−78.271	2.555
1700	66.944	210.288	155.084	93.845	−117.378	−75.779	2.328
1800	66.944	214.114	158.259	100.540	−115.877	−73.375	2.129
1900	66.944	217.734	161.294	107.234	−114.381	−71.055	1.953
2000	66.944	221.167	164.203	113.929	−112.889	−68.813	1.797
2100	66.944	224.433	166.994	120.623	−111.404	−66.646	1.658
2200	66.944	227.548	169.676	127.317	−109.924	−64.549	1.533
2300	66.944	230.524	172.257	134.012	−108.451	−62.519	1.420
2400	66.944	233.373	174.745	140.706	−106.986	−60.554	1.318
2500	66 944	236.105	177.145	147.401	−105.528	−58.649	1.225
2600	66.944	238.731	179.464	154.095	−104.079	−56.803	1.141
2700	66.944	241.257	181.706	160.789	−102.639	−55.012	1.064
2800	66.944	243.692	183.876	167.484	−101.209	−53.274	0.994
2900	66.944	246.041	185.980	174.178	−399.992	−45.591	0.821
3000	66.944	248.311	188.020	180.873	−397.786	−33.408	0.582

PREVIOUS: CURRENT: March 1966

Copper Chloride (CuCl) $Cl_1Cu_1(l)$

Copper Chloride (CuCl) CRYSTAL-LIQUID

0 to 703 K crystal
above 703 K liquid

Refer to the individual tables for details.

$M_r = 98.999$ Copper Chloride (CuCl) $Cl_1Cu_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	48.534	87.027	87.027	0.	−138.072	−120.876	21.177
300	48.771	87.328	87.028	0.090	−138.059	−120.769	21.028
400	56.902	102.675	89.065	5.444	−136.933	−115.157	15.038
500	59.831	115.711	93.128	11.291	−135.437	−109.882	11.479
600	61.505	126.773	97.838	17.361	−133.803	−104.924	9.134
700	62.760	136.354	102.671	23.578	−132.097	−100.244	7.480
703.000	62.791	136.623	102.815	23.767	CRYSTAL <--> LIQUID TRANSITION		
703.000	66.944	151.174	102.815	33.996			
800	66.944	159.827	109.215	40.490	−119.759	−97.249	6.350
900	66.944	167.712	115.285	47.184	−117.701	−94.560	5.488
1000	66.944	174.765	120.886	53.879	−115.709	−92.096	4.811
1100	66.944	181.146	126.079	60.573	−113.795	−89.828	4.266
1200	66.944	186.971	130.914	67.268	−111.976	−87.731	3.819
1300	66.944	192.329	135.435	73.962	−110.296	−85.779	3.447
1400	66.944	197.290	139.678	80.656	−121.908	−83.545	3.117
1500	66.944	201.909	143.675	87.351	−120.394	−80.857	2.816
1600	66.944	206.229	147.451	94.045	−118.884	−78.271	2.555
1700	66.944	210.288	151.029	100.740	−117.378	−75.779	2.328
1800	66.944	214.114	154.428	107.434	−115.877	−73.375	2.129
1900	66.944	217.734	157.666	114.128	−114.381	−71.055	1.953
2000	66.944	221.167	160.756	120.823	−112.889	−68.813	1.797
2100	66.944	224.433	163.711	127.517	−111.404	−66.646	1.658
2200	66.944	227.548	166.542	134.212	−109.924	−64.549	1.533
2300	66.944	230.524	169.260	140.906	−108.451	−62.519	1.420
2400	66.944	233.373	171.872	147.600	−106.986	−60.554	1.318
2500	66.944	236.105	174.387	154.295	−105.528	−58.649	1.225
2600	66.944	238.731	176.812	160.989	−104.079	−56.803	1.141
2700	66.944	241.257	179.152	167.684	−102.639	−55.012	1.064
2800	66.944	243.692	181.414	174.378	−101.209	−53.274	0.994
2900	66.944	246.041	183.602	181.072	−399.992	−45.591	0.821
3000	66.944	248.311	185.722	187.767	−397.786	−33.408	0.582

PREVIOUS: CURRENT: March 1966

Copper Chloride (CuCl) $Cl_1Cu_1(cr,l)$

Copper Chloride (CuCl) **IDEAL GAS** $M_r = 98.999$ **Copper Chloride (CuCl)** **$Cl_1Cu_1(g)$**

$S°(298.15\ K) = 237.207\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 91.21 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 91.09 \pm 1.7\ kJ \cdot mol^{-1}$

Electronic Level and Multiplicity

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 414.9\ cm^{-1}$ $\omega_e x_e = 1.577\ cm^{-1}$ $\sigma = 1$
$B_e = 0.1761\ cm^{-1}$ $\alpha_e = 0.001\ cm^{-1}$ $r_e = 2.050$ Å

Enthalpy of Formation

The enthalpy of formation was obtained from the equilibrium data of Brewer and Lofgren.[1] They studied the reaction $x Cu(cr) + x\ HCl(g) \rightarrow Cu_2Cl_2(g) + x/2\ H_2(g)$ by measuring the amount of CuCl formed when various ratios of $HCl:H_2$ were passed over heated copper. Brewer and Lofgren analyzed the data by a least squares fitting technique and deduced partial pressures of monomer and trimer. The monomer pressures were subjected to 2nd and 3rd law analysis and gave $\Delta_r H°(298.15\ K) = 46.85 \pm 3.2$ and $43.83 \pm 0.4\ kcal \cdot mol^{-1}$, respectively. The 3rd law value yields $\Delta_f H°(CuCl, g, 298.15\ K) = 21.77 \pm 0.4\ kcal \cdot mol^{-1}$, which was adopted.

Heat Capacity and Entropy

The molecular constants were corrected for normal isotopic abundance of both copper and chlorine and were calculated from the values for $^{65}Cu^{35}Cl$ given by Asundi *et al.*[2] The rotational constants were in good agreement with those reported by Lagerqvist and Lazarova–Girsamov[3] for $Cu^{65}Cl^{35}$.

References

[1] L. Brewer and N. L. Lofgren, J. Am. Chem. Soc. **72**, 3038 (1950).
[2] R. K. Asundi, P. R. Rao and J. K. Brody, Nature **192**, 444 (1961).
[3] A. Lagerqvist and V. Lazarova–Girsamov, Naturwissenschaften **48**, 68 (1961).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.471	91.212	91.212	INFINITE
100	29.899	201.663	267.142	−6.548	92.010	82.298	−42.988
200	33.356	223.487	240.381	−3.379	91.647	72.692	−18.985
250	34.503	231.061	237.784	−1.681	91.373	67.985	−14.205
298.15	35.261	237.207	237.207	0.	91.086	63.506	−11.126
300	35.285	237.425	237.208	0.065	91.074	63.335	−11.028
350	35.830	242.908	237.639	1.844	90.757	58.736	−8.766
400	36.220	247.719	238.605	3.646	90.426	54.184	−7.076
450	36.509	252.003	239.860	5.464	90.081	49.675	−5.766
500	36.730	255.861	241.270	7.295	89.724	45.204	−4.722
600	37.044	262.587	244.279	10.985	88.978	36.369	−3.166
700	37.257	268.315	247.314	14.701	88.184	27.663	−2.064
800	37.415	273.300	250.257	18.435	87.344	19.074	−1.245
900	37.538	277.715	253.067	22.183	86.455	10.594	−0.615
1000	37.641	281.675	255.733	25.942	85.512	2.215	−0.116
1100	37.729	285.267	258.258	29.710	84.500	−6.067	0.288
1200	37.807	288.553	260.647	33.487	83.401	−14.252	0.620
1300	37.879	291.582	262.912	37.272	82.171	−22.341	0.898
1400	37.945	294.392	265.061	41.063	67.656	−29.923	1.116
1500	38.008	297.012	267.105	44.860	66.274	−36.845	1.283
1600	38.068	299.467	269.052	48.664	64.893	−43.674	1.426
1700	38.126	301.777	270.909	52.474	63.514	−50.418	1.549
1800	38.182	303.957	272.685	56.289	62.136	−57.080	1.656
1900	38.236	306.023	274.386	60.110	60.759	−63.665	1.750
2000	38.290	307.986	276.017	63.937	59.382	−70.178	1.833
2100	38.342	309.855	277.585	67.768	58.005	−76.622	1.906
2200	38.394	311.640	279.092	71.605	56.627	−83.001	1.971
2300	38.445	313.348	280.545	75.447	55.247	−89.317	2.028
2400	38.496	314.985	281.946	79.294	53.866	−95.573	2.080
2500	38.546	316.558	283.299	83.146	52.481	−101.771	2.126
2600	38.595	318.070	284.608	87.003	51.093	−107.913	2.168
2700	38.645	319.528	285.874	90.865	49.700	−114.003	2.206
2800	38.694	320.934	287.101	94.732	48.303	−120.040	2.239
2900	38.743	322.293	288.292	98.604	−253.302	−120.032	2.162
3000	38.792	323.607	289.447	102.481	−253.914	−115.426	2.010
3100	38.840	324.880	290.570	106.362	−254.581	−110.799	1.867
3200	38.889	326.114	291.661	110.249	−255.304	−106.150	1.733
3300	38.937	327.311	292.723	114.140	−256.081	−101.476	1.606
3400	38.985	328.474	293.758	118.036	−256.913	−96.779	1.487
3500	39.033	329.605	294.766	121.937	−257.798	−92.057	1.374
3600	39.081	330.705	295.749	125.843	−258.734	−87.308	1.267
3700	39.129	331.777	296.708	129.753	−259.719	−82.533	1.165
3800	39.176	332.821	297.645	133.668	−260.750	−77.730	1.068
3900	39.224	333.839	298.560	137.588	−261.825	−72.900	0.976
4000	39.272	334.833	299.455	141.513	−262.939	−68.042	0.889
4100	39.319	335.803	300.329	145.443	−264.089	−63.155	0.805
4200	39.367	336.751	301.185	149.377	−265.272	−58.240	0.724
4300	39.414	337.678	302.023	153.316	−266.484	−53.296	0.647
4400	39.462	338.585	302.844	157.260	−267.721	−48.324	0.574
4500	39.509	339.472	303.648	161.209	−268.980	−43.324	0.503
4600	39.556	340.341	304.436	165.162	−270.256	−38.295	0.435
4700	39.604	341.192	305.209	169.120	−271.547	−33.239	0.369
4800	39.651	342.027	305.968	173.083	−272.850	−28.155	0.306
4900	39.698	342.845	306.712	177.050	−274.160	−23.043	0.246
5000	39.745	343.647	307.443	181.022	−275.476	−17.905	0.187
5100	39.793	344.435	308.160	184.999	−276.795	−12.740	0.130
5200	39.840	345.208	308.865	188.981	−278.114	−7.550	0.076
5300	39.887	345.967	309.558	192.967	−279.431	−2.334	0.023
5400	39.934	346.713	310.239	196.958	−280.744	2.906	−0.028
5500	39.981	347.446	310.909	200.954	−282.053	8.171	−0.078
5600	40.028	348.167	311.568	204.954	−283.354	13.460	−0.126
5700	40.075	348.876	312.216	208.959	−284.647	18.771	−0.172
5800	40.122	349.573	312.855	212.969	−285.932	24.106	−0.217
5900	40.169	350.260	313.483	216.984	−287.208	29.462	−0.261
6000	40.216	350.935	314.101	221.003	−288.473	34.840	−0.303

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

Copper Chloride (CuCl) **$Cl_1Cu_1(g)$**

Hydrochloric Acid-d (DCl) **IDEAL GAS** **$M_r = 37.467102$ Hydrochloric Acid-D (DCl)** **$Cl_1D_1(g)$**

$S°(298.15\ K) = 192.741\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -93.131 \pm 0.21\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -93.345 \pm 0.21\ kJ{\cdot}mol^{-1}$

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
	Electronic States and Molecular Constants ($\sigma = 1$)						
$X^1\Sigma^+$	0	1	2144.0	26.90	5.4444	0.1121	1.2746
$B^1\Pi$	75160	2	2199.0	[26.9]	5.1793	[0.1121]	
$V^1\Sigma^+$	76520	1	684.6	[26.9]	1.555	[0.1121]	2.43
$C^1\Pi$	77525	2	2114.1	[26.9]	4.9605	[0.1121]	

Enthalpy of Formation (Provisional–evaluation incomplete)

The enthalpy of formation was calculated from the selected value of $\Delta_f H°(298.15\ K)$ of HCl(g) given by JANAF,[1] the appropriate thermal functions (refer to H_2, D_2, DCl tables, and HCl[1]) and zero point energies. The zero point energies of $H_2(g)$ and $D_2(g)$ are taken from Herzberg and Monfile.[2] The zero point energies of HCl(g) and DCl(g), including the Dunham correction, were calculated from the molecular constants taken from Rosen.[3]

Heat Capacity and Entropy

The vibrational and rotational constants at the respective electronic levels were taken from Rosen[3] and were adjusted to $Cl^{35} = 75.4\%$ and $Cl^{37} = 24.6\%$.

The National Bureau of Standards prepared this table[4] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[4] we recalculate the table in terms of 1973 fundamental constants,[5] 1975 atomic weights,[6] and current JANAF reference states for the elements.

References

[1] JANAF Thermochemical Tables, 2nd ed., NSRDS-NBS 37, (June 1971).
[2] G. Herzberg and A. Monfils, J. Mol. Spectrosc. 5, 482 (1960).
[3] B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, Oxford, (1970).
[4] S. Abramowitz *et al.*, U. S. Natl. Bur. Stand. Rept. 10904, 239, (1972).
[5] CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, (December 1973).
[6] IUPAC Commission on Atomic Weights, Pure and Applied Chem. 47, 75 (1976); 37, 589 (1974).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.661	−93.131	−93.131	INFINITE
100	29.113	160.924	218.642	−5.772	−93.073	−94.076	49.140
200	29.124	181.107	195.407	−2.860	−93.157	−95.051	24.825
250	29.136	187.606	193.221	−1.404	−93.240	−95.516	19.957
298.15	29.170	192.741	192.741	0.	−93.345	−95.945	16.809
300	29.172	192.921	192.741	0.054	−93.349	−95.961	16.708
350	29.256	197.424	193.097	1.514	−93.478	−96.387	14.385
400	29.406	201.339	193.887	2.981	−93.618	−96.793	12.640
450	29.627	204.815	194.912	4.456	−93.763	−97.181	11.280
500	29.911	207.951	196.062	5.944	−93.905	−97.553	10.191
600	30.610	213.464	198.515	8.969	−94.170	−98.257	8.554
700	31.383	218.240	200.999	12.069	−94.397	−98.920	7.381
800	32.142	222.481	203.424	15.245	−94.582	−99.553	6.500
900	32.843	226.308	205.757	18.495	−94.732	−100.164	5.813
1000	33.467	229.801	207.990	21.811	−94.851	−100.762	5.263
1100	34.015	233.017	210.121	25.186	−94.948	−101.348	4.813
1200	34.491	235.998	212.154	28.612	−95.027	−101.926	4.437
1300	34.905	238.775	214.096	32.082	−95.094	−102.498	4.118
1400	35.266	241.375	215.953	35.591	−95.152	−103.065	3.845
1500	35.580	243.820	217.730	39.134	−95.205	−103.629	3.609
1600	35.857	246.125	219.433	42.706	−95.254	−104.189	3.401
1700	36.101	248.306	221.068	46.304	−95.301	−104.746	3.218
1800	36.318	250.376	222.639	49.925	−95.347	−105.300	3.056
1900	36.512	252.345	224.152	53.567	−95.395	−105.852	2.910
2000	36.687	254.222	225.608	57.227	−95.445	−106.401	2.779
2100	36.845	256.016	227.014	60.904	−95.498	−106.947	2.660
2200	36.989	257.733	228.372	64.596	−95.556	−107.491	2.552
2300	37.121	259.380	229.684	68.301	−95.619	−108.032	2.453
2400	37.242	260.963	230.955	72.019	−95.689	−108.570	2.363
2500	37.355	262.486	232.186	75.749	−95.766	−109.105	2.280
2600	37.460	263.953	233.380	79.490	−95.852	−109.637	2.203
2700	37.558	265.368	234.538	83.241	−95.946	−110.166	2.131
2800	37.650	266.736	235.664	87.002	−96.050	−110.691	2.065
2900	37.736	268.059	236.758	90.771	−96.164	−111.211	2.003
3000	37.819	269.339	237.823	94.549	−96.289	−111.728	1.945
3100	37.897	270.581	238.860	98.334	−96.424	−112.241	1.891
3200	37.971	271.785	239.870	102.128	−96.569	−112.749	1.840
3300	38.043	272.955	240.855	105.929	−96.724	−113.252	1.793
3400	38.111	274.091	241.816	109.736	−96.889	−113.750	1.748
3500	38.177	275.197	242.754	113.551	−97.063	−114.244	1.705
3600	38.241	276.273	243.670	117.372	−97.245	−114.732	1.665
3700	38.302	277.322	244.565	121.199	−97.434	−115.215	1.627
3800	38.362	278.344	245.441	125.032	−97.630	−115.693	1.590
3900	38.420	279.341	246.298	128.871	−97.831	−116.166	1.556
4000	38.477	280.315	247.136	132.716	−98.036	−116.633	1.523
4100	38.532	281.266	247.957	136.567	−98.245	−117.096	1.492
4200	38.586	282.195	248.761	140.422	−98.454	−117.553	1.462
4300	38.638	283.103	249.549	144.284	−98.665	−118.005	1.433
4400	38.690	283.992	250.322	148.150	−98.874	−118.452	1.406
4500	38.741	284.862	251.080	152.022	−99.082	−118.895	1.380
4600	38.790	285.714	251.823	155.898	−99.286	−119.333	1.355
4700	38.839	286.549	252.553	159.780	−99.486	−119.767	1.331
4800	38.888	287.367	253.270	163.666	−99.681	−120.196	1.308
4900	38.935	288.170	253.974	167.557	−99.869	−120.622	1.286
5000	38.982	288.957	254.666	171.453	−100.049	−121.043	1.265
5100	39.028	289.729	255.346	175.353	−100.221	−121.462	1.244
5200	39.074	290.487	256.015	179.259	−100.383	−121.876	1.224
5300	39.119	291.232	256.672	183.168	−100.535	−122.288	1.205
5400	39.164	291.964	257.319	187.082	−100.675	−122.697	1.187
5500	39.208	292.683	257.955	191.001	−100.803	−123.104	1.169
5600	39.252	293.390	258.582	194.924	−100.918	−123.508	1.152
5700	39.296	294 085	259.198	198.851	−101.020	−123.911	1.136
5800	39.339	294.769	259.806	202.783	−101.107	−124.312	1.120
5900	39.382	295 441	260.404	206.719	−101.180	−124.711	1.104
6000	39.424	296.104	260.994	210.660	−101.236	−125.110	1.089

PREVIOUS: June 1977 (1 atm) CURRENT June 1977 (1 bar)

Hydrochloric Acid–D (DCl) **$Cl_1D_1(g)$**

Hypochlorous Acid–d, (DOCl) IDEAL GAS $M_r = 53.466502$ Hypochlorous Acid–d, (DOCl) $Cl_1D_1O_1(g)$

$\Delta_f H°(0\ K) = -75.34 \pm 2.1\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 240.25 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -78.24 \pm 2.1\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1A'$	0	1
$^3A''$	[22000]	3

Vibrational Frequencies and Degeneracies

ν, cm^{-1}
2666(1)
911(1)
728(1)

Point Group: C_s $\sigma = 1$

Bond Distances: O–Cl = 1.689 ± 0.003 Å; O–D = 0.960 ± 0.004 Å

Bond Angle: D–O–Cl = 102.5 ± 0.5°

Product of the Moments of Inertia: $I_A I_B I_C = 9.0222 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°$(DOCl, g, 298.15 K) is calculated from the JANAF selection[1] for $\Delta_f H°$(298.15 K) of HOCl(g), the JANAF thermal functions,[1] and the zero point energies of $H_2(g)$, $D_2(g)$, HOCl(g), and DOCl(g). The zero point energies of $H_2(g)$ and $D_2(g)$ are those given by Herzberg and Monfils.[2] The zero–point energies of HOCl(g) and DOCl(g) are estimated from vibrational frequencies as listed by JANAF[1] using the first–order relation, zero–point energy = $(\omega_1 + \omega_2 + \omega_3)/2$.

Heat Capacity and Entropy

The molecular constants B_0 and C_0 are from the microwave work of Mirri *et al.*[3] The constant A_0 is calculated from the molecular structure given by Mirri *et al.*[3] and is somewhat uncertain. The rotational constants $A_0 = 11.105\ cm^{-1}$, $B_0 = 0.474852\ cm^{-1}$, and $C_0 = 0.454208\ cm^{-1}$ have been adjusted for the natural isotopic abundance of Cl. The vibrational frequencies are from the infrared spectroscopic work of Ashby[4] and that of Schwager and Arkell[5] and have not been corrected for isotopic abundances.

References

[1] JANAF Thermochemical Tables: HOCl(g), 3–31–79.

[2] G. Herzberg and A. Monfils, J. Mol. Spectrosc. 5, 482 (1960).

[3] A. M. Mirri, F. Scappini, and G. Cazzoli, J. Mol. Spectrosc. 38, 218 (1971).

[4] R. A. Ashby, J. Mol. Spectrosc. 23, 439 (1967); 40, 639 (1971).

[5] I. Schwager and A. Arkell, J. Amer. Chem. Soc. 89, 6006 (1967).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−10.319	−75.344	−75.344	INFINITE
100	33.286	202.209	272.143	−6.993	−76.301	−72.767	38.010
200	34.993	225.626	243.654	−3.606	−77.365	−68.814	17.972
250	36.758	233.619	240.871	−1.813	−77.840	−66.621	13.920
298.15	38.540	240.246	240.246	0.	−78.241	−64.422	11.287
300	38.607	240.485	240.247	0.071	−78.255	−64.337	11.202
350	40.306	246.566	240.724	2.045	−78.609	−61.988	9.251
400	41.785	252.048	241.802	4.098	−78.909	−59.593	7.782
450	43.057	257.045	243.222	6.220	−79.166	−57.162	6.635
500	44.157	261.639	244.837	8.401	−79.386	−54.705	5.715
600	45.987	269.858	248.339	12.912	−79.746	−49.734	4.330
700	47.488	277.063	251.938	17.588	−80.023	−44.709	3.336
800	48.767	283.490	255.487	22.402	−80.240	−39.649	2.589
900	49.872	289.299	258.927	27.335	−80.408	−34.564	2.006
1000	50.830	294.604	262.233	32.371	−80.538	−29.463	1.539
1100	51.659	299.489	265.401	37.497	−80.639	−24.350	1.156
1200	52.376	304.015	268.432	42.700	−80.716	−19.230	0.837
1300	52.997	308.233	271.334	47.969	−80.775	−14.103	0.567
1400	53.534	312.180	274.112	53.296	−80.822	−8.973	0.335
1500	54.000	315.890	276.774	58.673	−80.860	−3.840	0.134
1600	54.406	319.388	279.330	64.094	−80.894	1.296	−0.042
1700	54.760	322.698	281.784	69.553	−80.927	6.434	−0.198
1800	55.070	325.837	284.145	75.045	−80.961	11.574	−0.336
1900	55.342	328.821	286.419	80.566	−80.999	16.716	−0.460
2000	55.583	331.666	288.610	86.112	−81.044	21.860	−0.571
2100	55.796	334.384	290.726	91.681	−81.097	27.006	−0.672
2200	55.986	336.984	292.770	97.270	−81.162	32.156	−0.763
2300	56.156	339.476	294.747	102.878	−81.239	37.308	−0.847
2400	56.310	341.869	296.661	108.501	−81.330	42.464	−0.924
2500	56.449	344.171	298.515	114.139	−81.436	47.624	−0.995
2600	56.577	346.387	300.314	119.791	−81.559	52.789	−1.061
2700	56.696	348.525	302.060	125.454	−81.699	57.959	−1.121
2800	56.807	350.589	303.757	131.129	−81.857	63.135	−1.178
2900	56.912	352.584	305.406	136.815	−82.034	68.316	−1.230
3000	57.013	354.515	307.011	142.512	−82.228	73.503	−1.280
3100	57.111	356.386	308.574	148.218	−82.440	78.698	−1.326
3200	57.207	358.201	310.097	153.934	−82.670	83.899	−1.370
3300	57.303	359.963	311.581	159.659	−82.916	89.108	−1.410
3400	57.400	361.675	313.030	165.395	−83.177	94.325	−1.449
3500	57.499	363.340	314.443	171.139	−83.453	99.550	−1.486
3600	57.600	364.962	315.824	176.894	−83.740	104.783	−1.520
3700	57.704	366.541	317.174	182.660	−84.039	110.023	−1.553
3800	57.812	368.081	318.493	188.435	−84.346	115.273	−1.585
3900	57.924	369.585	319.784	194.222	−84.661	120.530	−1.614
4000	58.041	371.052	321.047	200.020	−84.981	125.795	−1.643
4100	58.162	372.487	322.285	205.830	−85.303	131.069	−1.670
4200	58.289	373.890	323.497	211.653	−85.627	136.350	−1.696
4300	58.421	375.263	324.685	217.488	−85.950	141.639	−1.721
4400	58.559	376.608	325.849	223.337	−86.270	146.935	−1.744
4500	58.701	377.926	326.992	229.200	−86.585	152.239	−1.767
4600	58.849	379.217	328.113	235.078	−86.893	157.549	−1.789
4700	59.002	380.485	329.214	240.970	−87.194	162.867	−1.810
4800	59.160	381.728	330.295	246.878	−87.484	168.190	−1.830
4900	59.322	382.950	331.358	252.802	−87.763	173.520	−1.850
5000	59.488	384.150	332.401	258.743	−88.029	178.855	−1.868
5100	59.659	385.330	333.428	264.700	−88.281	184.195	−1.887
5200	59.833	386.490	334.437	270.675	−88.518	189.540	−1.904
5300	60.011	387.631	335.430	276.667	−88.739	194.890	−1.921
5400	60.191	388.755	336.407	282.677	−88.942	200.243	−1.937
5500	60.375	389.861	337.369	288.705	−89.128	205.600	−1.953
5600	60.560	390.950	338.316	294.752	−89.295	210.960	−1.968
5700	60.747	392.024	339.249	300.817	−89.444	216.323	−1.982
5800	60.935	393.082	340.168	306.901	−89.572	221.689	−1.997
5900	61.124	394.125	341.074	313.004	−89.681	227.056	−2.010
6000	61.314	395.154	341.966	319.126	−89.771	232.425	−2.023

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

Chlorine Fluoride (ClF) IDEAL GAS $M_r = 54.451403$ Chlorine Fluoride (ClF) $Cl_1F_1(g)$

$S°(298.15\ K) = 217.938\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -50.197 \pm 0.42\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -50.292 \pm 0.42\ kJ{\cdot}mol^{-1}$

Electronic States and Molecular Constants ($\sigma = 1$)

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
X $^1\Sigma^+$	0	1	784.49	6.201	0.51409	0.004329	1.6281
A $^3\Pi_0$	18721	6	312.74	2.207	0.37026	0.01390	1.92

Enthalpy of Formation

The selected value, $\Delta_fH°(ClF, 298.15\ K) = -12.02 \pm 0.1\ kcal{\cdot}mol^{-1}$, is based on spectroscopic data. Three studies of the visible absorption bands of ClF, by Wahrahftig,[1] by Schmitz and Schumacher,[2] and by Stricker[3] agree in indicating a band convergence limit at 21,514 ± 10 cm^{-1}. Assignment of this limit to $Cl(^2P_{1/2}) + F(^2P_{3/2})$ is supported by the dissociative ionization threshold for ClF reported by Dibeler *et al.*[4] whose ion–pair threshold, when reassigned to a hot band, corroborates this choice. From this assignment it follows that $D_0°(ClF) = 58.98 \pm 0.02\ kcal{\cdot}mol^{-1}$.

Combining this value with $D_0°(F_2) = 36.7 \pm 0.2\ kcal{\cdot}mol^{-1}$, reported by Berkowitz *et al.*,[5] and with $D_0°(Cl_2) = 57.177 \pm 0.006\ kcal{\cdot}mol^{-1}$, given by Douglas *et al.*,[6] one obtains $\Delta_fH°(ClF, 0\ K) = -12.0 \pm 0.1\ kcal{\cdot}mol^{-1}$ ($-50.200 \pm 0.42\ kJ{\cdot}mol^{-1}$).

Calorimetric values for $\Delta_fH°(298.15\ K)$, which bracket the selected value, are as follows: $-11.6\ kcal{\cdot}mol^{-1}$, Wicke;[7] $-11.7\ kcal{\cdot}mol^{-1}$, Wicke and Friz;[8] -14.34 and $-15.0\ kcal{\cdot}mol^{-1}$, Schmitz and Schumacher;[9] and $-14.4 \pm 0.8\ kcal{\cdot}mol^{-1}$, Nuttall and Armstrong.[10]

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels are taken from Rosen[11] and are adjusted to $Cl^{35} = 75.4\%$ and $Cl^{37} = 24.6\%$. The value of α_e listed for the ground state by Rosen[11] has been divided by 10 to agree with the original data.[12] The National Bureau of Standards prepared this table[13] by critical analysis of data existing is 1972 but used the incorrect value[11] for α_e of the ground state. Using the correct molecular constants and $\Delta_fH°$ selected by NBS,[13] we recalculate the table in terms of 1973 fundamental constants,[14] 1975 atomic weights,[15] and current JANAF reference states for the elements. The thermodyanmic functions of this table may be biased at temperatures above about 3000 K due to neglect of rotational cut–off.

References

[1] A. L. Wahrhaftig, J. Chem. Phys. 10, 248 (1942).
[2] H. Schmitz and H. J. Schumacher, Z. Naturforsch. 29, 359 (1947).
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[12] D. A. Gilbert, A. Roberts, and P. A. Griswold, Phys. Rev. 76, 1723 (1949).
[13] S. Abramowitz *et al.*, U. S. Nat. Bur. Stand. Report 10904, 239, (1972).
[14] CODATA Task Group on Fundamental Constants, CODATA Bulletin 11, (December 1973).
[15] IUPAC Commission on Atomic Weights, Pure and Applied Chem. 47, 75 (1976).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−8.908	−50.197	−50.197	INFINITE
100	29.124	185.156	245.153	−6.000	−50.198	−50.745	26.506
200	30.126	205.546	220.809	−3.052	−50.234	−51.282	13.393
298.15	32.082	217.938	217.938	0.	−50.292	−51.784	9.072
300	32.118	218.136	217.939	0.059	−50.293	−51.793	9.018
400	33.751	227.613	219.220	3.358	−50.339	−52.285	6.828
500	34.866	235.273	221.689	6.792	−50.373	−52.768	5.513
600	35.619	241.700	224.503	10.319	−50.399	−53.244	4.635
700	36.143	247.233	227.364	13.908	−50.421	−53.717	4.008
800	36.522	252.085	230.157	17.542	−50.442	−54.186	3.538
900	36.807	256.404	232.838	21.210	−50.462	−54.653	3.172
1000	37.030	260.294	235.392	24.902	−50.483	−55.117	2.879
1100	37.210	263.832	237.819	28.614	−50.506	−55.580	2.639
1200	37.360	267.076	240.124	32.343	−50.531	−56.040	2.439
1300	37.487	270.072	242.314	36.085	−50.559	−56.498	2.270
1400	37.598	272.854	244.397	39.840	−50.591	−56.953	2.125
1500	37.697	275.451	246.382	43.605	−50.627	−57.407	1.999
1600	37.788	277.887	248.275	47.379	−50.667	−57.857	1.889
1700	37.873	280.181	250.085	51.162	−50.711	−58.305	1.792
1800	37.956	282.348	251.818	54.953	−50.758	−58.751	1.705
1900	38.040	284.402	253.479	58.753	−50.808	−59.193	1.627
2000	38.131	286.356	255.075	62.562	−50.858	−59.633	1.557
2100	38.233	288.219	256.609	66.380	−50.908	−60.071	1.494
2200	38.354	290.000	258.087	70.209	−50.954	−60.506	1.437
2300	38.500	291.708	259.512	74.051	−50.993	−60.939	1.384
2400	38.682	293.350	260.888	77.910	−51.020	−61.371	1.336
2500	38.908	294.934	262.218	81.789	−51.031	−61.802	1.291
2600	39.189	296.465	263.506	85.694	−51.018	−62.233	1.250
2700	39.535	297.950	264.754	89.629	−50.976	−62.665	1.212
2800	39.959	299.395	265.966	93.603	−50.895	−63.100	1.177
2900	40.470	300.806	267.143	97.624	−50.767	−63.538	1.144
3000	41.079	302.188	268.288	101.701	−50.580	−63.981	1.114
3100	41.796	303.547	269.404	105.843	−50.323	−64.432	1.086
3200	42.629	304.886	270.491	110.064	−49.983	−64.892	1.059
3300	43.587	306.212	271.554	114.373	−49.548	−65.364	1.035
3400	44.674	307.529	272.593	118.785	−49.004	−65.852	1.012
3500	45.894	308.842	273.610	123.312	−48.335	−66.356	0.990
3600	47.251	310.153	274.606	127.969	−47.528	−66.882	0.970
3700	48.742	311.468	275.585	132.767	−46.567	−67.433	0.952
3800	50.365	312.789	276.547	137.721	−45.437	−68.012	0.935
3900	52.115	314.120	277.493	142.844	−44.125	−68.622	0.919
4000	53.983	315.462	278.425	148.148	−42.617	−69.269	0.905
4100	55.960	316.819	279.345	153.645	−40.900	−69.956	0.891
4200	58.032	318.193	280.254	159.343	−38.964	−70.688	0.879
4300	60.184	319.583	281.152	165.254	−36.797	−71.469	0.868
4400	62.399	320.992	282.042	171.382	−34.392	−72.302	0.858
4500	64.658	322.420	282.923	177.735	−31.743	−73.193	0.850
4600	66.941	323.866	283.797	184.315	−28.845	−74.146	0.842
4700	69.228	325.330	284.665	191.123	−25.697	−75.164	0.835
4800	71.496	326.811	285.528	198.160	−22.297	−76.252	0.830
4900	73.725	328.308	286.386	205.421	−18.649	−77.413	0.825
5000	75.895	329.820	287.239	212.903	−14.757	−78.652	0.822
5100	77.985	331.344	288.089	220.597	−10.628	−79.970	0.819
5200	79.978	332.877	288.936	228.497	−6.269	−81.372	0.817
5300	81.858	334.419	289.779	236.589	−1.691	−82.860	0.817
5400	83.612	335.965	290.620	244.864	3.094	−84.436	0.817
5500	85.226	337.515	291.459	253.307	8.073	−86.102	0.818
5600	86.694	339.064	292.295	261.904	13.232	−87.861	0.820
5700	88.007	340.610	293.129	270.641	18.555	−89.713	0.822
5800	89.163	342.151	293.961	279.500	24.027	−91.660	0.825
5900	90.160	343.684	294.791	288.468	29.633	−93.702	0.830
6000	90.999	345.206	295.618	297.527	35.355	−95.841	0.834

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

Lithium Chlorofluoride (Li_2ClF) IDEAL GAS M_r = 68.333403 Lithium Chloride Fluoride (Li_2ClF) $Cl_1F_1Li_2(g)$

$S°(298.15\ K) = 267.931\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -749.128\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [-753.957]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is from NBS.[1]

Heat Capacity and Entropy

Data is from Koppang *et. al.*[2]

References

[1] U.S. National Bureau of Standards Report No. 6297, "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine (Revised)," (January 1959).

[2] R. R. Koppang, C. M. Sherwood, and G. S. Bahn, "Some Provisional Tables of Species Thermodynamic Properties" Marquardt Corp., Van Nuys, California., (October 1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−13.422	−749.132	−749.132	INFINITE
100	35.723	215.376	315.709	−10.033	−749.642	−751.742	392.670
200	51.877	245.279	273.438	−5.632	−751.907	−752.971	196.656
298.15	62.839	268.040	268.040	0.	−753.957	−753.043	131.930
300	62.986	268.429	268.041	0.116	−753.992	−753.038	131.116
400	69.601	287.518	270.599	6.768	−755.887	−752.436	98.258
500	73.601	303.506	275.626	13.940	−764.049	−750.717	78.427
600	76.128	317.161	281.439	21.433	−766.074	−747.856	65.107
700	77.801	329.029	287.408	29.134	−767.836	−744 677	55.568
800	78.948	339.496	293.278	36.974	−769.442	−741.258	48.399
900	79.772	348.845	298.942	44.912	−770.974	−737.642	42.812
1000	80.383	357.282	304.361	52.921	−772.451	−733.859	38.333
1100	80.759	364.961	309.526	60.978	−773.891	−729.930	34.661
1200	81.096	372.003	314.443	69.071	−775.303	−725.871	31.596
1300	81.396	378.506	319.124	77.196	−776.694	−721.695	28.998
1400	81.657	384.548	323.584	85.349	−778.059	−717.413	26.767
1500	81.881	390.190	327.839	93.526	−779.398	−713.034	24.830
1600	82.014	395.478	331.903	101.721	−780.716	−708.567	23.132
1700	82.136	400.454	335.790	109.929	−1072.490	−689.665	21.191
1800	82.245	405.152	339.514	118.148	−1072.271	−667.153	19.360
1900	82.343	409.601	343.087	126.378	−1072.054	−644.652	17.723
2000	82.429	413.827	346.519	134.616	−1071.842	−622.163	16.249
2100	82.488	417.851	349.821	142.862	−1071.637	−599.684	14.916
2200	82.543	421.689	353.001	151.114	−1071.441	−577.215	13.705
2300	82.593	425.359	356.068	159.371	−1071.255	−554.754	12.599
2400	82.639	428.876	359.029	167.632	−1071.082	−532.301	11.585
2500	82.680	432.250	361.891	175.898	−1070.924	−509.855	10.653
2600	82.712	435.493	364.660	184.168	−1070.782	−487.415	9.792
2700	82.741	438.615	367.341	192.440	−1070.661	−464.980	8.996
2800	82.769	441.625	369.941	200.716	−1070.560	−442.550	8.256
2900	82.794	444.530	372.463	208.994	−1070.485	−420.122	7.567
3000	82.818	447.337	374.912	217.275	−1070.435	−397.697	6.925
3100	82.838	450.053	377.293	225.558	−1070.415	−375.273	6.323
3200	82.857	452.683	379.608	233.842	−1070.427	−352.849	5.760
3300	82.874	455.233	381.861	242.129	−1070.471	−330.424	5.230
3400	82.891	457.708	384.056	250.417	−1070.551	−307.997	4.732
3500	82.906	460.111	386.194	258.707	−1070.669	−285.567	4.262
3600	82.919	462.446	388.280	266.998	−1070.825	−263.133	3.818
3700	82.932	464 718	390.316	275.291	−1071.024	−240.695	3.398
3800	82.944	466.930	392.303	283.585	−1071.265	−218.251	3.000
3900	82.954	469.085	394.244	291.880	−1071.550	−195.799	2.622
4000	82.965	471.185	396.141	300.176	−1071.882	−173.340	2.264
4100	82.973	473.234	397.997	308.472	−1072.263	−150.872	1.922
4200	82.981	475.234	399.812	316.770	−1072.694	−128.394	1.597
4300	82.988	477.186	401.589	325.069	−1073.177	−105.905	1.286
4400	82.995	479.094	403.329	333.368	−1073.673	−83.407	0.990
4500	83.002	480.959	405.033	341.668	−1074.247	−60.895	0.707
4600	83.009	482.784	406.704	349.968	−1074.881	−38.369	0.436
4700	83.015	484.569	408.341	358.269	−1075.573	−15.829	0.176
4800	83.021	486.317	409.948	366.571	−1076.325	6.726	−0.073
4900	83.027	488.029	411.524	374.874	−1077.140	29.298	−0.312
5000	83.031	489.706	413.071	383.176	−1078.019	51.887	−0.542
5100	83.035	491.350	414.590	391.480	−1078.954	74.494	−0.763
5200	83.039	492.963	416.081	399.784	−1079.969	97.120	−0.976
5300	83.042	494.545	417.547	408.088	−1081.056	119.767	−1.180
5400	83.045	496.097	418.987	416.392	−1082.220	142.435	−1.378
5500	83.048	497.621	420.403	424.697	−1083.463	165.125	−1.568
5600	83.051	499.117	421.795	433.002	−1084.788	187.838	−1.752
5700	83.054	500.587	423.165	441.307	−1086.199	210.576	−1.930
5800	83.056	502.032	424.512	449.612	−1087.698	233.339	−2.101
5900	83.059	503.451	425.838	457.918	−1089.289	256.129	−2.268
6000	83.061	504.847	427.143	466.224	−1090.974	278.947	−2.428

PREVIOUS: December 1960 (1 atm) CURRENT: December 1960 (1 bar)

Magnesium Chloride Fluoride (MgClF) IDEAL GAS $M_r = 78.756403$ Magnesium Chloride Fluoride (MgClF) $Cl_1F_1Mg_1(g)$

$\Delta_f H°(0\ K) = [-567.5 \pm 21]\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = [265.990]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-569.2 \pm 21]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[719](1)
[205](1)
[453](1)

Ground State Quantum Weight: [1] $\sigma = [1]$
Point Group: C_1
Bond Distances: Mg–Cl = [2.18] Å; Mg–F = [1.77] Å
Bond Angle: Cl–Mg–F = [170]°
Product of the Moments of Inertia: $I_A I_B I_C = [8.66593 \times 10^{-116}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation is based on an estimated $\Delta_r H°(298.15\ K) = 0$ for the reaction $MgCl_2(g) + MgF_2(g) \rightarrow 2MgClF(g)$, using $\Delta_f H°(298.15\ K) = -95.85$ and $-176.2\ kcal \cdot mol^{-1}$ for $MgCl_2(g)$ and $MgF_2(g)$, respectively.

Heat Capacity and Entropy

The bond angle is taken to be the value we have adopted for $MgCl_2(g)$. The Mg–Cl and Mg–F bond distances are assumed to be the same as those in $MgCl_2(g)$ and $MgF_2(g)$. The vibrational frequencies are the averages of those for $MgCl_2(g)$ and $MgF_2(g)$. The principal moments of inertia are: $I_A = 0.0766 \times 10^{-39}$, $I_B = 33.5997 \times 10^{-39}$ and $I_C = 33.6763 \times 10^{-39}\ g \cdot cm^2$.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−12.330	−567.533	−567.533	INFINITE
100	38.027	218.339	306.941	−8.860	−567.615	−570.529	298.014
200	45.162	246.994	270.419	−4.685	−568.430	−573.138	149.688
250	47.875	257.375	266.801	−2.356	−568.833	−574.269	119.987
298.15	49.911	265.990	265.990	.000	−569.204	−575.282	100.787
300	49.979	266.299	265.991	.092	−569.218	−575.319	100.172
350	51.581	274.129	266.605	2.633	−569.593	−576.306	86.009
400	52.798	281.100	267.989	5.244	−569.966	−577.240	75.380
450	53.732	287.375	269.801	7.908	−570.344	−578.127	67.107
500	54.455	293.075	271.847	10.614	−570.731	−578.971	60.485
600	55.478	303.101	276.244	16.114	−571.551	−580.543	50.541
700	56.142	311.706	280.710	21.698	−572.452	−581.971	43.427
800	56.595	319.234	285.064	27.336	−573.456	−583.264	38.083
900	56.915	325.920	289.239	33.012	−574.586	−584.424	33.919
1000	57.149	331.929	293.213	38.716	−584.451	−584.738	30.544
1100	57.326	337.384	296.984	44.440	−585.893	−584.696	27.765
1200	57.461	342.378	300.562	50.180	−587.338	−584.524	25.444
1300	57.568	346.982	303.958	55.931	−588.788	−584.231	23.475
1400	57.653	351.252	307.186	61.693	−717.653	−580.658	21.665
1500	57.723	355.232	310.257	67.461	−717.764	−570.869	19.879
1600	57.780	358.959	313.186	73.237	−717.881	−561.072	18.317
1700	57.827	362.463	315.983	79.017	−718.007	−551.268	16.938
1800	57.867	365.770	318.658	84.802	−718.139	−541.456	15.713
1900	57.901	368.899	321.220	90.590	−718.279	−531.637	14.616
2000	57.930	371.870	323.679	96.382	−718.426	−521.809	13.628
2100	57.955	374 697	326.042	102.176	−718.578	−511.975	12.735
2200	57.976	377.394	328.315	107.973	−718.736	−502.133	11.922
2300	57.995	379.971	330.506	113.771	−718.898	−492.284	11.180
2400	58.012	382.440	332.618	119.572	−719.065	−482.428	10.500
2500	58.027	384.808	334.659	125.374	−719.234	−472.564	9.874
2600	58.040	387.084	336.632	131.177	−719.407	−462.694	9.296
2700	58.051	389.275	338.541	136.981	−719.581	−452.817	8.760
2800	58.062	391.387	340.391	142.787	−719.758	−442.934	8.263
2900	58.071	393.424	342.185	148.594	−719.936	−433.044	7.800
3000	58.080	395.393	343.926	154.401	−720.117	−423.148	7.368
3100	58.087	397.298	345.617	160.210	−720.299	−413.246	6.963
3200	58.094	399.142	347.261	166.019	−720.484	−403.338	6.584
3300	58.101	400.930	348.860	171.829	−720.671	−393.424	6.227
3400	58.106	402.664	350.417	177.639	−720.861	−383.505	5.892
3500	58.112	404.349	351.934	183.450	−721.056	−373.580	5.575
3600	58.117	405.986	353.413	189.261	−721.254	−363.649	5.276
3700	58.121	407.578	354.856	195.073	−721.458	−353.713	4.994
3800	58.125	409.128	356.264	200.885	−721.669	−343.771	4.725
3900	58.129	410.638	357.639	206.698	−721.886	−333.824	4.471
4000	58.133	412.110	358.982	212.511	−722.112	−323.871	4.229
4100	58.136	413.545	360.295	218.325	−722.348	−313.912	3.999
4200	58.139	414.946	361.580	224.138	−722.594	−303.947	3.780
4300	58.142	416.314	362.837	229.952	−722.852	−293.976	3.571
4400	58.144	417.651	364.068	235.767	−723.123	−283.999	3.371
4500	58.147	418.958	365.273	241.581	−723.409	−274 016	3.181
4600	58.149	420.236	366.454	247.396	−723.710	−264.026	2.998
4700	58.151	421.486	367.612	253.211	−724.029	−254.029	2.823
4800	58.153	422.711	368.747	259.026	−724.366	−244.026	2.656
4900	58.155	423.910	369.860	264.842	−724.724	−234.015	2.495
5000	58.157	425.085	370.953	270.657	−725.103	−223.997	2.340
5100	58.159	426.236	372.026	276.473	−725.505	−213.971	2.192
5200	58.160	427.366	373.079	282.289	−725.932	−203.937	2.049
5300	58.162	428.474	374.114	288.105	−726.383	−193.894	1.911
5400	58.163	429.561	375.131	293.922	−726.863	−183.843	1.778
5500	58.165	430.628	376.130	299.738	−727.370	−173.782	1.650
5600	58.166	431.676	377.113	305.554	−727.908	−163.712	1.527
5700	58.167	432.706	378.079	311.371	−728.477	−153.632	1.408
5800	58.168	433.717	379.030	317.188	−729.079	−143.542	1.293
5900	58.169	434.712	379.965	323.005	−729.716	−133.441	1.181
6000	58.170	435.689	380.886	328.822	−730.387	−123.329	1.074

PREVIOUS· March 1966 (1 atm) CURRENT: March 1966 (1 bar)

Sulfuryl Chloride Fluoride (SO_2ClF) IDEAL GAS $M_r = 118.510203$

$S°(298.15\ K) = 302.849 \pm 1.7\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [-549.1 \pm 21]\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [-556.5 \pm 21]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1228(1)	510(1)	1467(1)
824(1)	423(1)	474(1)
629(1)	300(1)	308(1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: S–O = [1.404] Å; S–F = [1.530] Å; S–Cl = [2.011] Å
Bond Angles: O–S–O = [123.5]° Cl–S–F = [98.06]°
Product of the Moments of Inertia: $I_AI_BI_C = [1.40403 \times 10^{-113}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

$\Delta_fH°$ is estimated as the mean of the $\Delta_fH°$ values[1] for $SO_2F_2(g)$ and $SO_2Cl_2(g)$. This corresponds to use of the mean bond energies, $D_0°(S–F) = 74$ and $D_0°(S–Cl) = 36\ kcal{\cdot}mol^{-1}$, from SO_2F_2 and SO_2Cl_2, respectively. The resulting values of $\Delta_fG°$ are consistent with those methods of preparation for which thermodynamic tests are possible. Insufficient data preclude tests for preparation of SO_2ClF from AgF_2, CoF_3, MnF_3 and SbF_3. In other cases the tests are not stringent, since the calculated values of $\Delta_fG°$ are large and negative for the observed reactions.

Heat Capacity and Entropy

The point group and symmetry number are consistent with analysis of the spectral data, but the detailed structure is estimated from known coordinates of SO_2Cl in SO_2Cl_2[1,2] and SF in SO_2F_2.[1,3] This estimate should be quite reliable since the SO_2 coordinates are almost identical in SO_2Cl_2 and SO_2F_2. The resulting structure has an O–S–Cl angle of 107.7°, an O–S–F angle of 108.4° and pricipal moments of inertia of $I_A = 16.4743 \times 10^{-39}$, $I_B = 29.0842 \times 10^{-39}$ and $I_C = 29.3031 \times 10^{-39}\ g{\cdot}cm^2$.

Vibrational frequencies are based on infrared spectra of the vapor[4] and confirmed by Raman spectra of the liquid.[5] Birchall and Gillespie[4] assigned δ(FSCl) to a weak Raman band at 195 cm^{-1}, but force–constant calculations based on SO_2Cl_2 and SO_2F_2 predict a value near 300 cm^{-1}.[1,6,7] It appears that the twist(FSCl) and δ(FSCl) are nearly accidentally degenerate, so we assign them arbitrarily to the Raman band at 308 cm^{-1} and the infrared band at 300 cm^{-1}. The adopted assignments are those of Toyuki and Shimizu[6] and Pfeiffer.[7] All adopted values lie between the analogous modes for SO_2Cl_2 and $SO_2F_2{\cdot}\delta(FSCl) = 195$ cm^{-1} is unlikely since it would lie below δ(ClSCl) = 209 cm^{-1} in SO_2Cl_2; also the intensity of such bending modes should be strong not weak.[7]

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Sulfuryl Chloride Fluoride (SO_2ClF) $Cl_1F_1O_2S_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−14.701	−549.075	−549.075	INFINITE
100	38.907	244.096	356.685	−11.259	−552.137	−539.994	282.064
200	57.944	276.982	308.997	−6.403	−554.817	−526.728	137.567
250	65.602	290.764	303.995	−3.308	−555.760	−519.591	108.563
298.15	71.592	302.849	302.849	0.	−556.472	−512.558	89.798
300	71.799	303.292	302.850	0.133	−556.496	−512.285	89.197
350	76.869	314.753	303.744	3.853	−557.072	−504.869	75.348
400	81.066	325.300	305.788	7.805	−559.737	−497.292	64.940
450	84.571	335.057	308.505	11.949	−560.757	−489.433	56.812
500	87.514	344.124	311.619	16.253	−561.744	−481.452	50.297
600	92.099	360.508	318.431	25.246	−563.048	−465.260	40.505
700	95.414	374.968	325.496	34.630	−563.877	−448.892	33.497
800	97.855	387.876	332.501	44.300	−564.410	−432.426	28.235
900	99.686	399.512	339.311	54.181	−617.878	−414.825	24.076
1000	101.086	410.091	345.868	64.223	−616.868	−392.318	20.493
1100	102.174	419.779	352.153	74.388	−615.818	−369.913	17.566
1200	103.034	428.707	358.165	84.650	−614.746	−347.605	15.131
1300	103.724	436.983	363.914	94.989	−613.663	−325.387	13.074
1400	104.284	444.690	369.412	105.391	−612.580	−303.253	11.315
1500	104.745	451.902	374.673	115.843	−611.503	−281.196	9.792
1600	105.129	458.674	379.714	126.337	−610.438	−259.210	8.462
1700	105.451	465.058	384.548	136.866	−609.390	−237.291	7.291
1800	105.724	471.093	389.190	147.426	−608.362	−215.433	6.252
1900	105.957	476.816	393.652	158.010	−607.356	−193.631	5.323
2000	106.157	482.256	397.948	168.616	−606.373	−171.881	4.489
2100	106.331	487.439	402.087	179.240	−605.414	−150.180	3.736
2200	106.483	492.390	406.080	189.881	−604.479	−128.524	3.052
2300	106.616	497.126	409.936	200.536	−603.568	−106.910	2.428
2400	106.733	501.666	413.664	211.204	−602.680	−85.336	1.857
2500	106.837	506.025	417.272	221.883	−601.815	−63.798	1.333
2600	106.929	510.217	420.767	232.571	−600.971	−42.294	0.850
2700	107.012	514.254	424.155	243.268	−600.146	−20.822	0.403
2800	107.086	518.147	427.443	253.973	−599.340	0.620	−0.012
2900	107.153	521.906	430.636	264.685	−598.551	22.033	−0.397
3000	107.213	525.540	433.739	275.403	−597.778	43.419	−0.756
3100	107.268	529.056	436.757	286.127	−597.019	64.780	−1.092
3200	107.317	532.463	439.695	296.857	−596.272	86.116	−1.406
3300	107.363	535.766	442.557	307.591	−595.536	107.429	−1.700
3400	107.404	538.972	445.345	318.329	−594.809	128.720	−1.978
3500	107.442	542.086	448.065	329.071	−594.089	149.990	−2.238
3600	107.477	545.113	450.719	339.817	−593.376	171.240	−2.485
3700	107.509	548.058	453.310	350.567	−592.666	192.469	−2.717
3800	107.539	550.925	455.841	361.319	−591.960	213.680	−2.937
3900	107.567	553.719	458.315	372.074	−591.255	234.872	−3.146
4000	107.592	556.443	460.735	382.832	−590.550	256.045	−3.344
4100	107.616	559.100	463.102	393.593	−589.844	277.201	−3.532
4200	107.638	561.693	465.418	404.355	−589.136	298.340	−3.710
4300	107.658	564.226	467.687	415.120	−588.425	319.463	−3.881
4400	107.677	566.702	469.909	425.887	−587.709	340.568	−4.043
4500	107.695	569.122	472.087	436.656	−586.989	361.656	−4.198
4600	107.712	571.489	474.222	447.426	−586.264	382.729	−4.346
4700	107.728	573.806	476.317	458.198	−585.533	403.786	−4.488
4800	107.742	576.074	478.371	468.972	−584.797	424.828	−4.623
4900	107.756	578.295	480.388	479.747	−584.054	445.855	−4.753
5000	107.769	580.473	482.368	490.523	−583.306	466.866	−4.877
5100	107.782	582.607	484.313	501.300	−582.552	487.862	−4.997
5200	107.793	584.700	486.223	512.079	−581.793	508.842	−5.111
5300	107.804	586.753	488.101	522.859	−581.030	529.810	−5.222
5400	107.814	588.768	489.946	533.640	−580.262	550.761	−5.328
5500	107.824	590.747	491.761	544.422	−579.492	571.698	−5.430
5600	107.834	592.690	493.546	555.205	−578.718	592.623	−5.528
5700	107.842	594.598	495.302	565.989	−577.944	613.532	−5.622
5800	107.851	596.474	497.030	576.773	−577.169	634.430	−5.714
5900	107.859	598.318	498.732	587.559	−576.395	655.311	−5.802
6000	107.866	600.131	500.406	598.345	−575.623	676.182	−5.887

PREVIOUS: June 1971 (1 atm) CURRENT June 1971 (1 bar)

Perchloryl Fluoride (ClO_3F) IDEAL GAS M_r = 102.449603 Perchloryl Fluoride (ClO_3F) $Cl_1F_1O_3(g)$

$S°(298.15\ K) = 278.984 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -12.69 \pm 2.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -21.42 \pm 2.9\ kJ \cdot mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}	ν, cm^{-1}
1061(1)	1315(2)
715(1)	589(2)
549(1)	405(2)

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distances: F–Cl = [1.63] Å; O–Cl = [1.46] Å
Bond Angles: F–Cl–O = [95° 10']; O–Cl–O = [119° 12']
Product of the Moments of Inertia: $I_A I_B I_C = [4.29248 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Neugebauer and Margrave[1] measured the enthalpy of reaction of perchloryl fluoride and hydrogen.

$$ClO_3F(g) + 4H_2(g) = HF(aq., 0.6M) + HCl(aq, 0.6M) + 3H_2O(l)$$

The necessary, additional thermal data for the calculation of the enthalpy of formation was obtained by them from NBS.[2] Dibeler *et al.*[3] obtain a value of -5.3 ± 4 kcal·mol^{-1} from the observed appearance potential of Cl^+.

Heat Capacity and Entropy

The assignment of Lide and Mann,[4] based upon the infrared spectra of the gas is supported by the Raman measurements of Powell and Lippincott.[5]

The value of the spectroscopic constant B was obtained by Madden and Benedict[6] from a high resolution infrared spectrograph. The Cl–F bond distance was estimated assuming a single covalent bond with no ionic character as evidenced by the low dipole moment obtained by Maryott and Kreidler.[7] Electron spin resonance results are explained by Brownstein,[8] on the basis of a low dipole moment. The Cl–O distance was estimated to be that found in the chlorate ion, Pauling.[9] The resulting values of the bond angles and I_C are consistent with the measured I_B and the assumed bond lengths. The principal moments of inertia are: $I_A = I_B = [15.9597 \times 10^{-39}]$ and $I_C = [16.8522 \times 10^{-39}]\ g \cdot cm^2$.

A calorimetric entropy of 60.17 cal·K^{-1}·mol^{-1} at 226.48 K was obtained by Koehler and Giauque[10] for the ideal gas. If the lattice doesn't discriminate between F and O atoms then at 0 K a residual entropy of 2.75 cal·K^{-1}·mol^{-1} exists and the third law entropy would be 62.92 cal·K^{-1}·mol^{-1}. This value may be compared with 62.64 obtained statistically. The difference 0.3 cal·K^{-1}·mol^{-1} is within the range found for other molecules and explained on the basis of some discrimination in the lattice, see Koehler and Giauque,[10] for references.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.299	−12.693	−12.693	INFINITE
100	35.404	227.211	326.596	−9.939	−16.599	4.645	−2.426
200	50.513	256.003	284.485	−5.696	−19.707	27.199	−7.104
250	58.338	268.132	280.018	−2.971	−20.729	39.051	−8.159
298.15	64.924	278.984	278.984	0.	−21.422	50.632	−8.871
300	65.158	279.387	278.986	0.120	−21.444	51.079	−8.894
350	70.991	289.881	279.801	3.528	−21.905	63.206	−9.433
400	75.945	299.693	281.681	7.205	−22.161	75.384	−9.844
450	80.137	308.887	284.199	11.110	−22.253	87.584	−10.167
500	83.677	317.519	287.104	15.208	−22.215	99.788	−10.425
600	89.199	333.291	293.513	23.867	−21.848	124.159	−10.809
700	93.178	347.356	300.219	32.996	−21.212	148.446	−11.077
800	96 092	359.998	306.915	42.467	−20.401	172.629	−11.272
900	98.267	371.448	313.459	52.190	−19.473	196.703	−11.416
1000	99.922	381.891	319.788	62.103	−18.466	220.669	−11.527
1100	101.204	391.477	325.875	72.162	−17.406	244.532	−11.612
1200	102.214	400.328	331.716	82.335	−16.310	268.297	−11.679
1300	103.022	408.543	337.313	92.598	−15.193	291.969	−11.731
1400	103.677	416.202	342.678	102.934	−14.063	315.554	−11.773
1500	104.215	423.374	347.821	113.330	−12.930	339.058	−11.807
1600	104.662	430.115	352.756	123.774	−11.801	362.488	−11.834
1700	105.036	436.471	357.495	134.260	−10.680	385.846	−11.856
1800	105.353	442.484	362.051	144.779	−9.573	409.139	−11.873
1900	105.624	448.188	366.436	155.329	−8.482	432.371	−11.887
2000	105.857	453.612	370.660	165.903	−7.411	455.546	−11.898
2100	106.058	458.781	374.734	176.499	−6.361	478.668	−11.906
2200	106.234	463.719	378.668	187.114	−5.333	501.741	−11.913
2300	106.388	468.445	382.469	197.745	−4.329	524.767	−11.918
2400	106.524	472.976	386.146	208.391	−3.349	547.749	−11.921
2500	106.644	477.327	389.707	219.049	−2.393	570.692	−11.924
2600	106.751	481.512	393.158	229.719	−1.459	593.597	−11.926
2700	106.846	485.542	396.506	240.399	−0.548	616.467	−11.926
2800	106.932	489.430	399.755	251.088	0.341	639.303	−11.926
2900	107.009	493.183	402.913	261.785	1.210	662.107	−11.926
3000	107.079	496.812	405.982	272.489	2.059	684.883	−11.925
3100	107.142	500.324	408.969	283.201	2.891	707.630	−11.923
3200	107.199	503.727	411.878	293.918	3.706	730.350	−11.922
3300	107.252	507.026	414.711	304.640	4.507	753.045	−11.920
3400	107.300	510.229	417.474	315.368	5.296	775.716	−11.917
3500	107.344	513.340	420.169	326.100	6.074	798.364	−11.915
3600	107.384	516.364	422.799	336.836	6.843	820.990	−11.912
3700	107.421	519.307	425.368	347.577	7.604	843.594	−11.909
3800	107.455	522.172	427.878	358.321	8.361	866.180	−11.906
3900	107.487	524.964	430.331	369.068	9.114	888.745	−11.903
4000	107.516	527.686	432.731	379.818	9.865	911.289	−11.900
4100	107.544	530.341	435.080	390.571	10.615	933.815	−11.897
4200	107.569	532.933	437.379	401.327	11.367	956.323	−11.894
4300	107.593	535.464	439.631	412.085	12.121	978.814	−11.890
4400	107.615	537.938	441.837	422.845	12.879	1001.286	−11.887
4500	107.636	540.357	443.999	433.608	13.641	1023.740	−11.883
4600	107.655	542.723	446.120	444.372	14.408	1046.178	−11.880
4700	107.673	545.038	448.200	455.139	15.180	1068.600	−11.876
4800	107.690	547.305	450.241	465.907	15.959	1091.005	−11.873
4900	107.706	549.526	452.245	476.677	16.744	1113.395	−11.869
5000	107.721	551.702	454.212	487.448	17.534	1135.767	−11.865
5100	107.735	553.835	456.145	498.221	18.330	1158.124	−11.862
5200	107.748	555.927	458.044	508.995	19.132	1180.464	−11.858
5300	107.761	557.980	459.910	519.770	19.938	1202.791	−11.854
5400	107.773	559.994	461.745	530.547	20.747	1225.100	−11.850
5500	107.784	561.972	463.549	541.325	21.560	1247.395	−11.847
5600	107.795	563.914	465.324	552.104	22.373	1269.677	−11.843
5700	107.805	565.822	467.070	562.884	23.187	1291.942	−11.839
5800	107.815	567.697	468.789	573.665	23.999	1314.195	−11.836
5900	107.824	569.540	470.481	584.447	24.808	1336.431	−11.832
6000	107.832	571.352	472.148	595.230	25.612	1358.656	−11.828

PREVIOUS: March 1961 (1 atm) CURRENT. March 1961 (1 bar)

Phosphoryl Chloride Fluoride ($POClF_2$) IDEAL GAS $M_r = 120.422966$

$S°(298.15\ K) = 301.689\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-961.8]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-970.7]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
274(1)	424(2)	948(2)
410(1)	618(1)	1358(1)
895(1)		

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: P–Cl = 2.01 ± 0.04 Å; P–F = 1.51 ± 0.03 Å; P–O = 1.55 ± 0.03 Å
Bond Angles: F–P–F = 103°; F–P–Cl = 103°
Product of the Moments of Inertia: $I_A I_B I_C = 1.90249 \times 10^{-113}\ g\ cm^6$

Enthaply of Formation

The $\Delta_f H°(298.15\ K)$ of $POClF_2$ was estimated to be $-232\ kcal \cdot mol^{-1}$ from the $\Delta_f H°(298.15\ K)$ of POF_3 by assuming bond energies of 120 kcal for $D_0°(P\text{–}F)$ and 80 kcal for $D_0°(P\text{–}Cl)$. The $D_0°(P\text{–}F)$ and $D_0°(P\text{–}Cl)$ values were taken from Neale and Williams[1] and Neale *et al.*[2]

Essentially the same $\Delta_f H°(298.15\ K)$ may be obtained by assuming a $\Delta_r H° = 0$ for the following reaction: $POCl_3(g) + POF_3(g) \rightarrow POCl_2F(g) + POF_2Cl(g)$.

Heat Capacity and Entropy

The molecular constants were determined by Brockway and Beach[3] and by Williams *et al.*[4] Brockway and Beach[3] used electron diffraction. Williams *et al.*[4] measured microwave spectra. Brockway and Beach[3] assumed that the F–P–F and F–P–Cl angles were equal in POF_2Cl and $POFCl_2$. An analysis of Brockway and Beach's data by Williams *et al.*[4] indicates that the angles in POF_2Cl, $POFCl_2$, $POCl_3$, and POF_3 should be 103 rather than the reported 106 ± 3. The principal moments of inertia are: $I_A = 18.7062 \times 10^{-39}$, $I_B = 31.3539 \times 10^{-39}$, and $I_C = 32.4373 \times 10^{39}\ g \cdot cm^2$.
The Raman spectra and vibrational frequencies for POF_2Cl were reported by Delwaulle and Francois.[5] The frequencies were reassigned by Delwaulle and Francois.[6]

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Phosphoryl Chloride Fluoride ($POClF_2$) $Cl_1F_2O_1P_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.198	−961.769	−961.769	INFINITE
100	38.154	245.398	353.098	−10.770	−965.044	−952.662	497.620
200	55.039	277.016	307.567	−6.110	−968.551	−939.053	245.256
250	62.542	290.122	302.789	−3.167	−969.739	−931.537	194.634
298.15	68.838	301.689	301.689	0.	−970.688	−924.090	161.897
300	69.062	302.116	301.691	0.128	−970.721	−923.801	160.848
350	74.631	313.192	302.553	3.724	−972.247	−915.844	136.682
400	79.327	323.473	304.533	7.576	−972.964	−907.735	118.538
450	83.259	333.051	307.176	11.644	−973.527	−899.546	104.417
500	86.541	341.998	310.216	15.891	−973.963	−891.302	93.114
600	91.583	358.249	316.895	24.812	−974.544	−874.709	76.150
700	95.154	372.650	323.851	34.159	−974.844	−858.043	64.028
800	97.736	385.534	330.771	43.810	−974.953	−841.348	54.934
900	99.646	397.161	337.512	53.684	−974.929	−824 648	47.861
1000	101.088	407.738	344.014	63.724	−974.811	−807.955	42.203
1100	102.200	417.427	350.254	73.891	−974.626	−791.278	37.575
1200	103.073	426.358	356.228	84.156	−1037.967	−773.542	33.671
1300	103.768	434.637	361.945	94.499	−1036.928	−751.548	30.198
1400	104.331	442.348	367.416	104.905	−1035.873	−729.635	27.223
1500	104.792	449.563	372.655	115.362	−1034.810	−707.798	24.648
1600	105.174	456.338	377.675	125.861	−1033.744	−686.032	22.397
1700	105.495	462.725	382.492	136.395	−1032.679	−664.333	20.412
1800	105.765	468.762	387.119	146.958	−1031.618	−642.696	18.651
1900	105.996	474.487	391.568	157.547	−1030.564	−621.118	17.076
2000	106.194	479.929	395.851	168.157	−1029.516	−599.596	15.660
2100	106.366	485.115	399.979	178.785	−1028.476	−578.125	14.380
2200	106.516	490.066	403.962	189.429	−1027.441	−556.704	13.218
2300	106.646	494.804	407.810	200.087	−1026.411	−535.330	12.158
2400	106.762	499.345	411.530	210.758	−1025.383	−514.001	11.187
2500	106.864	503.706	415.130	221.439	−1024.357	−492.714	10.295
2600	106.955	507.899	418.618	232.130	−1023.330	−471.469	9.472
2700	107.036	511.937	422.000	242.830	−1022.300	−450.263	8.711
2800	107.108	515.831	425.282	253.537	−1021.264	−429.095	8.005
2900	107.174	519.591	428.469	264.251	−1020.221	−407.965	7.348
3000	107.233	523.225	431.568	274.972	−1019.168	−386.871	6.736
3100	107.287	526.742	434.581	285.698	−1018.103	−365.811	6.164
3200	107.335	530.149	437.515	296.429	−1017.024	−344.787	5.628
3300	107.380	533.453	440.372	307.165	−1015.930	−323.797	5.125
3400	107.420	536.659	443.157	317.905	−1014.817	−302.839	4.653
3500	107.458	539.773	445.874	328.649	−1013.685	−281.916	4.207
3600	107.492	542.801	448.524	339.396	−1012.532	−261.024	3.787
3700	107.523	545.746	451.112	350.147	−1011.357	−240.165	3.391
3800	107.552	548.614	453.640	360.901	−1010.157	−219.338	3.015
3900	107.579	551.408	456.112	371.657	−1008.931	−198.542	2.659
4000	107.604	554.132	458.528	382.416	−1007.679	−177.779	2.322
4100	107.627	556.790	460.893	393.178	−1006.398	−157.048	2.001
4200	107.649	559.384	463.207	403.942	−1005.089	−136.347	1.696
4300	107.669	561.917	465.473	414.708	−1003.750	−115.679	1.405
4400	107.688	564.392	467.693	425.476	−1002.381	−95.042	1.128
4500	107.705	566.812	469.869	436.245	−1000.980	−74.436	0.864
4600	107.721	569.180	472.002	447.017	−999.548	−53.863	0.612
4700	107.737	571.497	474.095	457.789	−998.084	−33.320	0.370
4800	107.751	573.765	476.148	468.564	−996.588	−12.808	0.139
4900	107.765	575.987	478.163	479.340	−995.060	7.672	−0.082
5000	107.777	578.164	480.141	490.117	−993.500	28.120	−0.294
5100	107.789	580.299	482.084	500.895	−991.909	48.536	−0.497
5200	107.801	582.392	483.993	511.675	−990.286	68.921	−0.692
5300	107.811	584.445	485.869	522.455	−988.632	89.275	−0.880
5400	107.821	586.461	487.713	533.237	−986.948	109.597	−1.060
5500	107.831	588.439	489.527	544.019	−985.234	129.887	−1.234
5600	107.840	590.382	491.310	554.803	−983.491	150.147	−1.401
5700	107.849	592.291	493.065	565.587	−981.720	170.374	−1.561
5800	107.857	594.167	494.792	576.373	−979.922	190.571	−1.716
5900	107.864	596.011	496.492	587.159	−978.098	210.736	−1.866
6000	107.872	597.824	498.166	597.946	−976.248	230.870	−2.010

PREVIOUS: March 1963 (1 atm) CURRENT: March 1963 (1 bar)

Chlorine Fluoride (ClF$_3$) IDEAL GAS M_r = 92.448209 Chlorine Fluoride (ClF$_3$) Cl$_1$F$_3$(g)

$\Delta_f H^\circ(0\ \text{K}) = -154.69 \pm 2.9\ \text{kJ·mol}^{-1}$

$S^\circ(298.15\ \text{K}) = 281.600\ \text{J·K}^{-1}\text{·mol}^{-1}$ $\Delta_f H^\circ(298.15\ \text{K}) = -158.87 \pm 2.9\ \text{kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
752 (1)	703 (1)
528 (1)	434 (1)
326 (1)	364 (1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2v}

Bond Distances: Cl–F$_1$ = Cl–F$_3$ = 1.698 Å; Cl–F$_2$ = 1.598 Å

Bond Angles: F$_1$–Cl–F$_2$ = F$_2$–Cl–F$_3$ = 87° 29'; F$_3$–Cl–F$_1$ = 185° 02'

Product of Moments of Inertia: $I_A I_B I_C = 2.69336 \times 10^{-114}\ \text{g}^3\text{·cm}^6$

Enthalpy of Formation

The $\Delta_f H^\circ(298.15\ \text{K}) = -37.97\ \text{kcal·mol}^{-1}$ was calculated from $\Delta_r H^\circ(298.15\ \text{K}) = 25.83\ \text{kcal·mol}^{-1}$ obtained by third law analysis of the equilibrium data of Schmitz and Schumacher[1] for the reaction ClF$_3$(g) = ClF(g) + F$_2$(g). Similar values are obtained from the equilibrium data of Schafer and Wicke.[2] Calorimetric values scatter widely, as summarized below; these were given little weight.

Source	Method	Reaction	Observation kcal·mol^{-1}	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H^\circ$(298.15 K) kcal·mol^{-1}
1a	K_p°(523–623 K)	$ClF_3(g) \rightarrow ClF(g) + F_2(g)$	$\Delta_r H^\circ$(298.15 K) = 25.83	0.8 ± 0.3	−37.97
2a	K_p°(733 K)	$ClF_3(g) \rightarrow ClF(g) + F_2(g)$	$\Delta_r H^\circ$(298.15 K) = 25.77	—	−37.91
2b	K_p°(570–680 K)	$ClF_3(g) \rightarrow ClF(g) + F_2(g)$	$\Delta_r H^\circ$(298.15 K) = 26.12	6 ± 3	−38.26
1b	Calorimetric	$3\ NaCl + ClF_3 \rightarrow 3\ NaF + 2\ Cl_2$	$\Delta_r H^\circ$(291 K) = −76.5		−40.02
1c	Calorimetric	$NaCl + 0.5\ F_2 = NaF + 0.5\ Cl_2$	$\Delta_r H^\circ$(291 K) = −39.5		−42.0*
3	Calorimetric	$3\ NaCl + ClF_3 \rightarrow 3\ NaF + 2\ Cl_2$	$\Delta_r H^\circ$(298.15 K) = −86.8		−29.7
4	Calorimetric	$0.5\ F_2 + NaCl \rightarrow NaF + 0.5\ Cl_2$	$\Delta_r H^\circ$(293 K) = −39.3		−31.1**
5	Flow Reaction	$0.5\ Cl_2(g) + 1.5\ F_2(g) = ClF_3(g)$	$\Delta_r H^\circ$(473 K) = −26.4		−26.4
		* from combination of 1b and 1c	**from combination of 3 and 4		

Heat Capacity and Entropy

The structural constants were obtained from the microwave study of Smith.[6] The planar distorted "T" structure is similar to that derived from X–ray studies of the solid by Burbank and Bensey.[7] Fundamental frequencies are taken from the infrared and Raman spectra of Claassen *et al.*[8] These data confirm the "T" structure as opposed to the pyramidal structure used in earlier spectral analyses.

Claassen *et al.*[8] calculate thermodynamic functions virtually identical with the JANAF values. These authors also correct the third law entropy reported by Grisard *et al.*[9] from measurements of heat capacity (14–285 K) and vapor pressure (226–303 K). The entropy at the normal boiling point becomes $S^\circ(284.91\ \text{K}) = 67.04\ \text{kcal·mol}^{-1}$ when a non-ideality correction consistent with the dimer–monomer vapor equilibrium is applied. The corresponding statistical entropy, $S^\circ(284.91\ \text{K}) = 66.59\ \text{kcal·mol}^{-1}$, is consistent with the third law value within the probable error in the entropy of the liquid and the entrophy of vaporization. The principal moments of inertia are: $I_A = 6.1123 \times 10^{-39}$, $I_B = 18.1568 \times 10^{-39}$ and $I_C = 24.2691 \times 10^{-39}\ \text{g·cm}^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K$_f$
0	0.	0.	INFINITE	−13.648	−154.687	−154.687	INFINITE
100	37.121	227.838	330.328	−10.249	−157.104	−144.882	75.679
200	52.643	258.307	287.119	−5.762	−158.530	−131.999	34.475
250	59.050	270.771	282.625	−2.964	−158.794	−125.331	26.187
298.15	63.845	281.600	281.600	0.	−158.866	−118.877	20.827
300	64.005	281.995	281.601	0.118	−158.867	−118.629	20.655
350	67.760	292.157	282.395	3.417	−158.811	−111.926	16.704
400	70.605	301.399	284.202	6.879	−158.669	−105.237	13.743
450	72.781	309.847	286.589	10.466	−158.471	−98.569	11.442
500	74.465	317.606	289.308	14.149	−158.234	−91.926	9.603
600	76.839	331.409	295.203	21.723	−157.686	−78.715	6.853
700	78.380	343.377	301.249	29.489	−157.083	−65.600	4.895
800	79.428	353.916	307.187	37.383	−156.453	−52.574	3.433
900	80.170	363.317	312.911	45.365	−155.813	−39.627	2.300
1000	80.713	371.793	318.382	53.410	−155.171	−26.752	1.397
1100	81.121	379.506	323.594	61.503	−154.533	−13.941	0.662
1200	81.435	386.578	328.552	69.631	−153.904	−1.188	0.052
1300	81.681	393.106	333.270	77.788	−153.288	11.513	−0.463
1400	81.879	399.167	337.763	85.966	−152.687	24.168	−0.902
1500	82.039	404.822	342.047	94.162	−152.102	36.780	−1.281
1600	82.171	410.121	346.138	102.373	−151.534	49.353	−1.611
1700	82.280	415.106	350.050	110.596	−150.984	61.892	−1.902
1800	82.372	419.812	353.796	118.828	−150.449	74.398	−2.159
1900	82.451	424.267	357.389	127.070	−149.930	86.875	−2.388
2000	82.517	428.498	360.839	135.318	−149.421	99.326	−2.594
2100	82.575	432.526	364.158	143.573	−148.922	111.751	−2.780
2200	82.625	436.368	367.353	151.833	−148.426	124.152	−2.948
2300	82.669	440.042	370.434	160.098	−147.931	136.531	−3.101
2400	82.708	443.561	373.409	168.367	−147.431	148.888	−3.240
2500	82.742	446.938	376.283	176.639	−146.923	161.224	−3.369
2600	82.772	450.184	379.063	184.915	−146.402	173.540	−3.486
2700	82.799	453.308	381.755	193.193	−145.863	185.835	−3.595
2800	82.823	456.320	384.365	201.474	−145.302	198.110	−3.696
2900	82.844	459.227	386.897	209.758	−144.717	210.365	−3.789
3000	82.864	462.036	389.355	218.043	−144.102	222.599	−3.876
3100	82.882	464.753	391.743	226.331	−143.455	234.811	−3.957
3200	82.898	467.385	394.066	234.620	−142.773	247.003	−4.032
3300	82.912	469.936	396.327	242.910	−142.053	259.172	−4.102
3400	82.926	472.411	398.528	251.202	−141.293	271.319	−4.168
3500	82.938	474.815	400.674	259.495	−140.490	283.443	−4.230
3600	82.949	477.152	402.766	267.790	−139.643	295.544	−4.288
3700	82.960	479.425	404.807	276.085	−138.750	307.620	−4.343
3800	82.969	481.637	406.800	284.381	−137.809	319.671	−4.394
3900	82.978	483.792	408.747	292.679	−136.819	331.698	−4.443
4000	82.986	485.893	410.649	300.977	−135.778	343.698	−4.488
4100	82.994	487.943	412.509	309.276	−134.687	355.671	−4.531
4200	83.001	489.943	414.329	317.576	−133.544	367.618	−4.572
4300	83.007	491.896	416.111	325.876	−132.349	379.536	−4.610
4400	83.014	493.804	417.855	334.177	−131.101	391.426	−4.647
4500	83.019	495.670	419.563	342.479	−129.799	403.287	−4.681
4600	83.025	497.495	421.238	350.781	−128.444	415.119	−4.714
4700	83.030	499.280	422.879	359.084	−127.035	426.920	−4.745
4800	83.034	501.028	424.489	367.387	−125.573	438.691	−4.774
4900	83.039	502.740	426.069	375.691	−124.058	450.431	−4.802
5000	83.043	504.418	427.619	383.995	−122.489	462.140	−4.828
5100	83.047	506.063	429.141	392.299	−120.868	473.816	−4.853
5200	83.051	507.675	430.636	400.604	−119.195	485.461	−4.877
5300	83.054	509.257	432.104	408.909	−117.469	497.072	−4.899
5400	83.057	510.810	433.548	417.215	−115.693	508.651	−4.920
5500	83.060	512.334	434.966	425.521	−113.866	520.196	−4.940
5600	83.063	513.830	436.361	433.827	−111.988	531.708	−4.960
5700	83.066	515.301	437.733	442.134	−110.062	543.184	−4.978
5800	83.069	516.745	439.083	450.440	−108.087	554.628	−4.995
5900	83.071	518.165	440.412	458.747	−106.065	566.037	−5.011
6000	83.074	519.562	441.719	467.055	−103.996	577.411	−5.027

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

Chlorotrifluorosilane ($SiClF_3$) IDEAL GAS $M_r = 120.533709$ Chlorotrifluorosilane ($SiClF_3$) $Cl_1F_3Si_1(g)$

$S°(298.15 \text{ K}) = [308.68 \pm 16.7] \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = [-1314 \pm 63] \text{ kJ·mol}^{-1}$

$\Delta_f H°(298.15 \text{ K}) = [-1318 \pm 63] \text{ kJ·mol}^{-1}$

Vibrational Frequencies and Quantum Weights ν, cm^{-1}
[870](1)
[550](1)
[275](1)
[900](2)
[400](2)
[200](2)

Ground State Quantum Weight: 1 $\sigma = 3$

Point Group: C_{3v}

Product of the Moments of Intertia: $I_A I_B I_C = 29.869 \times 10^{-114} \text{ g}^3\text{·cm}^6$

Enthalpy of Formation

All data taken from Henderson and Scheffee.[1]

Heat Capacity and Entropy

All data is taken from Henderson and Scheffee.[1] The principal moments of inertia are: $I_A = [19.9 \times 10^{-39}]$, $I_B = [33.9 \times 10^{-39}]$ and $I_C = [39.9 \times 10^{-39}] \text{ g·cm}^2$.

Reference

[1] C. B. Henderson and R. S. Scheffee, "Survey of Thermochemical Data," Atlantic Research Corp., Alexandria, Va., (January 1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.612	−1313.526	−1313.526	INFINITE
100	46.502	240.797	369.839	−12.904	−1315.901	−1304.592	681.449
200	66.344	279.593	315.556	−7.193	−1317.280	−1292.674	337.612
250	73.615	295.204	309.955	−3.688	−1317.689	−1286.473	268.794
298.15	79.372	308.679	308.679	0.	−1317.960	−1280.434	224.327
300	79.571	309.171	308.681	0.147	−1317.968	−1280.201	222.903
350	84.392	321.812	309.668	4.250	−1318.142	−1273.891	190.118
400	88.261	333.343	311.918	8.570	−1318.230	−1267.563	165.527
450	91.361	343.925	314.894	13.064	−1318.250	−1261.227	146.399
500	93.851	353.684	318.292	17.696	−1318.216	−1254.893	131.098
600	97.504	371.141	325.680	27.276	−1318.039	−1242.243	108.147
700	99.969	386.368	333.286	37.158	−1317.768	−1229.631	91.756
800	101.689	399.836	340.779	47.246	−1317.454	−1217.061	79.466
900	102.929	411.889	348.022	57.480	−1317.123	−1204.531	69.909
1000	103.847	422.783	354.962	67.821	−1316.796	−1192.039	62.266
1100	104.544	432.715	361.586	78.242	−1316.486	−1179.578	56.014
1200	105.085	441.836	367.899	88.724	−1316.202	−1167.145	50.804
1300	105.512	450.264	373.914	99.255	−1315.952	−1154.734	46.398
1400	105.855	458.097	379.651	109.824	−1315.742	−1142.341	42.621
1500	106.134	465.410	385.127	120.424	−1315.578	−1129.961	39.349
1600	106.365	472.267	390.361	131.049	−1315.461	−1117.590	36.486
1700	106.557	478.721	395.371	141.695	−1365.572	−1104.779	33.946
1800	106.719	484.817	400.172	152.359	−1365.326	−1089.445	31.615
1900	106.857	490.590	404.781	163.038	−1365.089	−1074.125	29.530
2000	106.975	496.074	409.209	173.730	−1364.857	−1058.817	27.653
2100	107.077	501.296	413.471	184.433	−1364.628	−1043.521	25.956
2200	107.165	506.280	417.577	195.145	−1364.401	−1028.235	24.413
2300	107.243	511.045	421.538	205.865	−1364.169	−1012.960	23.005
2400	107.311	515.611	425.364	216.593	−1363.930	−997.695	21.714
2500	107.371	519.993	429.062	227.327	−1363.680	−982.441	20.527
2600	107.424	524.205	432.641	238.067	−1363.414	−967.196	19.431
2700	107.472	528.260	436.107	248.812	−1363.129	−951.962	18.417
2800	107.515	532.169	439.469	259.561	−1362.820	−936.740	17.475
2900	107.553	535.943	442.731	270.315	−1362.483	−921.528	16.599
3000	107.588	539.590	445.899	281.072	−1362.117	−906.329	15.781
3100	107.620	543.118	448.978	291.832	−1361.716	−891.143	15.016
3200	107.648	546.535	451.974	302.596	−1361.279	−875.970	14.299
3300	107.674	549.848	454.890	313.362	−1360.803	−860.811	13.626
3400	107.698	553.063	457.730	324.131	−1360.286	−845.668	12.992
3500	107.720	556.185	460.499	334.902	−1359.725	−830.540	12.395
3600	107.740	559.220	463.199	345.675	−1743.271	−804.968	11.680
3700	107.758	562.172	465.834	356.449	−1742.203	−778.918	10.996
3800	107.775	565.046	468.408	367.226	−1741.089	−752.899	10.349
3900	107.791	567.846	470.922	378.005	−1739.927	−726.909	9.736
4000	107.806	570.575	473.379	388.784	−1738.715	−700.949	9.153
4100	107.819	573.237	475.782	399.566	−1737.452	−675.021	8.600
4200	107.832	575.836	478.134	410.348	−1736.138	−649.123	8.073
4300	107.843	578.373	480.435	421.132	−1734.770	−623.258	7.571
4400	107.854	580.852	482.689	431.917	−1733.349	−597.425	7.092
4500	107.865	583.276	484.898	442.703	−1731.874	−571.625	6.635
4600	107.874	585.647	487.062	453.490	−1730.345	−545.859	6.198
4700	107.883	587.967	489.185	464.278	−1728.762	−520.126	5.781
4800	107.891	590.239	491.266	475.066	−1727.125	−494.427	5.380
4900	107.899	592.463	493.309	485.856	−1725.434	−468.764	4.997
5000	107.907	594.643	495.314	496.646	−1723.688	−443.135	4.629
5100	107.914	596.780	497.283	507.437	−1721.890	−417.542	4.277
5200	107.920	598.876	499.216	518.229	−1720.038	−391.984	3.938
5300	107.927	600.931	501.116	529.021	−1718.134	−366.463	3.612
5400	107.932	602.949	502.983	539.814	−1716.179	−340.978	3.298
5500	107.938	604.929	504.819	550.608	−1714.172	−315.530	2.997
5600	107.943	606.874	506 624	561.402	−1712.116	−290.118	2.706
5700	107.948	608.785	508.400	572.196	−1710.010	−264.745	2.426
5800	107.953	610.662	510.147	582.992	−1707.858	−239.408	2.156
5900	107.958	612.508	511.866	593.787	−1705.658	−214.108	1.896
6000	107.962	614.322	513.559	604.583	−1703.412	−188.847	1.644

PREVIOUS December 1960 (1 atm) CURRENT: December 1960 (1 bar)

Chlorine Fluoride (ClF_5) IDEAL GAS $M_r = 130.445015$ Chlorine Fluoride (ClF_5) $Cl_1F_5(g)$

$S°(298.15\ K) = 310.739\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [-229.8 \pm 63]\ kJ{\cdot}mol^{-1}$

$\Delta_fH°(298.15\ K) = [-238.5 \pm 63]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
712(1)	488(1)	732 (2)
541(1)	346(1)	[440](2)
486(1)	375(1)	302 (2)

Ground State Quantum Weight: [1] $\sigma = 4$

Point Group: C_{4v}

Bond Distances: $(Cl–F)_{basal} = 1.72$ Å; $(Cl–F)_{axial} = 1.62$ Å

Bond Angle: F–Cl–F = 90°

Product of the Moments of Inertia: $I_AI_BI_C = 2.47347 \times 10^{-113}\ g^3{\cdot}cm^6$

Enthalpy of Formation

The heat of formation was estimated by assuming that the ratio [(A·B·E(ClF)–A·B·E(ClF_3))/[A·B·E(ClF_3)–A·B·E(ClF_5)] was equal to [A·B·E(BrF)–A·B·E(BrF_3)]/[A·B·E(BrF_3)–A·B·E(BrF_5)], where A·B·E represents average bond energy. All values were taken from these tables. A·B·E(ClF_5) was thus calculated to be 36 $kcal{\cdot}mol^{-1}$ which leads to $\Delta_fH° = -57 \pm 15\ kcal{\cdot}mol^{-1}$.

Heat Capacity and Entropy

Begun *et al.*[1] have reported the infrared spectra of the gas and the Raman spectra of the liquid. Their assignments have been adopted here, including one frequency ν_8 obtained from a valence force–field treatment. The values are consistent with those of $IF_5(g)$ and $BrF_5(g)$. Smith[2] had previously reported three infrared bands. The structure of the molecule has not been determined but the spectra can only be interpreted assuming C_{4v} symmetry, this is in accord with IF_5 and $BrF_5(g)$. Begun[1] assumed a square pyramidal structure with the chlorine in the base of the pyramid. There is some evidence that the chlorine may not lie in the basal plane but this would not appreciably affect the calculations. The structure adopted was that given by Begun *et al.*[1] The principal moments of inertia are $I_A = 37.3328 \times 10^{-39}$ and $I_B = I_C = 25.7400 \times 10^{-39}\ g{\cdot}cm^2$.

References

[1] G. M. Begun, W. H. Fletcher, and D. F. Smith, J. Chem. Phys. 42, 2236 (1965).

[2] D. F. Smith, Science 141, 1039 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−17.930	−229.765	−229.765	INFINITE
100	42.206	236.844	381.117	−14.427	−234.986	−206.628	107.931
200	75.005	276.255	319.001	−8.549	−237.949	−176.878	46.196
250	87.822	294.433	312.290	−4.464	−238.430	−161.544	33.753
298.15	97.165	310.739	310.739	0.	−238.488	−146.725	25.706
300	97.474	311.341	310.741	0.180	−238.484	−146.156	25.448
350	104.652	326.933	311.956	5.242	−238.254	−130.783	19.518
400	110.018	341.275	314.737	10.615	−237.832	−115.457	15.077
450	114.082	354.478	318.429	16.222	−237.281	−100.192	11.630
500	117.206	366.667	322.651	22.008	−236.639	−84.993	8.879
600	121.580	388.453	331.847	33.964	−235.183	−54.798	4.771
700	124.400	407.422	341.318	46.273	−233.589	−24.858	1.855
800	126.310	424.165	350.648	58.814	−231.922	4.847	−0.317
900	127.658	439.125	359.663	71.516	−230.215	34.341	−1.993
1000	128.641	452.628	368.295	84.333	−228.491	63.644	−3.324
1100	129.380	464.925	376.529	97.236	−226.763	92.774	−4.405
1200	129.948	476.208	384.372	110.204	−225.041	121.747	−5.299
1300	130.394	486.628	391.842	123.222	−223.332	150.576	−6.050
1400	130.751	496.305	398.962	136.280	−221.642	179.275	−6.689
1500	131.040	505.336	405.756	149.370	−219.974	207.853	−7.238
1600	131.277	513.801	412.247	162.486	−218.329	236.321	−7.715
1700	131.475	521.766	418.457	175.624	−216.709	264.687	−8.133
1800	131.641	529.285	424.408	188.780	−215.111	292.959	−8.501
1900	131.782	536.407	430.117	201.951	−213.533	321.141	−8.829
2000	131.902	543.169	435.602	215.135	−211.970	349.242	−9.121
2100	132.006	549.607	440.878	228.331	−210.417	377.264	−9.384
2200	132.097	555.750	445.961	241.536	−208.865	405.212	−9.621
2300	132.176	561.624	450.863	254.750	−207.310	433.091	−9.836
2400	132.245	567.251	455.596	267.971	−205.741	460.900	−10.031
2500	132.306	572.651	460.171	281.199	−204.152	488.645	−10.210
2600	132.361	577.841	464.598	294.432	−202.535	516.325	−10.373
2700	132.409	582.837	468.885	307.671	−200.883	543.942	−10.523
2800	132.452	587.653	473.041	320.914	−199.188	571.497	−10.661
2900	132.491	592.302	477.074	334.161	−197.444	598.991	−10.789
3000	132.527	596.794	480.990	347.412	−195.645	626.424	−10.907
3100	132.558	601.140	484.796	360.666	−193.786	653.795	−11.016
3200	132.587	605.349	488.498	373.923	−191.862	681.106	−11.118
3300	132.614	609.430	492.101	387.184	−189.868	708.356	−11.212
3400	132.638	613.389	495.611	400.446	−187.802	735.544	−11.300
3500	132.660	617.234	499.031	413.711	−185.659	762.670	−11.382
3600	132.680	620.972	502.367	426.978	−183.437	789.735	−11.459
3700	132.699	624.607	505.622	440.247	−181.135	816.736	−11.530
3800	132.716	628.146	508.800	453.518	−178.751	843.673	−11.597
3900	132.732	631.594	511.904	466.790	−176.282	870.547	−11.660
4000	132.747	634.955	514.939	480.064	−173.728	897.357	−11.718
4100	132.760	638.233	517.906	493.339	−171.089	924.101	−11.773
4200	132.773	641.432	520.809	506.616	−168.364	950.781	−11.825
4300	132.785	644.556	523.651	519.894	−165.552	977.393	−11.873
4400	132.796	647.609	526.433	533.173	−162.655	1003.940	−11.918
4500	132.806	650.593	529.159	546.453	−159.671	1030.421	−11.961
4600	132.816	653.512	531.831	559.734	−156.603	1056.833	−12.001
4700	132.825	656.369	534.451	573.016	−153.449	1083.178	−12.038
4800	132.833	659.165	537.020	586.299	−150.211	1109.456	−12.073
4900	132.841	661.904	539.541	599.583	−146.891	1135.665	−12.106
5000	132.849	664.588	542.015	612.867	−143.488	1161.804	−12.137
5100	132.856	667.219	544.444	626.153	−140.004	1187.876	−12.166
5200	132.862	669.799	546.830	639.438	−136.441	1213.879	−12.194
5300	132.869	672.330	549.174	652.725	−132.799	1239.812	−12.219
5400	132.875	674.813	551.478	666.012	−129.080	1265.675	−12.243
5500	132.880	677.252	553.743	679.300	−125.285	1291.468	−12.265
5600	132.885	679.646	555.970	692.588	−121.417	1317.194	−12.286
5700	132.891	681.998	558.160	705.877	−117.475	1342.847	−12.306
5800	132.895	684.309	560.315	719.166	−113.462	1368.432	−12.324
5900	132.900	686.581	562.436	732.456	−109.380	1393.948	−12.341
6000	132.904	688.815	564.524	745.746	−105.229	1419.392	−12.357

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

Sulfur Chloride Fluoride (SClF$_5$) IDEAL GAS M_r = 162.505015 Sulfur Chloride Fluoride (SClF$_5$) Cl$_1$F$_5$S$_1$(g)

$\Delta_fH°(0\ K) = -1026.3 \pm 10.5\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = 319.931 \pm 1.3\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -1038.9 \pm 10.5\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
855(1)	625 (1)	579(2)
707(1)	[332] (1)	441(2)
602(1)	505 (1)	287(2)
402(1)	909 (2)	

Ground State Quantum Weight: [1] $\sigma = 4$

Point Group = C_{4v}

Bond Distances: S–F* = 1.566 ± 0.003 Å; S–F** = 1.588 ± 0.009 Å

S–Cl = 2.047 ± 0.003 Å

Bond Angles: Cl–S–F* = 90.7 ± 0.2°; F*–S–F* = 90°

(* – equatorial ** – axial)

Product of Moments of Inertia: $I_AI_BI_C = 6.65952 \times 10^{-113}\ g^3\cdot cm^6$

Enthalpy Reference Temperature = T_r = 298.15 K						Standard State Pressure = $p°$ = 0.1 MPa	
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K$_f$
0	0.	0.	INFINITE	−18.458	−1026.280	−1026.280	INFINITE
100	42.459	243.875	393.298	−14.942	−1032.178	−1003.270	524.055
200	77.049	283.704	328.677	−8.995	−1036.714	−972.405	253.966
250	92.376	302.598	321.585	−4.747	−1038.051	−956.161	199.779
298.15	104.342	319.931	319.931	0.	−1038.887	−940.307	164.738
300	104.749	320.577	319.933	0.193	−1038.912	−939.696	163.616
350	114.465	337.485	321.246	5.684	−1039.419	−923.115	137.767
400	122.040	353.285	324.274	11.604	−1041.881	−906.393	118.363
450	127.964	368.015	328.326	17.860	−1042.606	−889.421	103.241
500	132.635	381.749	332.989	24.380	−1043.234	−872.363	91.135
600	139.350	406.569	343.230	38.003	−1043.695	−838.132	72.966
700	143.792	428.406	353.870	52.175	−1043.585	−803.874	59.986
800	146.853	447.818	364.423	66.716	−1043.129	−769.658	50.254
900	149.039	465.248	374.674	81.516	−1095.580	−734.432	42.625
1000	150.648	481.038	384.534	96.505	−1093.542	−694.413	36.272
1100	151.864	495.456	393.972	111.633	−1091.459	−654.601	31.084
1200	152.804	508.712	402.989	126.868	−1089.357	−614.979	26.769
1300	153.545	520.973	411.599	142.187	−1087.250	−575.533	23.125
1400	154.138	532.375	419.823	157.573	−1085.150	−536.249	20.008
1500	154.621	543.026	427.685	173.011	−1083.066	−497.115	17.311
1600	155.019	553.018	435.210	188.494	−1081.004	−458.119	14.956
1700	155.350	562.427	442.419	204.013	−1078.965	−419.251	12.882
1800	155.628	571.314	449.335	219.562	−1076.951	−380.502	11.042
1900	155.865	579.735	455.979	235.137	−1074.958	−341.866	9.399
2000	156.068	587.735	462.368	250.734	−1072.984	−303.333	7.922
2100	156.243	595.354	468.521	266.350	−1071.023	−264.899	6.589
2200	156.395	602.626	474.453	281.982	−1069.067	−226.558	5.379
2300	156.528	609.581	480.178	297.628	−1067.111	−188.305	4.277
2400	156.645	616.246	485.709	313.287	−1065.145	−150.138	3.268
2500	156.748	622.642	491.060	328.957	−1063.163	−112.054	2.341
2600	156.840	628.792	496.240	344.636	−1061.156	−74.049	1.488
2700	156.922	634.713	501.259	360.324	−1059.116	−36.122	0.699
2800	156.995	640.421	506.128	376.020	−1057.036	1.729	−0.032
2900	157.061	645.931	510.854	391.723	−1054.910	39.505	−0.712
3000	157.120	651.257	515.446	407.432	−1052.732	77.206	−1.344
3100	157.174	656.410	519.911	423.147	−1050.496	114.833	−1.935
3200	157.223	661.401	524.255	438.867	−1048.196	152.388	−2.487
3300	157.268	666.239	528.484	454.591	−1045.830	189.870	−3.005
3400	157.308	670.935	532.605	470.320	−1043.393	227.279	−3.492
3500	157.346	675.495	536.623	486.053	−1040.883	264.616	−3.949
3600	157.380	679.928	540.542	501.789	−1038.297	301.880	−4.380
3700	157.412	684.241	544.368	517.529	−1035.633	339.070	−4.787
3800	157.441	688.439	548.104	533.272	−1032.889	376.187	−5.171
3900	157.468	692.529	551.755	549.017	−1030.064	413.232	−5.535
4000	157.492	696.516	555.325	564.765	−1027.158	450.203	−5.879
4100	157.516	700.405	558.816	580.515	−1024.170	487.100	−6.206
4200	157.537	704.201	562.233	596.268	−1021.100	523.924	−6.516
4300	157.557	707.908	565.578	612.023	−1017.948	560.672	−6.811
4400	157.576	711.531	568.854	627.780	−1014.715	597.347	−7.091
4500	157.593	715.072	572.064	643.538	−1011.400	633.948	−7.359
4600	157.610	718.536	575.210	659.298	−1008.005	670.474	−7.613
4700	157.625	721.926	578.296	675.060	−1004.530	706.925	−7.857
4800	157.639	725.245	581.323	690.823	−1000.977	743.302	−8.089
4900	157.653	728.495	584.294	706.588	−997.347	779.604	−8.311
5000	157.665	731.680	587.210	722.354	−993.640	815.830	−8.523
5100	157.677	734.803	590.073	738.121	−989.859	851.982	−8.726
5200	157.689	737.864	592.886	753.889	−986.005	888.060	−8.921
5300	157.699	740.868	595.650	769.658	−982.079	924.062	−9.107
5400	157.709	743.816	598.366	785.429	−978.082	959.990	−9.286
5500	157.719	746.710	601.037	801.200	−974.016	995.842	−9.458
5600	157.728	749.552	603.664	816.973	−969.883	1031.621	−9.623
5700	157.736	752.344	606.248	832.746	−965.685	1067.324	−9.781
5800	157.744	755.087	608.791	848.520	−961.422	1102.954	−9.933
5900	157.752	757.784	611.293	864.295	−957.097	1138.510	−10.080
6000	157.759	760.435	613.757	880.070	−952.710	1173.991	−10.221

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

Heat of Formation

Leach and Roberts[1] have reported calorimetric measurements on the heat of hydrolysis of liquid sulfur chloride pentafluoride in aqueous caustic. Re–evaluation of their data using more recent auxiliary heats of formation[2] for aqueous NaOH, Na$_2$SO$_4$, NaCl, and NaF leads to $\Delta_fH°$(ClSF$_4$, l, 298.15 K) = −252.9 ± 2.0 kcal·mol^{-1}. The adopted value for the gas is obtained from that for the liquid by addition of the heat of vaporization at 298.15 K. We estimate a value for $\Delta_{vap}H°$(298.15 K) equal to 4.6 ± 0.5 kcal·mol^{-1} from $\Delta_{vap}H°$ = 5.19 kcal·mol^{-1} reported by Griffiths[3] from an analysis of vapor pressure data. We assume that the reported $\Delta_{vap}H°$ value refers to a boiling temperature of 251.85 K, and we estimate the $\Delta_pC°$ of vaporization as −12 cal·K^{-1}·mol^{-1}. Earlier vapor pressure measurements[4] lead to a lower value (3.9 kcal·mol^{-1}) for $\Delta_{vap}H°$(298.15 K), however, we believe the earlier vapor pressure data are less reliable than the measurements of Griffiths.[3]

Electron–impact studies by Harland and Thynne[5] on SF$_6$ and ClSF$_5$ have provided information on the appearance potentials (AP) for the formation of SF$_5^+$ and SF$_5^-$ from these neutral molecules. Our analysis of their AP data[5] leads to $\Delta_fH°$ values which are more than 15 kcal·mol^{-1} different than the adopted result.

The heat of atomization, $\Delta_aH°$(0 K), and S–Cl bond dissociation energy are calculated to be 431.8 ± 4.5 kcal·mol^{-1} and 59.6 ± 6.0 kcal·mol^{-1}, respectively. The latter value appears reasonable when compared with the mean values for the S–Cl bond strength in SCl$_2$(63.8 kcal·mol^{-1}).

Heat Capacity and Entropy

The structural parameters are taken from a study by Marsden and Bartell[6] who established the C_{4v} structure of ClSF$_5$ by a simultaneous least–squares analysis of electron diffraction and microwave spectroscopic data. The microwave data were based on the measurements of Kewley *et al.*[7] We use r_g distances to calculate the principal moments of inertia of $I_A = 30.9468 \times 10^{-38}$ and $I_B = I_C = 46.3888 \times 10^{-38}$ g·cm^2.

The vibrational spectrum of ClSF$_5$ has been studied using various spectroscopic techniques.[3,8,9] The observed vibratonal frequencies show good agreement, but conflicting assignments have been reported. Griffiths[3] has argued that the fundamentals assigned as ν_6 = 396 cm^{-1} and ν_{11} = 270 cm^{-1} by Cross *et al.*[8] should be reversed. A recent Raman study[9] of ClSF ν_5 isolated in an argon matrix has identified the band at 396 cm^{-1} as the Cl component of the S–Cl stretching frequency (ν_4). A comparison of the vibrational spectra of ClSF$_5$ and ClSeF$_5$[10] and results from two force field studies[6, 11] suggest that the low–frequency SF$_5$ bending mode (ν_{11}) should lie in the range 270–290 cm^{-1} We adopt ν_{11} = 287 cm^{-1} which was observed in the gas phase infrared spectra by Griffiths.[3] As suggested by others[10 11] we believe that the SF$_2$ out–of–plane deformation (ν_6) has not been resolved, and we use an estimated value (332 cm^{-1}) calculated from a general valency–force field.[11] An independent force–field calculation[6] supports this value (ν_6 = 317 cm^{-1}). All other fundamentals are rounded values taken from the gas phase infrared and liquid phase Raman study of Griffiths.[3]

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Iron Chloride (FeCl) IDEAL GAS $M_r = 91.300$ Iron Chloride (FeCl) $Cl_1Fe_1(g)$

$S°(298.15\ K) = [257.573]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 249.8 \pm 84\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 251.0 \pm 84\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^6\Sigma$	0	6
	[200]	[8]
	[1000]	[8]
	[4000]	[8]

$\omega_e = 404.92\ cm^{-1}$ $\omega_e x_e = 1.19\ cm^{-1}$ $\sigma = 1$

$B_e = [0.17795]\ cm^{-1}$ $\alpha_e = [0.00075]\ cm^{-1}$ $r_e = [2.09]$

Enthalpy of Formation

The dissociation energy of FeCl(g) was reported as 3 ± 2 cal·K^{-1}·mol^{-1} (69 ± 46 kcal·mol^{-1}) by Gaydon.[1] The corresponding $\Delta_f H°$(FeCl, g, 298.15 K) was evaluated to be 56 ± 46 kcal·mol^{-1}. By comparing D_0°(Fe–O) = 101 kcal·mol^{-1} in FeO(g) with the coordinate bond energies obtained in organic complexes and iron carbonyl halides of E(Fe–O) = 59.4 and E(Fe–Cl) = 37.3 kcal·mol^{-1}, reported by Jones *et al.*,[2] the D_0°(Fe–Cl) in FeCl(g) was estimated as 101 × (37.3/59.4) = 63.3 kcal·mol^{-1}, yielding $\Delta_f H°$(FeCl, g, 298.15 K) = 64 kcal·mol^{-1}. The adopted value of $\Delta_f H°$(298.15 K) for FeCl(g) is 60 ± 20 kcal·mol^{-1} (251.040 ± 84 kJ·mol^{-1}).

Heat Capacity and Entropy

The ground state configuration, ω_e and $\omega_e x_e$ (corrected to the average isotopic species) were obtained from Herzberg.[3] The Fe–Cl bond distance was assumed to be the same as that in $FeCl_2(g)$. Hence the values of B_e and α_e were calculated. The electronic levels and quantum weights were estimated by comparison with the electronic levels in $Fe^+(g)$ reported by Moore,[4] using the reasoning suggested by Hougen *et al.*[5] The total 30 for the quantum weight was obtained from the ground multiplet of Fe^+ and was split arbitrarily. The entropy values may be in error by a few entropy units due to the uncertainties in the low lying electronic levels.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.377	249.760	249.760	INFINITE
100	34.442	217.748	290.602	−7.285	250.973	239.255	−124.974
200	36.906	242.585	261.028	−3.689	251.282	227.351	−59.378
250	37.603	250.896	258.199	−1.826	251.198	221.376	−46.254
298.15	38.223	257.573	257.573	0.	251.040	215.646	−37.780
300	38.245	257.810	257.574	0.071	251.033	215.426	−37.509
350	38.782	263.747	258.041	1.997	250.814	209.508	−31.267
400	39.189	268.954	259.087	3.947	250.546	203.625	−26.591
450	39.472	273.587	260.445	5.914	250.227	197.779	−22.958
500	39.654	277.756	261.971	7.892	249.853	191.971	−20.055
600	39.813	285.003	265.224	11.867	248.926	180.477	−15.712
700	39.833	291.143	268.499	15.850	247.747	169.159	−12.623
800	39.813	296.460	271.669	19.833	246.265	158.029	−10.318
900	39.801	301.149	274.690	23.813	244.357	147.109	−8.538
1000	39.810	305.343	277.549	27.794	241.722	136.435	−7.127
1100	39.840	309.138	280.251	31.776	238.187	126.091	−5.988
1200	39.885	312.606	282.805	35.762	235.202	116.013	−5.050
1300	39.939	315.801	285.222	39.753	233.863	106.135	−4.265
1400	39.997	318.763	287.513	43.750	232.442	96.362	−3.595
1500	40.052	321.524	289.689	47.753	230.938	86.694	−3.019
1600	40.104	324.111	291.761	51.760	229.352	77.129	−2.518
1700	40.150	326.544	293.736	55.773	226.732	67.685	−2.080
1800	40.189	328.840	295.623	59.790	224.644	58.389	−1.694
1900	40.222	331.014	297.429	63.811	208.373	49.913	−1.372
2000	40.248	333.077	299.160	67.834	205.875	41.638	−1.087
2100	40.269	335.042	300.822	71.860	203.374	33.488	−0.833
2200	40.284	336.915	302.421	75.888	200.869	25.457	−0.604
2300	40.295	338.706	303.960	79.917	198.359	17.539	−0.398
2400	40.303	340.421	305.444	83.947	195.842	9.732	−0.212
2500	40.307	342.067	306.876	87.977	193.318	2.029	−0.042
2600	40.309	343.648	308.260	92.008	190.785	−5.573	0.112
2700	40.310	345.169	309.599	96.039	188.244	−13.077	0.253
2800	40.309	346.635	310.896	100.070	185.693	−20.486	0.382
2900	40.307	348.049	312.152	104.101	183.132	−27.805	0.501
3000	40.304	349.416	313.372	108.131	180.561	−35.035	0.610
3100	40.302	350.737	314.556	112.162	177.981	−42.179	0.711
3200	40.299	352.017	315.707	116.192	−172.910	−41.815	0.683
3300	40.297	353.257	316.826	120.222	−173.609	−37.708	0.597
3400	40.295	354.460	317.915	124.251	−174.349	−33.579	0.516
3500	40.293	355.628	318.976	128.280	−175.130	−29.427	0.439
3600	40.292	356.763	320.010	132.310	−175.952	−25.253	0.366
3700	40.293	357.867	321.018	136.339	−176.815	−21.055	0.297
3800	40.293	358.941	322.002	140.368	−177.717	−16.833	0.231
3900	40.295	359.988	322.963	144.398	−178.659	−12.587	0.169
4000	40.298	361.008	323.901	148.427	−179.641	−8.316	0.109
4100	40.302	362.003	324.819	152.457	−180.661	−4.021	0.051
4200	40.306	362.975	325.716	156.488	−181.719	0.300	−0.004
4300	40.312	363.923	326.593	160.519	−182.816	4.647	−0.056
4400	40.319	364.850	327.452	164.550	−183.950	9.019	−0.107
4500	40.326	365.756	328.293	168.582	−185.121	13.418	−0.156
4600	40.335	366.642	329.117	172.616	−186.330	17.844	−0.203
4700	40.345	367.510	329.925	176.649	−187.575	22.295	−0.248
4800	40.355	368.360	330.717	180.684	−188.858	26.774	−0.291
4900	40.367	369.192	331.494	184.721	−190.177	31.280	−0.333
5000	40.379	370.007	332.256	188.758	−191.534	35.813	−0.374
5100	40.392	370.807	333.004	192.796	−192.929	40.374	−0.414
5200	40.406	371.592	333.738	196.836	−194.361	44.963	−0.452
5300	40.421	372.361	334.460	200.878	−195.833	49.579	−0.489
5400	40.436	373.117	335.169	204.920	−197.345	54.223	−0.525
5500	40.453	373.859	335.866	208.965	−198.897	58.896	−0.559
5600	40.470	374.588	336.551	213.011	−200.492	63.598	−0.593
5700	40.488	375.305	337.224	217.059	−202.132	68.328	−0.626
5800	40.506	376.009	337.887	221.109	−203.817	73.088	−0.658
5900	40.525	376.702	338.539	225.160	−205.550	77.877	−0.689
6000	40.545	377.383	339.181	229.214	−207.333	82.695	−0.720

PREVIOUS: June 1965 (1 atm) CURRENT: June 1965 (1 bar)

Iron Chloride (FeCl) $Cl_1Fe_1(g)$

Hydrogen Chloride (HCl)   IDEAL GAS $M_r = 36.46094$ Hydrogen Chloride (HCl) $Cl_1H_1(g)$

$S°(298.15\ K) = 186.901\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -92.127 \pm 0.21\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -92.312 \pm 0.21\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = 2889.59\ cm^{-1}$ $\omega_e x_e = 52.06\ cm^{-1}$ $\sigma = 1$
$B_e = 10.5884\ cm^{-1}$ $\alpha_e = 0.3037\ cm^{-1}$ $r_e = 1.2746$ Å

Enthalpy of Formation

The selected value, Rossini's flow calorimetric measurement[1] of the direct combination of the elements, is essentially the same as that in the revised version[2] of NBS Circular 500. JANAF analyses of the more recent measurements are summarized below, while the earlier measurements have been reviewed by Rossini.[1]

Experimenters	Date	Method	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}	References
Johnson, Ambrose	1963	Comparison of HCl, H_2SO_4 and SO_2 by solution calorimetry	−22.14 ± 0.12	2,3 4,5,6,7,8,9,10)
Lacher *et al.*	1949–52	Catalytic combination in flow calorimeter	−22.10 ± 0.12	11,12
Roth and Richter	1934	Direct combination in bomb calorimeter	−21.90 ± 0.05	13
von Wartenberg and Hanisch	1932	Direct combination in flow calorimeter	−21.90 ± 0.01	14
Rossini	1932	Direct combination in flow calorimeter	−22.063 ± 0.012	1
—	1922–63	$\Delta_f G°$ from e.m.f. and $\Delta_f S°$ from statistical mechanics	−22.02 ± 0.03	15 16,17 18,19,20
Lewis	1906	Equilibria for reaction HCl(g) + 1/4O_2(g) = 1/2 H_2O(g) + 1/2 Cl2(g)	−22.30 ± 0.44	21

The direct combination values of Roth and Richter[13] and von Wartenberg and Hanisch[14] are 0.7% less negative than that of Rossini;[1] however, all of the other methods favor the more negative value. The Roth and Richter value may be affected by errors in the measurement of the extent of reaction by HCl titration (9, 22), since a set of experiments based on determination of the amount of H_2 gave a value of −22.02 kcal·mol^{-1}.

Rossini's value is confirmed by a variety of independent methods. The solution calorimetry,[3] though it is related through a complex reaction scheme, is based on species which are now quite well known. Emf measurements[15–20] give $\Delta_f G°(298.15\ K) = -22.733$, assuming an uncertainty of 1.0 mv. in $E°$, this leads to $\Delta_f H°(29815K) = -22.02 \pm 0.03$ when combined with the statistical entropies The equilibria of Lewis (625–692 K) give $\Delta_f H°(298.15\ K)$[21] = −2220 ± 044(2nd law) and −22.30 ± 0.04 (3rd law).

Enthalpy Capacity and Entropy

Spectroscopic constants for HCl[35] and HCl[37] were selected from the work of Plyler *et al.*[23] and Haeusler and Barchewitz.[24] The values were adjusted to 75.53% HCl[35].

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.640	−92.127	−92.127	INFINITE
100	29.116	155.087	212.797	−5.771	−92.214	−93.236	48.702
200	29.124	175.270	189.566	−2.859	−92.168	−94.284	24.625
250	29.130	181.770	187.381	−1.403	−92.219	−94.809	19.809
298.15	29.136	186.901	186.901	0.	−92.312	−95.300	16.696
300	29.137	187.081	186.902	0.054	−92.316	−95.318	16.596
350	29.149	191.574	187.256	1.511	−92.443	−95.809	14.299
400	29.175	195.467	188.045	2.969	−92.589	−96.280	12.573
450	29.223	198.906	189.064	4.429	−92.747	−96.732	11.228
500	29.304	201.989	190.205	5.892	−92.913	−97.166	10.151
600	29.575	207.353	192.629	8.835	−93.251	−97.985	8.530
700	29.985	211.942	195.068	11.811	−93.579	−98.747	7.369
800	30.494	215.978	197.434	14.835	−93.881	−99.465	6.494
900	31.055	219.602	199.699	17.912	−94.152	−100.146	5.812
1000	31.628	222.903	201.857	21.046	−94.388	−100.799	5.265
1100	32.186	225.944	203.910	24.237	−94.591	−101.430	4.817
1200	32.713	228.768	205.866	27.482	−94.766	−102.044	4.442
1300	33.203	231.406	207.730	30.779	−94.916	−102.644	4.124
1400	33.651	233.883	209.510	34.122	−95.046	−103.234	3.852
1500	34.060	236.219	211.214	37.508	−95.160	−103.815	3.615
1600	34.431	238.429	212.846	40.932	−95.261	−104.388	3.408
1700	34.767	240.527	214.413	44.393	−95.351	−104.956	3.225
1800	35.071	242.523	215.920	47.885	−95.435	−105.519	3.062
1900	35.348	244.426	217.371	51.406	−95.514	−106.077	2.916
2000	35.600	246.246	218.769	54.953	−95.590	−106.631	2.785
2100	35.830	247.989	220.119	58.525	−95.665	−107.181	2.666
2200	36.040	249.660	221.424	62.119	−95.742	−107.727	2.558
2300	36.233	251.267	222.687	65.732	−95.820	−108.270	2.459
2400	36.411	252.812	223.910	69.365	−95.903	−108.810	2.368
2500	36.575	254.302	225.097	73.014	−95.991	−109.346	2.285
2600	36.728	255.740	226.248	76.679	−96.086	−109.878	2.207
2700	36.870	257.129	227.366	80.359	−96.188	−110 407	2.136
2800	37.002	258.472	228.453	84.053	−96.298	−110.932	2.069
2900	37.127	259.772	229.511	87.760	−96.418	−111.452	2.007
3000	37.243	261.033	230.540	91.478	−96.547	−111.968	1.950
3100	37.354	262.256	231.544	95.208	−96.685	−112.480	1.895
3200	37.458	263.444	232.522	98.949	−96.834	−112.987	1.844
3300	37.557	264.598	233.477	102.699	−96.992	−113.490	1.796
3400	37.651	265.720	234.409	106.460	−97.159	−113.987	1.751
3500	37.740	266.813	235.319	110.229	−97.334	−114.480	1.709
3600	37.826	267.878	236.209	114.008	−97.518	−114.967	1.668
3700	37.908	268.915	237.079	117.795	−97.708	−115.449	1.630
3800	37.987	269.927	237.930	121.589	−97.905	−115.926	1.594
3900	38.063	270.915	238.763	125.392	−98.107	−116.397	1.559
4000	38.137	271.879	239.579	129.202	−98.313	−116.864	1.526
4100	38.208	272.822	240.378	133.019	−98.521	−117.325	1.495
4200	38.276	273.744	241.162	136.843	−98.731	−117.781	1.465
4300	38.343	274.645	241.930	140.674	−98.942	−118.232	1.436
4400	38.408	275.527	242.684	144.512	−99.152	−118.678	1.409
4500	38.471	276.391	243.423	148.356	−99.360	−119.120	1.383
4600	38.532	277.237	244.149	152.206	−99.564	−119.557	1.358
4700	38.592	278.067	244.862	156.062	−99.764	−119.989	1.334
4800	38.651	278.880	245.562	159.924	−99.959	−120.417	1.310
4900	38.708	279.677	246.250	163.792	−100.147	−120.842	1.288
5000	38.764	280.460	246.927	167.666	−100.328	−121.262	1.267
5100	38.819	281.228	247.592	171.545	−100.499	−121.679	1.246
5200	38.873	281.982	248.246	175.430	−100.662	−122.093	1.226
5300	38.927	282.723	248.889	179.320	−100.814	−122.503	1.207
5400	38.979	283.451	249.523	183.215	−100.954	−122.911	1.189
5500	39.030	284.167	250.146	187.116	−101.083	−123.317	1.171
5600	39 081	284.871	250.760	191.021	−101.198	−123.720	1.154
5700	39.131	285.563	251.364	194.932	−101.300	−124.121	1.137
5800	39.181	286.244	251.960	198.847	−101.387	−124.520	1.121
5900	39.230	286.914	252.547	202.768	−101.460	−124.919	1.106
6000	39.278	287.574	253.125	206.693	−101.517	−125.316	1.091

PREVIOUS September 1964 (1 atm)   CURRENT· September 1964 (1 bar)

Hypochlororous Acid (HOCl) IDEAL GAS $M_r = 52.46034$ Hypochlorous Acid (HOCl) $Cl_1H_1O_1(g)$

$S°(298.15\ K) = 236.504 \pm 0.42\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -71.5 \pm 2.1\ kJ{\cdot}mol^{-1}$

$\Delta_f H°(298.15\ K) = -74.5 \pm 2.1\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1A'$	0	1
$^3A''$	[22000]	3

Vibrational Frequencies and Degeneracies ν, cm^{-1}
3609.5(1)
1239.4(1)
725 (1)

Point Group: C_s $\sigma = 1$

Bond Distances: O–Cl = 1.689 ± 0.003 Å; O–H = 0.960 ± 0.005 Å

Bond Angle: H–O–Cl = 102.5 ± 0.5°

Product of the Moments of Inertia: $4.2740 \times 10^{-117}\ g^3{\cdot}cm^6$

Enthalpy of Formation

Our adopted value of $\Delta_f H°$(HOCl, g, 298.15 K) is based on the ultraviolet photometric equilibrium measurements of Knauth *et al.*[1] who determined $K_{333} = 0.132 \pm 0.008$ for the reaction $Cl_2O(g) + H_2O(g) = 2\ HOCl(g)$. Combining this result with JANAF auxiliary data,[2] we obtain $\Delta_r H°(298.15\ K) = 2.66 \pm 0.10\ kcal{\cdot}mol^{-1}$. When this result is combined with $\Delta_f H°(H_2O, g, 298.15\ K) = -57.795 \pm 0.01\ kcal{\cdot}mol^{-1}$[3] and $\Delta_f H°(Cl_2O, g, 298.15\ K) = 19.46 \pm 0.4\ kcal{\cdot}mol^{-1}$ from Alqasmi *et al.*,[4] we obtain $\Delta_f H°(HOCl, g, 298.15\ K) = -17.8 \pm 0.5\ kcal{\cdot}mol^{-1}$. This is in agreement with $\Delta_f H°(HOCl, g, 298.15\ K) = -18.0\ kcal{\cdot}mol^{-1}$ derived from similar equilibrium measurements of Molina and Molina.[5] Niki *et al.*[6] also measured the gas phase equilibrium constant for the same reaction using an infrared method and obtained K(295 K) = 0.068 ± 0.01, from which we derive $\Delta_r H°(298.15\ K) = 2.75 \pm 0.2\ kcal{\cdot}mol^{-1}$, and $\Delta_f H°(HOCl, g, 298.15\ K) = -17.8 \pm 0.6\ kcal{\cdot}mol^{-1}$ using the same auxiliary data as above. Hirsch *et al.*[7] have calculated a value of $\Delta_f H°(HOCl, g, 298.15\ K) = -19.2 \pm 4\ kcal{\cdot}mol^{-1}$ from ab initio results.

Connick and Chia[8] determined $\Delta_r H°(298.15\ K) = 5.06 \pm 0.13\ kcal{\cdot}mol^{-1}$ for the reaction $Cl_2(aq) + H_2O(l) = H^+(aq) + Cl^-(aq) + HOCl(aq)$. The auxiliary data[3] $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315\ kcal{\cdot}mol^{-1}$, $\Delta_f H°(Cl^-, aq, 298.15\ K) = -39.933\ kcal{\cdot}mol^{-1}$ and $\Delta_f H°(Cl_2, aq, 298.15\ K) = -5.6\ kcal{\cdot}mol^{-1}$[9] give $\Delta_f H°(HOCl, aq, 298.15\ K) = -28.92 \pm 0.2\ kcal{\cdot}mol^{-1}$. Similarly, Morris[10] determined $\Delta_r G°(298.15\ K) = 10.282\ kcal{\cdot}mol^{-1}$ for the reaction $HOCl(aq) = H^+(aq) + OCl^-(aq)$. Using entropies from NBS Tech Note 270–3[9] we obtain $\Delta_r H°(298.15\ K) = 3.13 \pm 0.5\ kcal{\cdot}mol^{-1}$, which when combined with auxiliary data from NBS Tech Note 270–3,[9] leads to $\Delta_f H°(HOCl, aq, 298.15\ K) = -28.73 \pm 0.5\ kcal{\cdot}mol^{-1}$. Combining the former value of $\Delta_f H°$(HOCl, aq, 298.15 K) with our adopted value for $\Delta_f H°$(HOCl, g, 298.15 K), we obtain $\Delta_r H°(298.15\ K) = -11.8 \pm 0.6\ kcal{\cdot}mol^{-1}$ for the heat of solution at infinite dilution of HOCl(g).

Heat Capacity and Entropy

The molecular structure given above is taken from the microwave work of Mirri *et al.*[11] The rotational constants used to determine the moments of inertia are taken from the high resolution infrared spectrum of Wells *et al.*[12] for the ν_1 vibrational band and are in reasonable agreement with rotational constants calculated from the above structure (the product of the moments of inertia calculated is 2% lower than our adopted value of $I_AI_BI_C$). Rotational constants are adjusted for the natural isotopic abundance of Cl and are $A_0 = 20.463\ cm^{-1}$, $B_0 = 0.50214\ cm^{-1}$, and $C_0 = 0.48910\ cm^{-1}$ Vibrational frequencies are taken from Wells *et al.* (12 (ν_1)) and from Ashby (13 (ν_2, ν_3)) Values of are adjusted for the natural isotopic abundance of chlorine. The vibrations are expected to be anharmonic[11] but no anharmonicity constants are available. The lowest–lying excited state has been calculated to lie at 22,000 cm^{-1}.[14] Omission of this state reduces $C_p°$ by 0.02 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ and $S°$ by 0.002 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ at 3000 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.224	−71.533	−71.533	INFINITE
100	33.284	198.866	267.844	−6.898	−72.615	−69.350	36.225
200	34.588	222.209	239.823	−3.523	−73.561	−65.717	17.164
250	35.898	230.063	237.110	−1.762	−74.037	−63.701	13.310
298.15	37.285	236.504	236.504	0.	−74.475	−61.670	10.804
300	37.339	236.735	236.505	0.069	−74.491	−61.591	10.724
350	38.759	242.599	236.965	1.972	−74.911	−59.407	8.866
400	40.077	247.862	238.004	3.943	−75.291	−57.165	7.465
450	41.260	252.652	239.369	5.977	−75.634	−54.879	6.370
500	42.307	257.054	240.920	8.067	−75.943	−52.556	5.490
600	44.045	264.928	244.281	12.388	−76.483	−47.826	4.164
700	45.437	271.825	247.733	16.864	−76.939	−43.013	3.210
800	46.604	277.971	251.136	21.468	−77.330	−38.139	2.490
900	47.625	283.520	254.431	26.180	−77.667	−33.219	1.928
1000	48.538	288.586	257.597	30.989	−77.960	−28.265	1.476
1100	49.366	293.252	260.629	35.885	−78.213	−23.283	1.106
1200	50.118	297.580	263.530	40.860	−78.433	−18.279	0.796
1300	50.800	301.619	266.306	45.907	−78.624	−13.258	0.533
1400	51.418	305.406	268.965	51.018	−78.792	−8.224	0.307
1500	51.977	308.973	271.514	56.188	−78.942	−3.178	0.111
1600	52.481	312.344	273.962	61.411	−79.078	1.878	−0.061
1700	52.936	315.540	276.314	66.683	−79.204	6.941	−0.213
1800	53.346	318.577	278.579	71.997	−79.323	12.012	−0.349
1900	53.716	321.471	280.761	77.351	−79.439	17.089	−0.470
2000	54.049	324.235	282.866	82.739	−79.556	22.173	−0.579
2100	54.351	326.880	284.899	88.159	−79.675	27.262	−0.678
2200	54.625	329.415	286.865	93.608	−79.800	32.357	−0.768
2300	54.874	331.848	288.769	99.084	−79.933	37.458	−0.851
2400	55.101	334.189	290.613	104.583	−80.075	42.565	−0.926
2500	55.310	336.442	292.401	110.103	−80.229	47.678	−0.996
2600	55.502	338.615	294.137	115.644	−80.397	52.798	−1.061
2700	55.679	340.714	295.823	121.203	−80.578	57.924	−1.121
2800	55.846	342.741	297.463	126.779	−80.775	63.058	−1.176
2900	56.002	344.704	299.058	132.372	−80.987	68.198	−1.228
3000	56.151	346.605	300.612	137.980	−81.216	73.346	−1.277
3100	56.294	348.449	302.125	143.602	−81.460	78.502	−1.323
3200	56.432	350.238	303.601	149.238	−81.719	83.666	−1.366
3300	56.567	351.977	305.041	154.888	−81.993	88.839	−1.406
3400	56.699	353.667	306.446	160.551	−82.281	94.020	−1.444
3500	56.832	355.313	307.819	166.228	−82.582	99.209	−1.481
3600	56.964	356.916	309.161	171.918	−82.894	104.408	−1.515
3700	57.098	358.478	310.472	177.621	−83.215	109.615	−1.547
3800	57.233	360.003	311.756	183.337	−83.544	114.831	−1.578
3900	57.371	361.491	313.012	189.068	−83.879	120.056	−1.608
4000	57.512	362.945	314.242	194.812	−84.219	125.289	−1.636
4100	57.656	364.367	315.448	200.570	−84.561	130.532	−1.663
4200	57.805	365.758	316.629	206.343	−84.903	135.782	−1.689
4300	57.957	367.120	317.788	212.131	−85.243	141.040	−1.713
4400	58.113	368.455	318.924	217.935	−85.580	146.306	−1.737
4500	58.273	369.762	320.039	223.754	−85.911	151.580	−1.759
4600	58.438	371.045	321.134	229.589	−86.236	156.861	−1.781
4700	58.607	372.303	322.209	235.442	−86.551	162.149	−1.802
4800	58.779	373.539	323.266	241.311	−86.856	167.444	−1.822
4900	58.956	374.753	324.304	247.198	−87.149	172.745	−1.841
5000	59.136	375.946	325.325	253.102	−87.429	178.052	−1.860
5100	59.319	377.119	326.329	259.025	−87.695	183.365	−1.878
5200	59.505	378.272	327.317	264.966	−87.945	188.682	−1.895
5300	59.695	379.408	328.289	270.926	−88.178	194.004	−1.912
5400	59.886	380.525	329.246	276.905	−88.394	199.330	−1.928
5500	60.079	381.626	330.189	282.903	−88.592	204.660	−1.944
5600	60.274	382.710	331.117	288.921	−88.771	209.994	−1.959
5700	60.471	383.779	332.032	294.958	−88.931	215.330	−1.973
5800	60.668	384.832	332.933	301.015	−89.071	220.670	−1.987
5900	60.866	385.871	333.821	307.092	−89.191	226.010	−2.001
6000	61.063	386.895	334.697	313.188	−89.291	231.354	−2.014

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

Chlorosilane (SiH_3Cl) **IDEAL GAS** **M_r = 66.56232** **Chlorosilane (SiH_3Cl)** **$Cl_1H_3Si_1(g)$**

$S°(298.15\ K) = 250.761 \pm 0.21\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [-132.77 \pm 8]\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [-141.84 \pm 8]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
2201(1)	2211(2)
945(1)	952(2)
551(1)	663(2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: Si–H = 1.486 ± 0.008 Å; Si–Cl = 2.049 Å
Bond Angles: H–Si–H = 110.42° ± 0.5°; H–Si–Cl = 108.5° ± 0.5°
Product of the Moments of Inertia: $I_AI_BI_C = 1.60170 \times 10^{-115}\ g^3{\cdot}cm^6$

Enthalpy of Formation

$\Delta_fH°$(298.15 K) is estimated from values for $SiCl_4$, $SiHCl_3$ and SiH_4.[1] Data for $SiHCl_3$[1] suggest that $\Delta_fH°$ shows minor deviations from linearity in the chlorosilanes. We assume that $\Delta_fH°$ has a cubic variation with a constant third difference of −1.5 kcal·mol^{-1}. $\Delta_fH°$ values of the chloromethanes yield an almost constant third difference of about −2.5 kcal·mol^{-1}.[2,3,1] This approximation corresponds to Allen's bond additivity scheme involving near–neighbor interactions taken two and three at a time.[2] Our adopted $\Delta_fH°$ is 0.4 kcal·mol^{-1} more negative than that estimated by linear interpolation between $SiCl_4$ and SiH_4.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Kewley *et al.*[4] for isotopic forms of the four monohalosilanes. The authors concluded that the silyl group is effectively the same in all four halides. We adopt effective (r_o) structural parameters rather than substitutional (r_s) parameters. These are in reasonable agreement with previous structures obtained by various methods.[5] The principal moments of inertia are $I_A = 0.9972 \times 10^{-39}$ and $I_B = I_C = 12.6739 \times 10^{-39}\ g{\cdot}cm^2$.

Shimanouchi[6] selected vibrational frequencies from gas–phase infrared spectra of SiH_3X (X=F, Cl, Br) observed by Newman *et al.*[7] These authors' assignments for SiH_3F and SiH_3Br have been modified slightly by new data[1] obtained at higher resolution. Unpublished gas–phase frequencies of SiH_3X from the thesis of Robiette were quoted by Ball *et al.*[8] These are more consistent with the new data for SiH_3F and SiH_3Br, so we adopt them for SiH_3Cl. Monfils also obtianed partially resolved spectra of SiH_3Cl; his final paper[9] is not available to us.

We neglect excited states and assume the electronic ground state to be $^1A_1$ by analogy with CH_3Cl.[10] Electronic absorption bands of SiH_3Cl were observed at ≥67000 cm^{-1} [11] and the absorption maximum in the lowest transition was estimated to be at ~62000 cm^{-1}.[12] Contributions of these high–lying states would be negligible.

References

[1] JANAF Thermochemical Tables: $Cl_3HSi(g)$, 12–31–76; $FH_3Si(g)$, $H_4Si(g)$ 6–30–76; $CH_3Cl(g)$ 6–30–72; $Cl_4Si(g)$, 12–31–70; $CCl_4(g)$, $CH_2Cl_2(g)$, CHCl3(g), 12–31–68, $CH_4(g)$, 3–31–61.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−11.441	−132.769	−132.769	INFINITE
100	33.561	207.803	288.915	−8.111	−135.660	−131.498	68.688
200	40.360	232.644	255.088	−4.489	−138.776	−126.152	32.948
250	45.846	242.233	251.574	−2.335	−140.376	−122.810	25.660
298.15	51.098	250.761	250.761	0.	−141.838	−119.292	20.900
300	51.292	251.078	250.762	0.095	−141.891	−119.152	20.746
350	56.258	259.365	251.406	2.786	−143.268	−115.252	17.200
400	60.660	267.171	252.893	5.711	−144.490	−111.164	14.517
450	64.557	274.545	254.893	8.843	−145.561	−106.932	12.412
500	68.034	281.530	257.210	12.160	−146.489	−102.589	10.717
600	74 008	294.480	262.361	19.272	−147.963	−93.663	8.154
700	78.961	306.272	267.804	26.928	−148.998	−84.525	6.307
800	83.092	317.093	273.298	35.036	−149.677	−75.265	4.914
900	86.538	327.085	278.726	43.523	−150.074	−65.937	3.827
1000	89.411	336.356	284.031	52.325	−150.257	−56.577	2.955
1100	91.809	344.994	289.185	61.390	−150.282	−47.206	2.242
1200	93.817	353.071	294.176	70.674	−150.195	−37.839	1.647
1300	95.504	360.649	299.001	80.142	−150.034	−28.482	1.144
1400	96.929	367.780	303.662	89.766	−149.830	−19.140	0.714
1500	98.140	374.510	308.163	99.521	−149.606	−9.812	0.342
1600	99.174	380.878	312.510	109.388	−149.382	−0.500	0.016
1700	100.062	386.917	316.711	119.351	−199.349	9.245	−0.284
1800	100.829	392.659	320.772	129.396	−198.933	21.504	−0.624
1900	101.496	398.129	324.701	139.513	−198.508	33.738	−0.928
2000	102.077	403.350	328.504	149.693	−198.082	45.951	−1.200
2100	102.587	408.343	332.188	159.926	−197.660	58.142	−1.446
2200	103.037	413.126	335.759	170.208	−197.247	70.313	−1.669
2300	103.435	417.715	339.223	180.532	−196.846	82.466	−1.873
2400	103.789	422.125	342.586	190.894	−196.460	94.602	−2.059
2500	104.105	426.368	345.853	201.289	−196.092	106.722	−2.230
2600	104.388	430.457	349.029	211.714	−195.745	118.828	−2.387
2700	104.642	434.402	352.118	222.165	−195.419	130.920	−2.533
2800	104.872	438.211	355.125	232.641	−195.116	143.001	−2.668
2900	105.079	441.895	358.054	243.139	−194.838	155.072	−2.793
3000	105.268	445.461	360.909	253.656	−194.585	167.133	−2.910
3100	105.439	448.915	363.692	264.192	−194.357	179.187	−3.019
3200	105.596	452.265	366.408	274.744	−194.156	191.233	−3.122
3300	105.739	455.517	369.059	285.311	−193.981	203.274	−3.218
3400	105.870	458.675	371.649	295.891	−193.831	215.310	−3.308
3500	105.991	461.746	374.179	306.484	−193.708	227.341	−3.393
3600	106.102	464.734	376.653	317.089	−577.761	249.831	−3.625
3700	106.205	467.642	379.073	327.705	−577.273	272.813	−3.851
3800	106.300	470.476	381.442	338.330	−576.811	295.782	−4.066
3900	106.388	473.238	383.760	348.964	−576.373	318.739	−4.269
4000	106.470	475.933	386.031	359.607	−575.958	341.685	−4.462
4100	106.546	478.563	388.256	370.258	−575.564	364.621	−4.645
4200	106.617	481.131	390.437	380.916	−575.191	387.548	−4.820
4300	106.683	483.641	392.575	391.581	−574.836	410.466	−4.986
4400	106.745	486.094	394.673	402.253	−574.499	433.376	−5.145
4500	106.803	488.493	396.731	412.930	−574.177	456.279	−5.296
4600	106.857	490.841	398.751	423.613	−573.870	479.174	−5.441
4700	106.908	493.140	400.735	434.302	−573.576	502.063	−5.580
4800	106.955	495.391	402.684	444.995	−573.293	524.947	−5.713
4900	107.000	497.597	404.599	455.693	−573.021	547.824	−5.840
5000	107.043	499.759	406.480	466.395	−572.758	570.696	−5.962
5100	107.083	501.879	408.330	477.101	−572.502	593.562	−6.079
5200	107.120	503.959	410.149	487.811	−572.252	616.424	−6.192
5300	107.156	506.000	411.938	498.525	−572.007	639.280	−6.300
5400	107.190	508.003	413.699	509.242	−571.766	662.133	−6.405
5500	107.222	509.970	415.432	519.963	−571.526	684.980	−6.505
5600	107.252	511.902	417.137	530.687	−571.288	707.824	−6.602
5700	107.280	513.801	418.816	541.413	−571.049	730.663	−6.696
5800	107.308	515.667	420.470	552.143	−570.809	753.498	−6.786
5900	107.334	517.502	422.099	562.875	−570.567	776.328	−6.873
6000	107.358	519.306	423.704	573.609	−570.319	799.155	−6.957

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

Ammonium Chloride (NH_4Cl) CRYSTAL $M_r = 53.49146$ Ammonium Chloride (NH_4Cl) $Cl_1H_4N_1(cr)$

$S°(298.15\ K) = 94.86 \pm 4.2\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs2} = 242.6\ K$
$T_{trs1} = 457.7\ K$
$T_{fus} = 793.2\ K$
$T_{dcm} = 612\ K$

$\Delta_fH°(0\ K) = -311.391 \pm 0.84\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -314.553 \pm 0.84\ kJ{\cdot}mol^{-1}$
$\Delta_{trs2} = 1.046\ kJ{\cdot}mol^{-1}$
$\Delta_{trs1} = 3.950\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The equilibrium pressures for the reaction $NH_4Cl(cr) = NH_3(g) + HCl(g)$, at 320–636 K, have been measured by many investigators. Smits and de Lange,[2] using the densi–tensimeter, determined the vapor pressure of $NH_4Cl(cr)$ and the density of the saturated vapor simultaneously. The results obtained indicate that within the range 527–626 K the saturated vapor completely dissociates into gaseous NH_3 and HCl. Based on this conclusion, the reported vapor pressure data were employed to evaluate the enthalpy of dissociation of $NH_4Cl(cr)$ by both the 2nd and 3rd law methods. The results are presented as follows.

Source	T/K	$\Delta_rH°(298.15\ K)$, $kcal{\cdot}mol^{-1}$ 2nd law	3rd law	Drift $cal{\cdot}K^{-1}{\cdot}mol^{-1}$
1	521.6–619.1	43.18 ± 0.08	42.11	−2.0 ± 0.2
2	527.9–625.6	42.16 ± 0.22	42.14	−0.2 ± 0.4
3	525.4–615.0	42.02 ± 0.06	42.20	0.2 ± 0.1
4	471.3–557.0	42.43 ± 0.09	42.08	−0.3 ± 0.2
5	319.0–352.7	43.83 ± 0.38	42.17	−4.9 ± 1.1
6	503.4–611.4	41.27 ± 0.38	42.12	1.3 ± 0.8

The value of $\Delta_rH°(298.15\ K)$ adopted is $42.15 \pm 0.10\ kcal{\cdot}mol^{-1}$, yielding $\Delta_fH°(NH_4Cl,\ cr,\ 298.15\ K) = -75.8 \pm 0.20\ kcal{\cdot}mol^{-1}$. The corresponding $\Delta_rH°(298.15\ K)$ value evaluated from solution data, selected by Parker[7] is $42.06\ kcal{\cdot}mol^{-1}$.

Heat Capacity and Entropy

The heat capacities (20.1–523.2 K) of $NH_4Cl(cr)$ have been measured by the following investigators: Ewald 138–301 K;[8] Simon 20.1–290.8 K;[9] Klinhardt 323.2–523.2 K;[10] Simon *et al.* 204.5–275.8 K;[11] Ziegler and Messer 107.2–320.2 K,[12] Extermann and Weigle 228.2–248.2[13] and Popov and Galchenko 373.2–523.2 K.[14] These $C_p°$ data were plotted and a smooth $C_p°$ curve was drawn and adopted. The $C_p°$ values above 523 K were obtained by graphical extrapolation of the previous $C_p°$ curve. $S°(298.15\ K)$ was derived from the adopted low temperature data, based on $S°(20.1\ K) = 0.114\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

Transition Data

There are two transitions reported in the literature. The low temperature transition data (T_{trs2} and $\Delta_{trs2}H°$) were derived based on the heat capacity (107–320 K) data reported by Ziegler and Messer,[12] in which the other T_{trs2} values given by previous investigators were reviewed. The high temperature transition data (T_{trs1} and $\Delta_{trs1}H°$) were taken from Klinkhardt.[10] However, $\Delta_{trs1}H° = 1030$ and $\Delta H°(463.5\ K) = 1059.1 \pm 8.0\ cal{\cdot}mol^{-1}$ were reported by Scheffer,[13] and Popov and Galchenko,[14] respectively. Markowitz and Boryta[6] determined T_{trs1} to be 459.5 ± 0.5 K.

Fusion Data

T_{fus} was obtained from Rassow.[15]

Decomposition Data

The value of T_{dcm} was calculated as the temperature at which the vapor pressure of the decomposition products (NH_3 and HCl) equals 1 atm. By differential thermal analysis, T_{dcm} for $NH_4Cl(cr)$ was determined to be 611.4 K by Markowitz and Boryta.[6]

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ ($J{\cdot}K^{-1}mol^{-1}$)	$S°$ ($J{\cdot}K^{-1}mol^{-1}$)	$-[G°-H°(T_r)]/T$ ($J{\cdot}K^{-1}mol^{-1}$)	$H°-H°(T_r)$ ($kJ{\cdot}mol^{-1}$)	$\Delta_fH°$ ($kJ{\cdot}mol^{-1}$)	$\Delta_fG°$ ($kJ{\cdot}mol^{-1}$)	log K_f
0	.000	.000	INFINITE	−22.698	−311.391	−311.391	INFINITE
100	37.656	24.552	163.795	−13.924	−311.523	−276.392	144.372
200	67.111	59.752	103.140	−8.678	−314.638	−239.828	62.637
298.15	86.441	94.860	94.860	.000	−314.553	−203.092	35.581
300	86.944	95.396	94.861	.160	−314.558	−202.400	35.241
400	102.968	122.642	98.467	9.670	−314.054	−165.049	21.553
457.700	109.956	136.945	102.428	15 798	II <– –> III		
457.700	85.898	145.537	102.428	19.731	TRANSITION		
500	90.500	153.330	106.407	23.462	−309.363	−128.299	13.403
600	101.671	170.818	115.701	33.071	−308.920	−92.110	8.019
700	112.801	187.327	124.764	43.795	−307.429	−56.079	4.185
800	123.888	203.114	133.577	55.629	−304.904	−20.332	1.328
900	134.976	218.360	142.155	68.585	−301.346	15.037	−.873
1000	144.557	233.090	150.517	82.573	−296.853	49.958	−2.610
1100	152.716	247.259	158.672	97.446	−291.583	84.389	−4.007
1200	159.829	260.861	166.625	113.083	−285.657	118.312	−5.150
1300	165.686	273.889	174.378	129.364	−279.201	151.717	−6.096
1400	171.000	286.365	181.935	146.203	−272.298	184.609	−6.888
1500	175.728	298.328	189.298	163.544	−265.002	216.992	−7.556

PREVIOUS December 1960   CURRENT: September 1965

Ammonium Perchlorate (NH_4ClO_4) CRYSTAL M_r = 117.48906 Ammonium Perchlorate (NH_4ClO_4) $Cl_1H_4N_1O_4(cr)$

$S°(298.15\ K) = 184.180 \pm 1.26\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs} = 513.15\ K$
$T_{dcm} = [513]\ K$

$\Delta_fH°(0\ K) = -277.78 \pm 0.17\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -295.77 \pm 0.17\ kJ{\cdot}mol^{-1}$
$\Delta_{trs}H° = 9.6 \pm 0.8\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Gilliland and Johnson[1] and Birky and Hepler[2] have derived the enthalpy of formation for NH_4ClO_4(cr) from solution–calorimetric measurements. Thier values are −70.74 ± 0.32 and −70.63 $kcal{\cdot}mol^{-1}$, respectively. The mean of these is adopted here.

Heat Capacity and Entropy

Justice and Westrum[3] have measured the heat capacity from 5 to 350 K. The $C_p°$ values above 350 K were extrapolated. From the partial molar entropies of NH_4^+(aq) and ClO_4^-(aq) and the entropy of solution, Birky and Hepler[2] calculated a value of 43.6 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ for $S°(298.15\ K)$. The fair agreement of this value with that derived from $C_p°$ suggests that there is no residual entropy at 0 K, as there would be if the NH_4^+ ion had a random orientation.

Transition and Decomposition Data

T_{trs} and $\Delta_{trs}H°$ were obtained (under a pressure of NH_3) by Markowitz.[4] T_{dcm} was estimated from the report by Markowitz.[4]

References

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[3] B. H. Justice and E. F. Westrum, Univ. of Michigan, Ann Arbor, Mich., personal communication, (April 1961).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	$\log K_f$
0	0.	0.	INFINITE	−25.238	−277.778	−277.778	INFINITE
100	79.622	72.894	283.140	−21.025	−288.280	−223.321	116.651
200	107.236	137.419	195.200	−11.556	−292.995	−156.325	40.828
298.15	128.072	184.180	184.180	0.	−295.767	−88.607	15.524
300	128.449	184.973	184.182	0.237	−295.804	−87.322	15.204
400	148.699	224.699	189.462	14.095	−296.894	−17.615	2.300
500	168.950	260.052	200.101	29.975	−296.232	52.165	−5.450
513.150	171.628	264.472	201.694	32.215	I <−−> II TRANSITION		
513.150	179.996	283.226	201.694	41.838			
600	197.568	312.708	215.652	58.234	−283.459	119.958	−10.443
700	217.819	344.684	231.823	79.003	−278.431	186.822	−13.941
800	238.070	375.092	247.845	101.797	−271.621	252.842	−16.509
900	258.456	404.312	263.616	126.626	−263.001	317.902	−18.451
1000	278.571	432.586	279.107	153.480	−252.567	381.904	−19.949
1100	299.569	460.142	294.317	182.408	−240.258	444.771	−21.120
1200	317.984	487.016	309.260	213.307	−226.169	506.437	−22.045
1300	333.816	513.111	323.943	245.919	−210.548	566.864	−22.777
1400	347.066	538.350	338.362	279.984	−193.645	626.039	−23.358
1500	357.732	562.674	352.510	315.246	−175.712	683.966	−23.818

PREVIOUS: September 1961 CURRENT: December 1962

Mercury Chloride (HgCl) IDEAL GAS $M_r = 236.043$ Mercury Chloride (HgCl) $Cl_1Hg_1(g)$

$S°(298.15\ K) = 260.005\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 82.54 \pm 9.6\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 78.45 \pm 9.6\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight State	ϵ_i, cm^{-1}	g_i
$^2\Sigma^+$	0	2

$\omega_e = 290.94\ cm^{-1}$ $\omega_e x_e = 1.5844\ cm^{-1}$ $\sigma = 1$
$B_e = [0.1121]\ cm^{-1}$ $\alpha_e = [0.0007]\ cm^{-1}$ $r_e = 2.23$ Å

Enthalpy of Formation

Gaydon[1] gives 23 ± 2.3 kcal·mol^{-1} for the heat of dissociation into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants from Wieland[2] were weighted according to their natural isotopic abundances. Rotational constants were estimated using equation III.[3] Bond length was given by Herzberg.[3]

References

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[2] K. Wieland, Z. Elektrochem. 64, 761 (1960).
[3] G. Herzberg, "Spectra of Diatomic Molecules," equation III, 123 p. 108, Van Nostrand, New York (1950).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.846	82.537	82.537	INFINITE
100	31.476	222.563	291.359	−6.880	82.342	73.258	−38.266
200	35.116	245.701	263.302	−3.520	81.598	64.458	−16.835
250	35.926	253.632	260.602	−1.743	78.869	60.376	−12.615
298.15	36.420	260.005	260.005	0.	78.450	56.853	−9.960
300	36.435	260.230	260.005	0.067	78.434	56.719	−9.876
350	36.778	265.874	260.450	1.898	78.016	53.133	−7.930
400	37.023	270.802	261.443	3.744	77.610	49.606	−6.478
450	37.207	275.173	262.730	5.599	77.211	46.130	−5.355
500	37.353	279.101	264.174	7.464	76.817	42.697	−4.461
600	37.574	285.932	267.248	11.211	76.034	35.947	−3.129
700	37.740	291.737	270.342	14.977	16.490	35.899	−2.679
800	37.878	296.786	273.339	18.758	16.342	38.682	−2.526
900	37.998	301.254	276.197	22.552	16.198	41.483	−2.408
1000	38.107	305.263	278.907	26.357	16.056	44.300	−2.314
1100	38.209	308.900	281.471	30.173	15.918	47.132	−2.238
1200	38.306	312.229	283.897	33.998	15.784	49.975	−2.175
1300	38.399	315.299	286.196	37.834	15.655	52.830	−2.123
1400	38.490	318.148	288.378	41.678	15.530	55.694	−2.078
1500	38.579	320.806	290.452	45.532	15.409	58.567	−2.039
1600	38.667	323.299	292.428	49.394	15.293	61.448	−2.006
1700	38.753	325.646	294.314	53.265	15.181	64.336	−1.977
1800	38.839	327.863	296.116	57.145	15.073	67.231	−1.951
1900	38.924	329.966	297.843	61.033	14.969	70.131	−1.928
2000	39.009	331.964	299.500	64.929	14.869	73.037	−1.908
2100	39.093	333.870	301.091	68.834	14.771	75.948	−1.889
2200	39.176	335.690	302.623	72.748	14.675	78.863	−1.872
2300	39.260	337.433	304.099	76.670	14.581	81.783	−1.857
2400	39.343	339.106	305.523	80.600	14.489	84.707	−1.844
2500	39.425	340.714	306.898	84.538	14.396	87.635	−1.831
2600	39.508	342.262	308.229	88.485	14.303	90.566	−1.819
2700	39.591	343.754	309.517	92.440	14.209	93.501	−1.809
2800	39.673	345.196	310.766	96.403	14.115	96.439	−1.799
2900	39.755	346.589	311.977	100.374	14.018	99.381	−1.790
3000	39.837	347.938	313 154	104.354	13.920	102.327	−1.782
3100	39.919	349.246	314.297	108.342	13.821	105.275	−1.774
3200	40.001	350.515	315.409	112.338	13.720	108.227	−1.767
3300	40.083	351.747	316.492	116.342	13.619	111.182	−1.760
3400	40.165	352.945	317.546	120.355	13.518	114.140	−1.754
3500	40.247	354.110	318.574	124.375	13.417	117.101	−1.748
3600	40.329	355.245	319.577	128.404	13.317	120.064	−1.742
3700	40.410	356.351	320.556	132.441	13.221	123.031	−1.737
3800	40.492	357.430	321.512	136.486	13.127	126.000	−1.732
3900	40.574	358.483	322.447	140.539	13.039	128.972	−1.727
4000	40.655	359.511	323.361	144 601	12.956	131.945	−1.723
4100	40.737	360.516	324.255	148.670	12.881	134.921	−1.719
4200	40.818	361.498	325.130	152.748	12.815	137.898	−1.715
4300	40.900	362.460	325.987	156.834	12.758	140.877	−1.711
4400	40.981	363.401	326.826	160.928	12.712	143.857	−1.708
4500	41.063	364.323	327.650	165.030	12.678	146.838	−1.704
4600	41.144	365.226	328.457	169.141	12.657	149.820	−1.701
4700	41.226	366.112	329.248	173.259	12.650	152.802	−1.698
4800	41.307	366.981	330.026	177.386	12.658	155.784	−1.695
4900	41.389	367.833	330.788	181.521	12.682	158.765	−1.692
5000	41.470	368.670	331.538	185.664	12.723	161.746	−1.690
5100	41.551	369.492	332.274	189.815	12.781	164.726	−1.687
5200	41.633	370.300	332.997	193.974	12.856	167.705	−1.685
5300	41.714	371.094	333.709	198.141	12.950	170.682	−1.682
5400	41.796	371.874	334.408	202.317	13.062	173.657	−1.680
5500	41.877	372.642	335.097	206.500	13.192	176.630	−1.677
5600	41.958	373.397	335.774	210.692	13.341	179.600	−1.675
5700	42.040	374.141	336.440	214.892	13.509	182.567	−1.673
5800	42.121	374.873	337.097	219.100	13.695	185.532	−1.671
5900	42.202	375.593	337.743	223.316	13.900	188.493	−1.669
6000	42.284	376.303	338.380	227.541	14.122	191.450	−1.667

PREVIOUS· December 1961 (1 atm) CURRENT: December 1961 (1 bar)

Iodine Chloride (ICl) **CRYSTAL** **M_r = 162.3575** **Iodine Chloride (ICl)** **$Cl_1I_1(cr)$**

$S°(298.15\ K) = 97.927\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 300.53\ K$

$\Delta_f H°(0\ K) = -36.395 \pm 0.105\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -35.422 \pm 0.105\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 11.602 \pm 0.008\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is that adopted by Calder and Giauque[1] from an analysis of the equilibrium data of McMorris and Yost[2] and Beeson and Yost.[3] This yielded a enthalpy of formation of ICl(g), from which the heat of formation of ICl(cr) was calculated by using the heat of vaporization determined by Calder and Giauque.[1]

Heat Capacity and Entropy

The heat capacity has been measured by Calder and Giauque[1] from 17–322 K. The entropy was calculated based on $S°(15\ K) = 0.592\ cal \cdot K^{-1} \cdot mol^{-1}$. Above 300 K the heat capacity data was extrapolated smoothly.

Fusion Data

All data were measured by Calder and Giauque.[1]

References

[1] G. V. Calder and W. F. Giauque, J. Phys. Chem. 69, 2443 (1965).
[2] J. McMorris and D. M. Yost, J. Amer. Chem. Soc. 54, 2247 (1932).
[3] C. M. Beeson and D. M. Yost, J. Chem. Phys. 7, 44 (1939).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.163	−36.395	−36.395	INFINITE
100	40.246	45.693	143.013	−9.732	−36.945	−29.015	15.156
200	49.539	77.011	102.805	−5.159	−36.357	−21.267	5.554
298.15	55.229	97.927	97.927	0.	−35.422	−14.049	2.461
300	55.325	98.268	97.928	0.102	−35.401	−13.917	2.423
300.530	55.589	98.366	97.928	0.131	--- CRYSTAL <--> LIQUID ---		
400	60.195	114.866	100.158	5.883	−42.174	−6.656	0.869
500	64.379	128.756	104.525	12.116	−61.826	4.083	−0.427
600	68.145	140.833	109.591	18.745	−58.889	16.995	−1.480
700	71.489	151.594	114.836	25.731	−55.624	29.389	−2.193
800	74.412	161.335	120.049	33.029	−52.065	41.294	−2.696
900	76.914	170.249	125.139	40.599	−48.250	52.737	−3.061
1000	78.994	178.464	130.066	48.398	−44.220	63.743	−3.330

PREVIOUS. September 1963 CURRENT: September 1965

Iodine Chloride (ICl) **$Cl_1I_1(cr)$**

Iodine Chloride (ICl) LIQUID $M_r = 162.3575$ Iodine Chloride (ICl) $Cl_1I_1(l)$

$S°(298.15\ K) = [136.167]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 300.53\ K$

$\Delta_f H°(298.15\ K) = [-23.929]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 11.602 \pm 0.008\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(300.53\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity from 300.53 to 317.76 K has been measured by Calder and Giauque.[1] Above 318 K it was extrapolated in a smooth manner. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Reference

[1] G. V. Calder and W. F. Giauque, J. Phys. Chem. 69, 2443 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	102.759	136.167	136.167	0.	−23.929	−13.958	2.445
300	102.851	136.802	136.168	0.190	−23.821	−13.896	2.420
300.530	103.856	136.972	136.170	0.241	--- CRYSTAL <--> LIQUID ---		
400	98.324	165.893	140.170	10.289	−26.275	−11.168	1.458
500	94.140	187.384	147.559	19.913	−42.536	−5.941	0.621
600	89.956	204.178	155.649	29.117	−37.025	0.853	−0.074
700	85.772	217.730	163.582	37.904	−31.958	6.759	−0.504
800	81.588	228.911	171.071	46.272	−27.329	11.969	−0.781
900	77.404	238.279	178.033	54.221	−23.135	16 625	−0.965
1000	73.220	246.217	184.465	61.753	−19.373	20.837	−1.088

PREVIOUS: September 1963 CURRENT: September 1965

Iodine Chloride (ICl) CRYSTAL-LIQUID $M_r = 162.3575$ Iodine Chloride (ICl) $Cl_1I_1(cr,l)$

0 to	300.53 K	crystal
above	300.53 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−12.163	−36.395	−36.395	INFINITE
100	40.246	45.693	143.013	−9.732	−36.945	−29.015	15.156
200	49.539	77.011	102.805	−5.159	−36.357	−21.267	5.554
298.15	55.229	97.927	97.927	0.	−35.422	−14.049	2.461
300	55.325	98.268	97.928	0.102	−35.401	−13.917	2.423
300.530	55.589	98.366	97.928	0.131	CRYSTAL <--> LIQUID		
300.530	103.856	136.972	97.928	11.734		TRANSITION	
400	98.324	165.893	111.438	21.782	−26.275	−11.168	1.458
500	94.140	187.384	124.573	31.405	−42.536	−5.941	0.621
600	89.956	204.178	136.494	40.610	−37.025	0.853	−0.074
700	85.772	217.730	147.164	49.397	−31.958	6.759	−0.504
800	81.588	228.911	156.705	57.765	−27.329	11.969	−0.781
900	77.404	238.279	165.263	65.714	−23.135	16.625	−0.965
1000	73.220	246.217	172.972	73.245	−19.373	20.837	−1.088

PREVIOUS: CURRENT: September 1965

Iodine Chloride (ICl) $Cl_1I_1(cr,l)$

Iodine Chloride (ICl) IDEAL GAS $M_r = 162.3575$ Iodine Chloride (ICl) $Cl_1I_1(g)$

$S°(298.15\ K) = 247.567\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 19.141 \pm 0.105\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = 17.506 \pm 0.105\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 382.18\ cm^{-1}$ $\omega_ex_e = 1.450\ cm^{-1}$ $\sigma = 1$
$B_e = 0.11298\ cm^{-1}$ $\alpha_e = 0.0005275\ cm^{-1}$ $r_e = 2.327$ Å

Enthalpy of Formation

The dissociation energy from spectroscopic measurements of ICl(g) has been summarized by Evans *et al.*[1] from which they adopt $D_0^\circ = 49.64$ kcal·mol^{-1}. McMorris and Yost[2] and Beeson and Yost[3] studied the equilibria $NOCl = NO + 0.5Cl_2$ and $NO + ICl = NOCl + 0.5I_2(g)$ from which the equilibrium constant of $ICl = 1/2\ Cl_2 + 1/2\ I_2(g)$ can be obtained. Calder and Giauque[4] have used 3rd law analysis to obtain $D_0^\circ = 49.578 \pm 0.025$ kcal·mol^{-1}. This value was adopted yielding $\Delta_fH°(298.15\ K) = 4.184 \pm 0.025$ kcal·mol^{-1} (17.506 ± 0.105 kJ·mol^{-1}).

Heat Capacity and Entropy

The molecular and vibrational constants were obtained from Herzberg.[5] The values were then adjusted for the normal isotopic abundance of chlorine.

References

[1] W. H. Evans, T. R. Munson and D. D. Wagman, J. Res. Nat. Bur. Stand. 55, 147 (1955).
[2] J. McMorris and D. M. Yost, J. Amer. Chem. Soc. 54, 2247 (1932).
[3] C. M. Beeson and D. M. Yost, J. Chem. Phys. 7, 44 (1939).
[4] G. V. Calder and W. F. Giauque, J. Phys. Chem. 69, 2443 (1965).
[5] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York (1950).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.555	19.141	19 141	INFINITE
100	30.179	211.592	277.844	−6.625	19.089	10.430	−5.448
200	33.787	233.701	250.772	−3.414	18.315	2.067	−0.540
250	34.859	241.364	248.149	−1.696	17.910	−1.948	0.407
298.15	35.548	247.567	247.567	0.	17.506	−5.737	1.005
300	35.570	247.787	247.568	0.066	17.490	−5.881	1.024
350	36.056	253.309	248.003	1.857	17.016	−9.740	1.454
400	36.401	258.147	248.975	3.669	8.539	−13.255	1.731
450	36.656	262.450	250.237	5.496	7.461	−15.914	1.847
500	36.849	266.323	251.655	7.334	−13.680	−16.554	1.729
600	37.125	273.067	254.678	11.033	−13.674	−17.130	1.491
700	37.313	278.805	257.725	14.756	−13.671	−17.706	1.321
800	37.452	283.797	260.679	18.494	−13.672	−18.283	1.194
900	37.562	288.215	263.498	22.245	−13.676	−18.859	1.095
1000	37.654	292.177	266.171	26.006	−13.685	−19.434	1.015
1100	37.734	295.770	268.701	29.776	−13.698	−20.009	0.950
1200	37.806	299.056	271.096	33.553	−13.718	−20.582	0.896
1300	37.871	302.085	273.364	37.336	−13.748	−21.152	0.850
1400	37.932	304.894	275.517	41.127	−13.792	−21.720	0.810
1500	37.991	307.513	277.564	44.923	−13.855	−22.285	0.776
1600	38.046	309.966	279.513	48.725	−13.942	−22.844	0.746
1700	38.100	312.274	281.373	52.532	−14.057	−23.397	0.719
1800	38.152	314.454	283.151	56.345	−14.204	−23.942	0.695
1900	38.203	316.518	284.853	60.162	−14.384	−24.478	0.673
2000	38.254	318.479	286.486	63.985	−14.600	−25.004	0.653
2100	38.303	320.346	288.054	67.813	−14.851	−25.518	0.635
2200	38.352	322.129	289.563	71.646	−15.134	−26.020	0.618
2300	38.400	323.835	291.016	75.483	−15.446	−26.508	0.602
2400	38.448	325.470	292.418	79.326	−15.783	−26.982	0.587
2500	38.495	327.041	293.772	83.173	−16.140	−27.441	0.573
2600	38.542	328.552	295.081	87.025	−16.513	−27.886	0.560
2700	38.589	330.007	296.347	90.881	−16.894	−28.316	0.548
2800	38.635	331.411	297.575	94.743	−17.281	−28.732	0.536
2900	38.682	332.768	298.765	98.608	−17.666	−29.134	0.525
3000	38.728	334.080	299.920	102.479	−18.046	−29.523	0.514
3100	38.774	335.351	301.043	106.354	−18.416	−29.899	0.504
3200	38.820	336.582	302.134	110.234	−18.773	−30.264	0.494
3300	38.866	337.778	303.196	114.118	−19.112	−30.618	0.485
3400	38.911	338.939	304.231	118.007	−19.431	−30.962	0.476
3500	38.957	340.067	305.239	121.900	−19.727	−31.296	0.467
3600	39.002	341.165	306.221	125.798	−19.997	−31.623	0.459
3700	39.048	342.234	307.180	129.701	−20.239	−31.943	0.451
3800	39.093	343.276	308.117	133.608	−20.453	−32.256	0.443
3900	39.138	344.292	309.031	137.519	−20.635	−32.564	0.436
4000	39.183	345.284	309.925	141.435	−20.785	−32.868	0.429
4100	39.229	346.252	310.799	145.356	−20.901	−33.169	0.423
4200	39.274	347.198	311.655	149.281	−20.984	−33.467	0.416
4300	39.319	348.123	312.492	153.211	−21.031	−33.763	0.410
4400	39.364	349.027	313.312	157.145	−21.042	−34.059	0.404
4500	39.409	349.912	314.116	161.083	−21.017	−34.355	0.399
4600	39.454	350.779	314.903	165.027	−20.955	−34.652	0.393
4700	39.499	351.628	315.676	168.974	−20.856	−34.951	0.388
4800	39.544	352.460	316.433	172.926	−20.720	−35.252	0.384
4900	39.589	353.276	317.177	176.883	−20.546	−35.557	0.379
5000	39.634	354.076	317.907	180.844	−20.335	−35.866	0.375
5100	39.678	354.861	318.624	184.810	−20.087	−36.178	0.371
5200	39.723	355.632	319.328	188.780	−19.801	−36.497	0.367
5300	39.768	356.389	320.020	192.754	−19.478	−36.821	0.363
5400	39.813	357.133	320.701	196.733	−19.118	−37.151	0.359
5500	39.858	357.864	321.370	200.717	−18.721	−37.489	0.356
5600	39.903	358.582	322.028	204.705	−18.288	−37.834	0.353
5700	39.947	359.289	322.676	208.698	−17.819	−38.187	0.350
5800	39.992	359.984	323.313	212.694	−17.314	−38.549	0.347
5900	40.037	360.668	323.940	216.696	−16.774	−38.919	0.345
6000	40.082	361.342	324.558	220.702	−16.199	−39.300	0.342

PREVIOUS September 1965 (1 atm) CURRENT September 1965 (1 bar)

Potassium Chloride (KCl) CRYSTAL $M_r = 74.5513$

$\Delta_f H°(0\ K) = -436.38 \pm 0.25\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = 82.55 \pm 0.17\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -436.68 \pm 0.25\ kJ \cdot mol^{-1}$
$T_{fus} = 1044\ K$ $\Delta_{fus} H° = 26.284\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was calculated from the enthalpy of hydrolysis of K(cr), the enthalpies of solution of HCl(g) and KCl(cr), and the standard enthalpy of neutralization of a strong acid and strong base. Extensive measurements are available for all these quantities. Values used in the calculation, in addition to the enthalpy of formation for HCl(g), are summarized below.

Source	Reaction	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1}
1–4	$K(cr) + H_2O(l) \rightarrow KOH(\infty H_2O) + 1/2\ H_2(g)$	−46.966 ± 0.05
5, 2, 6	$HCl(g) \rightarrow HCl(\infty H_2O)$	−17.88 ± 0.015
7	$KCl(\infty H_2O) \rightarrow KCl(cr)$	−4.115 ± 0.010
7	$KOH(\infty H_2O) + HCl(\infty H_2O) \rightarrow KCl(\infty H_2O) + H_2O(l)$	−13.345 ± 0.025

Heat Capacity and Entropy

Low temperature heat capacities were obtained from the data (2.8–275 K) of Berg and Morrison.[8] Previous measurements scatter around the selected values and are in good agreement. These include Strelkov *et al.* (12–298 K),[9] Clusius *et al.* (10–273 K),[10] and Southard and Nelson (17–285 K).[11] For other less extensive data see the review by Kelley and King.[12] The entropy is based on the extrapolation $S°(2.8\ K) = 0.0006\ cal \cdot K^{-1} \cdot mol^{-1}$.

High temperature values are based on enthalpy data (373–1038 K) from Douglas.[13] These values join smoothly with the low temperature values and are in excellent agreement with the enthalpy data (673–933 K) of Skuratov and Lapushkin[14] and the adiabatic heat capacities (334–721 K) of Mustajoki.[15]

Fusion Data

The melting point and enthalpy of melting are from Douglas.[13] Values of $T_{fus} = 1043$ K and 1045 K have been reported by Aukrust *et al.*[16] and Johnson and Bredig,[17] respectively. The enthalpy of melting is confirmed by $\Delta_{fus} H° = 6.34\ kcal \cdot mol^{-1}$ obtained from enthalpy data by Dworkin and Bredig[18] and $\Delta_{fus} H° = 6.4$ and $6.5\ kcal \cdot mol^{-1}$ based on enthalpy and phase diagram studies of Aukrust *et al.*,[16] respectively.

References

[1] S. R. Gunn and L. G. Green, J. Am. Chem. Soc. **80**, 4782 (1957).
[2] S. R. Gunn, UCRL–7992, Livermore, Calif., (July 1964).
[3] C. E. Messer, L. G. Fasolino and C. E. Thalmayer, J. Amer. Chem. Soc. **77**, 4524 (1955).
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Potassium Chloride (KCl) $Cl_1K_1(cr)$

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.368	−436.379	−436.379	INFINITE
100	39.200	31.773	125.871	−9.410	−437.610	−427.776	223.447
200	48.438	62.630	87.169	−4.908	−437.221	−418.052	109.184
298.15	51.287	82.554	82.554	0.	−436.684	−408.761	71.613
300	51.329	82.872	82.555	0.095	−436.675	−408.587	71.141
400	53.137	97.895	84.592	5.321	−438.662	−398.837	52.083
500	54.752	109.927	88.494	10.717	−438.160	−388.935	40.632
600	56.317	120.048	92.931	16.270	−437.462	−379.152	33.008
700	58.003	128.852	97.447	21.984	−436.580	−369.501	27.573
800	60.078	136.727	101.873	27.883	−435.508	−359.989	23.505
900	62.911	143.957	106.152	34.024	−434.210	−350.625	20.350
1000	66.969	150.782	110.276	40.505	−432.610	−341.420	17.834
1044.000	69.287	153.713	112.045	43.502	--- CRYSTAL <--> LIQUID ---		
1100	71.965	157.406	114.261	47.460	−509.549	−327.785	15.565
1200	76.149	163.853	118.126	54.872	−506.096	−311.410	13.555
1300	79.496	170.086	121.885	62.662	−502.272	−295.339	11.867
1400	82.006	176.075	125.543	70.744	−498.159	−279.574	10.431
1500	83.680	181.794	129.104	79.035	−493.843	−264.111	9.197

PREVIOUS: December 1961   CURRENT: March 1966

Potassium Chloride (KCl) $Cl_1K_1(cr)$

Potassium Chloride (KCl) LIQUID $M_r = 74.5513$ Potassium Chloride (KCl) $Cl_1K_1(l)$

$S°(298.15\ K) = [86.657]\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{fus}H° = 1044\ K$

$\Delta_fH°(298.15\ K) = [-421.791]\ kJ\cdot mol^{-1}$
$\Delta_{fus}H° = 26.284\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1044\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The constant heat capacity, 17.59 $cal\cdot K^{-1}\cdot mol^{-1}$, was derived from enthalpy data (1053–1173 K) of Douglas.[1] This value was extrapolated above and below the experimental range. A lower value of 16.7 $cal\cdot K^{-1}\cdot mol^{-1}$ was derived by Dworkin[2] from enthalpy data (1050–1110 K) obtained in an enthalpy of melting study. The entropy of the liquid is calculated in a manner analogous to that used for enthalpy of formation.

Fusion Data

The melting point and enthalpy of melting are from Douglas.[1] Values of $T_{fus} = 1043$ K and 1045 K have been reported by Aukrust *et al.*[3] and Johnson and Bredig,[4] respectively. The enthalpy of melting is confirmed by $\Delta_{fus}H° = 6.34\ kcal\cdot mol^{-1}$ obtained from enthalpy data by Dworkin and Bredig[5] and $\Delta_{fus}H° = 6.4$ and 6.5 $kcal\cdot mol^{-1}$ based on enthalpy and phase diagram studies of Aukrust *et al.*,[3] respectively.

Vaporization Data

T_{vap}(equilibrium vapor) = ~1710 K is the temperature resulting in unit total pressure based on the calculated partial pressures of KCl(g) and $K_2Cl_2(g)$. This value may be compared with boiling points of 1688 and 1690 K observed respectively by Ruff and Mugdan[6] and von Wartenburg and Albrecht.[7] $\Delta_{vap}H°$ (equilibrium vapor) at the boiling point is calculated as the enthalpy of vaporization of one mole of liquid to vapor containing 22.3 mole percent of dimer. According to the selected functions, the amount of dimer at lower temperatures increases gradually to about 32 mole percent at the melting point then decreases rapidly over the crystal. T_{vap} (monomer) = ~1750 K is taken as the temperature at which the calculated Gibbs energy change is zero for $KCl(l) \rightarrow KCl(g)$, while $\Delta_{vap}H°$ (monomer) is the corresponding enthalpy of vaporization.

Data on vapor pressures and dimer–monomer equilibrium are reviewed on the tables for KCl(g) and $K_2Cl_2(g)$, respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0							
100							
200							
298.15	73.597	86.657	86.657	0.	−421.791	−395.090	69.218
300	73.597	87.112	86.658	0.136	−421.740	−394.925	68.763
400	73.597	108.285	89.545	7.496	−421.594	−385.925	50.397
500	73.597	124.707	94.996	14.855	−419.128	−377.293	39.415
600	73.597	138.126	101.100	22.215	−416.624	−369.160	32.138
700	73.597	149.471	107.221	29.575	−414.096	−361.449	26.972
800	73.597	159.298	113.130	36.934	−411.563	−354.101	23.120
900	73.597	167.966	118.751	44.294	−409.046	−347.070	20.143
1000	73.597	175.721	124.067	51.654	−406.568	−340.317	17.776
1044.000	73.597	178.890	126.311	54.892	--- CRYSTAL <--> LIQUID ---		
1100	73.597	182.735	129.087	59.013	−483.102	−329.200	15.632
1200	73.597	189.139	133.828	66.373	−479.702	−315.359	13.727
1300	73.597	195.030	138.312	73.733	−476.307	−301.801	12.127
1400	73.597	200.484	142.561	81.092	−472.917	−288.505	10.764
1500	73.597	205.561	146.593	88.452	−469.533	−275.451	9.592
1600	73.597	210.311	150.429	95.812	−466.154	−262.622	8.574
1700	73.597	214.773	154.084	103.171	−462.781	−250.005	7.682
1800	73.597	218.980	157.574	110.531	−459.415	−237.586	6.895
1900	73.597	222.959	160.911	117.891	−456.058	−225.354	6.195
2000	73.597	226.734	164.109	125.250	−452.711	−213.298	5.571

PREVIOUS: December 1961 CURRENT: March 1966

Potassium Chloride (KCl) CRYSTAL-LIQUID

0	to	1044 K	crystal
above		1044 K	liquid

Refer to the individual tables for details.

$M_r = 74.5513$ Potassium Chloride (KCl) $Cl_1K_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−11.368	−436.379	−436.379	INFINITE
100	39.200	31.773	125.871	−9.410	−437.610	−427.776	223.447
200	48.438	62.630	87.169	−4.908	−437.221	−418.052	109.184
298.15	51.287	82.554	82.554	0.	−436.684	−408.761	71.613
300	51.329	82.872	82.555	0.095	−436.675	−408.587	71.141
400	53.137	97.895	84.592	5.321	−438.662	−398.837	52.083
500	54.752	109.927	88.494	10.717	−438.160	−388.935	40.632
600	56.317	120.048	92.931	16.270	−437.462	−379.152	33.008
700	58.003	128.852	97.447	21.984	−436.580	−369.501	27.573
800	60.078	136.727	101.873	27.883	−435.508	−359.989	23.505
900	62.911	143.957	106.152	34.024	−434.210	−350.625	20.350
1000	66.969	150.782	110.276	40.505	−432.610	−341.420	17.834
1044.000	69.287	153.713	112.045	43.502	CRYSTAL <−−> LIQUID TRANSITION		
1044.000	73.597	178.890	112.045	69.786			
1100	73.597	182.735	115.547	73.907	−483.102	−329.200	15.632
1200	73.597	189.139	121.417	81.267	−479.702	−315.359	13.727
1300	73.597	195.030	126.856	88.626	−476.307	−301.801	12.127
1400	73.597	200.484	131.922	95.986	−472.917	−288.505	10.764
1500	73.597	205.561	136.664	103.346	−469.533	−275.451	9.592
1600	73.597	210.311	141.121	110.705	−466.154	−262.622	8.574
1700	73.597	214.773	145.323	118.065	−462.781	−250.005	7.682
1800	73.597	218.980	149.299	125.425	−459.415	−237.586	6 895
1900	73.597	222.959	153.072	132.784	−456.058	−225.354	6.195
2000	73.597	226.734	156.662	140.144	−452.711	−213.298	5.571

PREVIOUS: CURRENT: March 1966

Potassium Chloride (KCl) IDEAL GAS $M_r = 74.5513$ Potassium Chloride (KCl) $Cl_1K_1(g)$

$S°(298.15\ K) = 239.087\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -212.89 \pm 0.4\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -214.68 \pm 0.4\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = 278.6\ cm^{-1}$ $\omega_ex_e = 1.157\ cm^{-1}$ $\sigma = 1$
$B_e = 0.127536\ cm^{-1}$ $\alpha_e = 0.0007799$ $r_e = 2.6667$ Å

Enthalpy of Formation

The enthalpy of formation was calculated from that of the liquid based on $\Delta_{vap}H°(298.15\ K) = 49.5\ kcal{\cdot}mol^{-1}$ as selected from vapor pressure analyses summarized below. Partial pressures for the monomer were obtained from data of the first four sources by combination of total vapor pressures with PVT data or with transpiration data. Mass spectrometric values[5] are based on temperature variation of ion intensity. These same five studies were used in selection of $\Delta_fH°(298.15\ K) = 45.0\ kcal{\cdot}mol^{-1}$ for the dimer–monomer equilibrium (see K_2Cl_2).

The resulting tables were tested by comparison with total pressure data over the range 819–1691 K. Dimer–monomer ratios calculated from the tables were used to convert observed total pressures to the monomer pressures which are analyzed below.[6–11] The results are consistent except near the boiling point where the observed pressures[10, 11] are 6–18% larger than those calculated. Knudsen effusion and transpiration studies over the crystal were not analyzed since they are in essential agreement with the torsion effusion data of source 6.

Source	Method	Data Points	T/K	$\Delta_{vap}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
1	PVT + Vap. Press. (a)	15	1310–1404	51.04 ± 0.40	49.67	−1.0 ± 0.4
2	Trans. + Vap. Press.	10	1253–1352	50.75 ± 0.80	49.49	−1.0 ± 0.6
3	Trans. + Vap. Press. (b)	5	1261–1372	50.26 ± 0.77	49.28	−0.8 ± 0.6
4	Trans. + Vap. Press.	7	1250–1473	49.67 ± 0.66	49.46	−0.1 ± 0.5
5	Mass Spectrometry	–	774–1016	49.6 ± 1.8	—	—
6	Total Vap. Press.	137	819–945	49.5	49.57	0.06
7	Total Vap. Press.	9	847–936	49.0	49.95	1.0 ± 0.6
8	Total Vap. Press.	9	1179–1378	50.3	49.44	−0.8 ± 0.2
9	Total Vap. Press.	9	1170–1466	51.0	49.42	−1.2 ± 0.2
10	Total Vap. Press.	7	1393–1688	53.6	49.48	−2.7 ± 0.4
11	Total Vap. Press.	16	1389–1691	50.2	49.22	−0.8 ± 0.5

(a) Total vapor pressure.[2,3,8] (b) 1235 K was omitted.

Heat Capacity and Entropy

Rotational and vibrational constants are based on the microwave studies of Clouser and Gordy.[12] Earlier microwave data of Honig *et al.*[13] and electric resonance data of Lee *et al.*[14] are in excellent agreement. Infrared spectra of Rice and Klemperer[15] yield $\omega_e = 261 \pm 6\ cm^{-1}$ which is in good agreement. The constants were adjusted to a natural isotopic composition of 24.4% ^{37}Cl and 6.8% ^{41}K.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.885	−212.893	−212.893	INFINITE
100	31.699	201.456	270.564	−6.911	−213.108	−220.243	115.043
200	35.270	224.739	242.394	−3.531	−213.841	−227.094	59.311
250	36.034	232.698	239.686	−1.747	−214.241	−230.362	48.131
298.15	36.496	239.087	239.087	0.	−214.681	−233.428	40.896
300	36.510	239.313	239.088	0.068	−214.700	−233.544	40.664
350	36.829	244.967	239.534	1.902	−217.616	−236.547	35.303
400	37.056	249.900	240.528	3.749	−218.231	−239.209	31.237
450	37.228	254.275	241.817	5.606	−218.826	−241.795	28.067
500	37.362	258.205	243.263	7.471	−219.403	−244.316	25.524
600	37.567	265.036	246.339	11.218	−220.511	−249.194	21.694
700	37.721	270.839	249.435	14.983	−221.578	−253.890	18.945
800	37.848	275.884	252.432	18.761	−222.626	−258.434	16.874
900	37.960	280.349	255.291	22.552	−223.679	−262.847	15.255
1000	38.061	284.354	258.000	26.353	−224.759	−267.141	13.954
1100	38.156	287.986	260.564	30.164	−304.842	−266.715	12.665
1200	38.246	291.309	262.989	33.984	−304.981	−263.243	11.459
1300	38.333	294.374	265.287	37.813	−305.117	−259.759	10.437
1400	38.417	297.218	267.468	41.651	−305.250	−256.265	9.561
1500	38.500	299.871	269.541	45.496	−305.379	−252.762	8.802
1600	38.582	302.359	271.515	49.351	−305.505	−249.250	8.137
1700	38.662	304.700	273.399	53.213	−305.630	−245.730	7.550
1800	38.742	306.912	275.200	57.083	−305.753	−242.203	7.029
1900	38.821	309.009	276.924	60.961	−305.878	−238.669	6.561
2000	38.900	311.002	278.579	64.847	−306.005	−235.129	6.141
2100	38.978	312.902	280.168	68.741	−306.136	−231.582	5.760
2200	39.056	314.717	281.698	72.643	−306.276	−228.028	5.414
2300	39.134	316.455	283.172	76.552	−306.425	−224.468	5.098
2400	39.211	318.122	284.593	80.470	−306.587	−220.902	4.808
2500	39.288	319.725	285.967	84.395	−306.766	−217.328	4.541
2600	39.365	321.267	287.295	88.327	−306.965	−213.746	4.294
2700	39.442	322.754	288.581	92.268	−307.187	−210.157	4.066
2800	39.519	324.190	289.827	96.216	−307.436	−206.559	3.853
2900	39.595	325.578	291.036	100.171	−307.714	−202.951	3.656
3000	39.672	326.922	292.210	104.135	−308.027	−199.333	3.471
3100	39.748	328.224	293.351	108.106	−308.376	−195.704	3.298
3200	39.825	329.487	294.461	112.084	−308.766	−192.064	3.135
3300	39.901	330.714	295.541	116.071	−309.190	−188.411	2.982
3400	39.977	331.906	296.593	120.065	−309.667	−184.744	2.838
3500	40.053	333.066	297.618	124.066	−310.191	−181.062	2.702
3600	40.130	334.195	298.619	128.075	−310.770	−177.365	2.573
3700	40.206	335.296	299.595	132.092	−311.404	−173.651	2.452
3800	40.282	336.369	300.549	136.116	−312.099	−169.918	2.336
3900	40.358	337.416	301.481	140.148	−312.856	−166.167	2.226
4000	40.434	338.439	302.392	144.188	−313.673	−162.396	2.121
4100	40.510	339.438	303.283	148.235	−314.560	−158.604	2.021
4200	40.586	340.415	304.156	152.290	−315.524	−154.788	1.925
4300	40.662	341.371	305.010	156.352	−316.565	−150.949	1.834
4400	40.738	342.307	305.847	160.422	−317.408	−147.112	1.746
4500	40.814	343.223	306.668	164.500	−318.543	−143.229	1.663
4600	40.889	344.121	307.472	168.585	−319.751	−139.320	1.582
4700	40.965	345.001	308.261	172.678	−321.016	−135.386	1.505
4800	41.041	345.865	309.036	176.778	−322.247	−131.436	1.430
4900	41.117	346.712	309.796	180.886	−323.658	−127.446	1.359
5000	41.193	347.543	310.543	185.001	−325.144	−123.427	1.289
5100	41.269	348.360	311.276	189.125	−326.705	−119.377	1.223
5200	41.344	349.162	311.997	193.255	−328.343	−115.296	1.158
5300	41.420	349.950	312.706	197.393	−330.056	−111.183	1.096
5400	41.496	350.725	313.403	201.539	−331.844	−107.037	1.035
5500	41.572	351.487	314.088	205.693	−333.706	−102.857	0.977
5600	41.648	352.237	314.763	209.854	−335.640	−98.642	0.920
5700	41.723	352.975	315.427	214.022	−337.300	−94.440	0.865
5800	41.799	353.701	316.080	218.198	−339.330	−90.162	0.812
5900	41.875	354.416	316.724	222.382	−341.422	−85.848	0.760
6000	41.951	355.120	317.358	226.573	−343.575	−81.498	0.710

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

Potassium Perchlorate ($KClO_4$) CRYSTAL M_r = 138.5489

$S°(298.15\ K) = 151.04 \pm 0.8\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs} = 572.7\ K$
$T_{fus} = 798\ K$

$\Delta_f H°(0\ K) = -422.1 \pm 1.0\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -430.1 \pm 4.0\ kJ{\cdot}mol^{-1}$
$\Delta_{trs} H° = 13.77\ kJ{\cdot}mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The enthalpy of decomposition of $KClO_4(cr)$ to $KCl(cr)$ and $O_2(g)$ was measured by Johnson and Gilliland,[1] yielding $\Delta_r H°(298.15\ K) = -103.22 \pm 0.15\ kcal{\cdot}mol^{-1}$. Hofmann and Martin[2] burned a mixture of paraffin and potassium perchlorate and obtained $\Delta_r E(298.15\ K) = -1.73\ kcal{\cdot}mol^{-1}$ for the constant volume process corresponding to the reaction: $KClO_4(cr) = KCl(cr) + 2\,O_2(g)$. Correction of their value for $\Delta(pV)$ gives $\Delta_r H°(298.15\ K) = -0.55\ kcal{\cdot}mol^{-1}$ which agrees reasonably well to the corresponding value, $-0.96 \pm 0.10\ kcal{\cdot}mol^{-1}$, reported by Johnson and Gilliland.[1] However, for the same reaction, $\Delta_r H°(298.15\ K) = -2.55 \pm 0.18\ kcal{\cdot}mol^{-1}$ was determined by Skuratov *et al.*[3] They measured this quantity by two different methods which gave concordant results. The value of $\Delta_f H°(298.15\ K)$ reported was $-101.9 \pm 0.2\ kcal{\cdot}mol^{-1}$. The value used here is the average of these four results.

Berthelot and Vieille[4] determined the difference between the enthalpy of explosion of ammonium picrate and that of an ammonium picrate–potassium perchlorate mixture, and also the difference between the enthalpy of explosion of potassium picrate and that of a potassium pricrate–potassium perchlorate mixture. They obtained $\Delta_r H° = 7.5\ kcal{\cdot}mol^{-1}$ for the reaction $KClO_4(cr) = KCl(cr) + 2\,O_2(g)$. From that the value of $\Delta_f H°(298.15\ K)$ was calculated to be $-111.9\ kcal{\cdot}mol^{-1}$. This value was not used.

Heat Capacity and Entropy

The low temperature heat capacities (12.53–298.07 K) were measured by Latimer and Ahlberg.[5] The heat capacities above 298.15 K were estimated by comparison with those of $NaClO_4(cr)$. $S°(298.15\ K)$ was reported by Kelley and King,[6] based on the low temperature heat capacities measured by Latimer and Ahlberg,[5] using $S°(12.59\ K, extrap) = 0.14\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

Transition Data

T_{trs} and $\Delta_{trs} H°$ were obtained from the U. S. National Bureau of Standards.[7]

Fusion Data

T_{fus} was taken from the National Research Council.[8]

References

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Potassium Perchlorate ($KClO_4$) $Cl_1K_1O_4(cr)$

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
0	0.	0.	INFINITE	−21.071	−422.147	−422.147	INFINITE
100	64.936	59.404	235.342	−17.594	−427.667	−385.936	201.592
200	88.408	112.278	161.419	−9.828	−429.837	−343.204	89.636
298.15	110.207	151.042	151.042	0.	−430.115	−300.282	52.608
300	112.968	151.733	151.045	0.206	−430.104	−299.477	52.144
400	138.490	187.967	155.809	12.863	−430.602	−255.709	33.392
500	153.971	220.606	165.568	27.519	−426.958	−212.379	22.187
572.700	162.758	242.115	173.939	39.045	I <−−> II TRANSITION		
572.700	162.661	266.151	173.939	52.810			
600	165.268	273.786	178.309	57.286	−408.365	−170.557	14.848
700	174.316	299.954	193.849	74.273	−402.719	−131.358	9.802
800	182.422	323.770	208.622	92.118	−396.375	−93.018	6.073
900	189.483	345.671	222.649	110.719	−389.427	−55.510	3.222
1000	195.811	365.969	235.979	129.990	−381.961	−18.803	0.982
1100	201.195	384.887	248.666	149.843	−453.021	21.744	−1.033
1200	206.271	402.613	260.764	170.219	−443.702	64.496	−2.807
1300	211.041	419.314	272.324	191.087	−433.965	106.454	−4.277
1400	215.504	435.119	283.392	212.417	−423.832	147.647	−5.509
1500	219.660	450.131	294.012	234.178	−413.329	188.102	−6.550

PREVIOUS: CURRENT: June 1963

Lithium Chloride (LiCl)　　CRYSTAL　　$M_r = 42.394$　Lithium Chloride (LiCl)　　$Cl_1Li_1(cr)$

$S°(298.15\ K) = 59.300 \pm 0.063\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 883 \pm 2\ K$

$\Delta_fH°(0\ K) = -408.359 \pm 1.142\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -408.266 \pm 1.142\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 19.832 \pm 0.42\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was obtained as follows:

	$\Delta_fH°(298.15\ K)$, kcal·mol^{-1}	Source
(1) LiOH(aq, 100 H_2O) → Hcl(aq, 100 H_2O) → LiCl(aq, 201 H_2O)	−13.704 ± 0.014	1
(2) Li(cr) + (aq, 1001 H_2O)(l) → LiOH(aq, 1000 H_2O) + 1/2 H_2(g)	−53.142 ± 0.019	2
(3) LiOH(aq, 1000 H_2O) → LiOH(aq, 100 H_2O) + (aq, 900 H_2O)(l)	0.153 ± 0.040	3
(4) 1/2 H_2(g) + 1/2 Cl_2(g) → HCl(g)	−21.97 ± 0.09	4
(5) HCl(g) + (aq, 100 H_2O)(l) → HCl(aq, 100 H_2O)	−17.575 ± 0.100	5, 6
(6) LiCl(aq, 201 H_2O) → LiCl(cr) + (aq, 201 H_2O)(l)	8.660 ± 0.010	7
(1)+(2)+(3)+(4)+(5)+(6) gives Li(cr) + 1/2 Cl (g) → LiCl(cr)	−97.578 ± 0.273	

A direct calorimetric determination by Siemonsen and Siemonsen[8] gave −94.8 ± 0.6 kcal·mol^{-1}. However, the solution route was thought to be inherently more accurate and was adopted.

Enthalpy Capacity and Entropy

The enthalpy capacity between 15 and 325 K has been measured by Shirley[9] and by Oetting *et al.*[10] The two sets of data are in substantial agreement and were plotted together and used to evalute the entropy at 298. The extrapolation to 0 K was done assuming a T^3 law and yielded $S°(15\ K) = 0.019\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. Above 298, Douglas *et al.*[11] have made enthalpy measurements to 1200 K. Rodigina *et al.*[12] also made enthalpy determinations to 1100 K. These two sets of measurements were averaged and joined smoothly to the low temperature values.

Fusion and Transition Data

The melting point has been reported as follows: 880 K, Douglas *et al.*,[11] 883 K, Rodigina *et al.*,[12] 883 K, Haendler *et al.*;[13] 879 K, Flood *et al.*;[14] 879 K, von Wartenberg and Schulz.[15] The highest value of 883 K was taken as representing the most pure samples. At this temperature the enthalpy equations of Douglas *et al.* yield a enthalpy of fusion of 4.718 kcal·mol^{-1}, those of Rodigina *et al.*, 4.669 kcal·mol^{-1}. Dworkin and Bredig[16] report a value of 4.76 ± 0.10 kcal·mol^{-1} and quote 4.83 kcal·mol^{-1} from a private communication from D. E. Smith. The average value $\Delta_{fus}H° = 4.74 \pm 0.10$ kcal·mol^{-1} was adopted.

A transition at 838 K has been reported by Kislova and Bergman[17] but is not supported by the enthalpy measurements quoted above.

References

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[2] S. R. Gunn and L. G. Green, J. Amer. Chem. Soc. 80, 4782 (1958).
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Enthalpy Reference Temperature = T_r = 298.15 K　　Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.305	−408.359	−408.359	INFINITE
100	36.313	13.585	98.646	−8.506	−409.511	−400.685	209.296
200	43.350	41.045	63.555	−4.502	−408.867	−392.114	102.410
298.15	48.028	59.300	59.300	0.	−408.266	−384.019	67.279
300	48.095	59.597	59.301	0.089	−408.254	−383.869	66.838
400	50.969	73.853	61.225	5.051	−407.628	−375.837	49.079
500	53.342	85.484	64.948	10.268	−410.130	−367.643	38.407
600	55.593	95.409	69.217	15.715	−409.482	−359.202	31.271
700	57.781	104.144	73.595	21.384	−408.574	−350.891	26.184
800	59.936	112.000	77.912	27.270	−407.434	−342.726	22.378
883.000	61.702	118.003	81.402	32.318	--- CRYSTAL <--> LIQUID ---		
900	62.061	119.183	82.105	33.370	−406.085	−334.716	19.426
1000	64.170	125.831	86.149	39.682	−404.528	−326.868	17.074
1100	66.266	132.045	90.042	46.204	−402.762	−319.185	15.157
1200	68.358	137.901	93.788	52.935	−400.788	−311.673	13.567
1300	70.452	143.455	97.397	59.876	−398.606	−304.334	12.228
1400	72.534	148.752	100.877	67.025	−396.213	−297.170	11.088
1500	74.598	153.827	104.239	74.381	−393.610	−290.186	10.105
1600	76.663	158.707	107.492	81.945	−390.796	−283.381	9.251
1700	78.731	163.417	110.644	89.714	−533.008	−269.583	8.283
1800	80.797	167.976	113.703	97.691	−529.021	−254.202	7.377
1900	82.863	172.399	116.676	105.874	−524.833	−239.047	6.572
2000	84.927	176.702	119.571	114.263	−520.446	−224.119	5.853

PREVIOUS:　　CURRENT. June 1962

Lithium Chloride (LiCl) LIQUID $M_r = 42.394$ Lithium Chloride (LiCl) $Cl_1Li_1(l)$

$S°(298.15\ K) = [78.435]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 883 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-390.755]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 19.832 \pm 0.42\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(LiCl, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(883\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity data from the melting point to 1100 K and 1200 K has been reported by Rodigina *et al.*[1] and Douglas *et al.*[2] The equation given by the former authors for the enthalpy of the liquid does not agree with their measurements and has been replaced by $H°(T;293.15) = 18.000T-1.5 \times 10^{-3}T^2-2279\ cal{\cdot}mol^{-1}$, which fits to ±0.3%. The two sets of results were averaged and the equations were assumed to hold up to the normal boiling point. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

The equilibrium boiling point, $T_{vap} = 1656$ K, was taken from von Wartenburg and Schultz.[3] The boiling point of the monomeric gas is defined as the temperature at which it reaches 1 bar pressure. This was obtained from the Gibbs energy crossover between liquid and monomeric gas.

References

[1] E. N. Rodigina, K. Z. Gomelski and V. F. Luginina, Zhur. Neorg. Khim. 4, 975 (1959).
[2] T. B. Douglas, J. L. Dever, and A. W. Harman, U.S. Nat. Bur. Stand. Report 6297, (1959).
[3] H. von Wartenburg and H. Schultz, Z. Electrochem. **27**, 568 (1921).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	48.028	78.435	78.435	0.	−390.755	−372.214	65.210
300	48.095	78.732	78.436	0.089	−390.743	−372.099	64.788
400	50.969	92.989	80.360	5.051	−390.117	−365.980	47.792
500	53.342	104 621	84.084	10.269	−392.618	−359.700	37.578
588.000	55.239	113.421	87.830	15.048	GLASS <--> LIQUID TRANSITION		
588.000	67.807	113.421	87.830	15.048			
600	67.693	114.790	88.355	15.861	−391.825	−353.174	30.747
700	66.747	125.154	92.893	22.583	−389.864	−346.888	25.885
800	65.802	134.005	97.492	29.210	−387.983	−340.878	22.257
883.000	65.015	140.463	101.233	34.639	--- CRYSTAL <--> LIQUID ---		
900	64.856	141.701	101.986	35.743	−386.201	−335.098	19.449
1000	63.911	148.485	106.304	42.182	−384.517	−329.511	17.212
1100	62.965	154.532	110.418	48.525	−382.929	−324.088	15.390
1200	62.015	159.970	114.325	54.774	−381.437	−318.806	13.877
1300	61.070	164.897	118.028	60.929	−380.041	−313.644	12.602
1400	60.124	169.388	121.539	66.988	−378.739	−308.586	11.513
1500	59.165	173.503	124.868	72.953	−377.527	−303.618	10.573
1600	58.216	177.291	128.028	78.822	−376.408	−298.727	9.752
1700	57.284	180.793	131.030	84.597	−520.614	−286.728	8.810
1800	56.346	184.040	133.886	90.278	−518.922	−273.020	7.923
1900	55.403	187.062	136.606	95.866	−517.330	−259.402	7.131
2000	54.455	189.879	139.200	101.359	−515.839	−245.866	6.421

PREVIOUS: CURRENT: June 1962

Lithium Chloride (LiCl) $Cl_1Li_1(l)$

Lithium Chloride (LiCl) CRYSTAL-LIQUID

0 to 883 K crystal
above 883 K liquid

Refer to the individual tables for details.

$M_r = 42.394$ Lithium Chloride (LiCl) $Cl_1Li_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.305	−408.359	−408.359	INFINITE
100	36.313	13.585	98.646	−8.506	−409.511	−400.685	209.296
200	43.350	41.045	63.555	−4.502	−408.867	−392.114	102.410
298.15	48.028	59.300	59.300	0.	−408.266	−384.019	67.279
300	48.095	59.597	59.301	0.089	−408.254	−383.869	66.838
400	50.969	73.853	61.225	5.051	−407.628	−375.837	49 079
500	53.342	85.484	64.948	10.268	−410.130	−367.643	38.407
600	55.593	95.409	69.217	15.715	−409.482	−359.202	31.271
700	57.781	104.144	73.595	21.384	−408.574	−350.891	26.184
800	59.936	112.000	77.912	27.270	−407.434	−342.726	22.378
883.000	61.702	118.003	81.402	32.318	CRYSTAL <−−> LIQUID		
883.000	65.015	140.463	81.402	52.150	TRANSITION		
900	64.856	141.701	82.529	53.254	−386.201	−335.098	19.449
1000	63.911	148.485	88.792	59.693	−384.517	−329.511	17.212
1100	62.965	154.532	94.499	66.036	−382.929	−324.088	15.390
1200	62.015	159.970	99.732	72.285	−381.437	−318.806	13.877
1300	61.070	164.897	104.558	78.440	−380.041	−313.644	12.602
1400	60.124	169.388	109.031	84 499	−378.739	−308.586	11.513
1500	59.165	173.503	113.194	90.464	−377.527	−303.618	10.573
1600	58.216	177.291	117.083	96.333	−376.408	−298.727	9.752
1700	57.284	180.793	120.729	102.108	−520.614	−286.728	8.810
1800	56.346	184.040	124.157	107.789	−518.922	−273.020	7.923
1900	55.403	187.062	127.390	113.377	−517.330	−259.402	7.131
2000	54.455	189.879	130.444	118.870	−515.839	−245.866	6.421

PREVIOUS: CURRENT June 1962

Lithium Chloride (LiCl) $Cl_1Li_1(cr,l)$

Lithium Chloride (LiCl) IDEAL GAS $M_r = 42.394$ Lithium Chloride (LiCl) $Cl_1Li_1(g)$

$S°(298.15\ K) = 212.919\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -195.57\ kJ{\cdot}mol^{-1}$

$\Delta_f H°(298.15\ K) = -195.72 \pm 12.6\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0.0	1

$\omega_e = 641.1 \pm 3.0\ cm^{-1}$ $\omega_e x_e = 4.2 \pm 0.3\ cm^{-1}$ $\sigma = 1$

$B_e = 0.7053\ cm^{-1}$ $\alpha_e = 0.0067\ cm^{-1}$ $r_e = 2.022$ Å

Enthalpy of Formation

Klemperer *et al.*[1] quote a private communication from W. H. Evans at the National Bureau of Standards giving $D_0^\circ = 4.35$ cal·K^{-1}·mol^{-1} which corresponds to $\Delta_f H°(0\ K) = -45.3 \pm 2.4$ kcal·mol^{-1}. A 3rd law analysis of the vapor pressure data of Nesmeyanov and Sazonov[2] in conjunction with the relative concentration of monomer, dimer, and trimer at 870 K from the work of Miller and Kusch[3] leads to a monomer enthalpy of sublimation at 298.15 K of 52.56 kcal·mol^{-1}, this gives $\Delta_f H°(298.15\ K) = -45.02$ kcal·mol^{-1} These values lead, however, to partial vapor pressures of the monomer which are less than half of the total vapor pressure near the boiling point. From the data of Miller and Kusch[3] it would be expected that the monomer would be the predominant species near the boiling point, a fact also substantiated by the work of Beusman,[4] on the average molecular weight of the vapor. Thus it was decided to change the enthalpy of sublimation so as to give the correct normal boiling point and vapor pressures in the region 1400–1600 K and to approximate the relative concentrations of monomer, dimer, and trimer as found by Miller and Kusch at 870 K. A monomer heat of sublimation at 298.15 K of 50.8 kcal·mol^{-1} was chosen, which gives $\Delta_f H°(298.15\ K) = -46.778$ kcal·mol^{-1}. The normal boiling point was taken as 1656 K as determined by von Wartenburg and Schulz[5] and the boiling point of LiCl(g) was found as 1701 K from the Gibbs energy crossover between liquid and gas.

Heat Capacity and Entropy

The spectroscopic constants were taken from Klemperer *et al.*[1] The value of α_e was calculated by the value of a_1 given by the Rittner potential function and the equation given by Klemperer *et al.*[1] The value of r_e was taken from Douglas *et al.*[6]

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[6] T. B. Douglas, J. L. Dever, and A. W. Harman, U.S. Nat. Bur. Stand. Report 6297, (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	-9.061	-195.567	-195.567	INFINITE
100	29.194	179.425	240.943	-6.152	-194.609	-202.367	105.706
200	31.011	200.100	215.893	-3.159	-194.976	-210.035	54.855
250	32.231	207.153	213.461	-1.577	-195.333	-213.759	44.663
298.15	33.245	212.919	212.919	0.	-195.719	-217.274	38.065
300	33.280	213.125	212.920	0.062	-195.735	-217.408	37.854
350	34.119	218.321	213.328	1.747	-196.171	-220.986	32.980
400	34.778	222.922	214.246	3.470	-196.661	-224.498	29.316
450	35.295	227.049	215.443	5.223	-197.220	-227.945	26.459
500	35.705	230.790	216.793	6.998	-200.852	-231.019	24.134
600	36.304	237.356	219.688	10.601	-202.049	-236.938	20.627
700	36.715	242.985	222.624	14.253	-203.158	-242.664	18.108
800	37.014	247.908	225.483	17.940	-204.217	-248.235	16.208
900	37.242	252.281	228.222	21.653	-205.255	-253.675	14.723
1000	37.425	256.215	230.828	25.387	-206.276	-259.000	13.529
1100	37.577	259.789	233.301	29.137	-207.282	-264.223	12.547
1200	37.707	263.065	235.647	32.901	-208.274	-269.356	11.725
1300	37.821	266.087	237.874	36.678	-209.256	-274.406	11.026
1400	37.924	268.894	239.990	40.465	-210.226	-279.381	10.424
1500	38.019	271.514	242.005	44.262	-211.182	-284.288	9.900
1600	38.107	273.970	243.927	48.069	-212.124	-289.131	9.439
1700	38.189	276.283	245.763	51.884	-358.291	-286.739	8.810
1800	38.268	278.468	247.520	55.706	-358.458	-282.525	8.199
1900	38.344	280.539	249.204	59.537	-358.622	-278.302	7.651
2000	38.417	282.508	250.820	63.375	-358.787	-274.071	7.158
2100	38.487	284.384	252.374	67.220	-358.952	-269.831	6.712
2200	38.556	286.176	253.870	71.073	-359.121	-265.583	6.306
2300	38.624	287.891	255.312	74.932	-359.294	-261.327	5.935
2400	38.690	289.537	256.704	78.797	-359.474	-257.064	5.595
2500	38.755	291.117	258.049	82.670	-359.663	-252.793	5.282
2600	38.820	292.639	259.351	86.548	-359.863	-248.515	4.993
2700	38.883	294.105	260.611	90.433	-360.077	-244.228	4.725
2800	38.946	295.520	261.833	94.325	-360.306	-239.933	4.476
2900	39.009	296.888	263.018	98.223	-360.552	-235.630	4.244
3000	39.071	298.211	264.169	102.127	-360.818	-231.318	4.028
3100	39.132	299.493	265.288	106.037	-361.105	-226.996	3.825
3200	39.193	300.737	266.376	109.953	-361.414	-222.665	3.635
3300	39.254	301.944	267.436	113.875	-361.747	-218.324	3.456
3400	39.314	303.116	268.468	117.804	-362.104	-213.973	3.287
3500	39.375	304.257	269.475	121.738	-362.487	-209.611	3.128
3600	39.435	305.367	270.456	125.679	-362.895	-205.237	2.978
3700	39.494	306.448	271.414	129.625	-363.331	-200.852	2.836
3800	39.554	307.502	272.350	133.578	-363.793	-196.454	2.700
3900	39.613	308.531	273.265	137.536	-364.282	-192.044	2.572
4000	39.673	309.534	274.159	141.500	-364.798	-187.621	2.450
4100	39.732	310.515	275.034	145.471	-365.342	-183.185	2.334
4200	39.791	311.473	275.890	149.447	-365.914	-178.735	2.223
4300	39.850	312.410	276.729	153.429	-366.514	-174.272	2.117
4400	39.909	313.327	277.550	157.417	-367.121	-169.795	2.016
4500	39.967	314.224	278.355	161.410	-367.768	-165.304	1.919
4600	40.026	315.103	279.144	165.410	-368.444	-160.797	1.826
4700	40.084	315.965	279.919	169.416	-369.148	-156.276	1.737
4800	40.143	316.809	280.678	173.427	-369.880	-151.739	1.651
4900	40.201	317.637	281.424	177.444	-370.641	-147.186	1.569
5000	40.260	318.450	282.157	181.467	-371.431	-142.618	1.490
5100	40.318	319.248	282.876	185.496	-372.244	-138.034	1.414
5200	40.376	320.031	283.583	189.531	-373.093	-133.434	1.340
5300	40.434	320.801	284.278	193.571	-373.974	-128.816	1.270
5400	40.492	321.557	284.962	197.618	-374.887	-124.182	1.201
5500	40.550	322.301	285.634	201.670	-375.833	-119.531	1.135
5600	40.608	323.032	286.295	205.728	-376.814	-114.862	1.071
5700	40.666	323.751	286.946	209.791	-377.831	-110.175	1.010
5800	40.724	324.459	287.587	213.861	-378.886	-105.470	0.950
5900	40.782	325.156	288.217	217.936	-379.978	-100.747	0.892
6000	40.840	325.842	288.839	222.018	-381.111	-96.005	0.836

PREVIOUS: June 1962 (1 atm) CURRENT: June 1962 (1 bar)

Lithium Hypochlorite (LiOCl) IDEAL GAS $M_r = 58.3934$ Lithium Hypochlorite (LiOCl) $Cl_1Li_1O_1(g)$

$S°(298.15\ K) = [256.417]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -11.5 \pm 84\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [-14.2 \pm 84]\ kJ{\cdot}mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
[1150](1)
[500](1)
[700](1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: [Cs]
Bond Distances: Li–O = 1.82 Å; O–Cl = 1.73 Å
Bond Angle: Li–O–Cl = 115°
Product of the Principal Moments of Inertia: $I_A I_B I_C = 1.83923 \times 10^{-115}\ g^3{\cdot}cm^6$

Enthalpy of Formation

Data from Hildenbrand.[1]

Enthalpy Capacity and Entropy

Data from Hildenbrand.[1] The principal moments of inertia are: $I_A = 1.4098 \times 10^{-39}$, $I_B = 10.7387 \times 10^{-39}$, and $I_C = 12.1485 \times 10^{-39}$ $g{\cdot}cm^2$.

Reference

[1] D. L. Hildenbrand, "Tables of Thermodynamic Data for Performance Calculations, "Aeronutronic Division of Ford Motor Company, Newport Beach, Calif., (September 1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

		$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.854	−11.525	−11.525	INFINITE
100	33.617	215.894	291.124	−7.523	−11.598	−14.337	7.489
200	37.908	240.313	260.189	−3.975	−12.866	−16.618	4.340
250	40.585	249.062	257.112	−2.012	−13.569	−17.475	3.651
298.15	42.961	256.417	256.417	0.	−14.226	−18.167	3.183
300	43.046	256.683	256.418	0.080	−14.250	−18.191	3.167
350	45.197	263.485	256.950	2.287	−14.903	−18.796	2.805
400	47.028	269.643	258.158	4.594	−15.557	−19.308	2.521
450	48.566	275.273	259.751	6.985	−16.236	−19.736	2.291
500	49.853	280.459	261.566	9.446	−19.953	−19.780	2.066
600	51.826	289.733	265.506	14.536	−21.242	−19.622	1.708
700	53.219	297.833	269.558	19.792	−22.374	−19.260	1.437
800	54.223	305.008	273.550	25.167	−23.414	−18.744	1.224
900	54.963	311.440	277.409	30.628	−24.407	−18.100	1.051
1000	55.520	317.261	281.107	36.153	−25.367	−17.348	0.906
1100	55.948	322.573	284.639	41.728	−26.303	−16.500	0.784
1200	56.284	327.456	288.006	47.340	−27.222	−15.569	0.678
1300	56.551	331.973	291.217	52.982	−28.130	−14.560	0.585
1400	56.767	336.172	294.280	58.649	−29.027	−13.483	0.503
1500	56.944	340.094	297.205	64.334	−29.915	−12.342	0.430
1600	57.090	343.774	300.002	70.036	−30.796	−11.141	0.364
1700	57.213	347.239	302.679	75.752	−176.908	−2.710	0.083
1800	57.316	350.512	305.247	81.478	−177.029	7.540	−0.219
1900	57.404	353.614	307.711	87.214	−177.158	17.798	−0.489
2000	57.480	356.560	310.081	92.959	−177.297	28.062	−0.733
2100	57.545	359.366	312.361	98.710	−177.449	38.334	−0.953
2200	57.602	362.044	314.559	104.467	−177.617	48.613	−1.154
2300	57.652	364.606	316.680	110.230	−177.801	58.900	−1.338
2400	57.696	367.061	318.728	115.998	−178.006	69.196	−1.506
2500	57.735	369.417	320.709	121.769	−178.233	79.501	−1.661
2600	57.770	371.682	322.626	127.545	−178.485	89.815	−1.804
2700	57.801	373.863	324.484	133.323	−178.764	100.139	−1.937
2800	57.828	375.965	326.285	139.105	−179.072	110.475	−2.061
2900	57.853	377.995	328.033	144.889	−179.411	120.821	−2.176
3000	57.876	379.957	329.732	150.675	−179.783	131.180	−2.284
3100	57.896	381.855	331.383	156.464	−180.189	141.553	−2.385
3200	57.915	383.693	332.989	162.254	−180.631	151.938	−2.480
3300	57.932	385.476	334.552	168.047	−181.109	162.338	−2.570
3400	57.947	387.205	336.076	173.841	−181.624	172.753	−2.654
3500	57.961	388.885	337.561	179.636	−182.178	183.184	−2.734
3600	57.974	390.518	339.009	185.433	−182.770	193.631	−2.810
3700	57.986	392.107	340.423	191.231	−183.401	204.095	−2.881
3800	57.997	393.653	341.803	197.030	−184.070	214.578	−2.950
3900	58.008	395.160	343.152	202.830	−184.779	225.078	−3.015
4000	58.017	396.629	344.471	208.632	−185.526	235.596	−3.077
4100	58.026	398.062	345.761	214.434	−186.313	246.134	−3.136
4200	58.034	399.460	347.023	220.237	−187.138	256.691	−3.192
4300	58.042	400.826	348.258	226.041	−188.003	267.269	−3.247
4400	58.049	402.160	349.468	231.845	−188.886	277.865	−3.299
4500	58.056	403.465	350.653	237.650	−189.821	288.483	−3.349
4600	58.062	404.741	351.815	243.456	−190.796	299.123	−3.397
4700	58.068	405.989	352.955	249.263	−191.810	309.784	−3.443
4800	58.073	407.212	354.072	255.070	−192.864	320.467	−3.487
4900	58.078	408.409	355.169	260.877	−193.958	331.173	−3.530
5000	58.083	409.583	356.246	266.685	−195.093	341.901	−3.572
5100	58.088	410.733	357.303	272.494	−196.265	352.653	−3.612
5200	58.092	411.861	358.341	278.303	−197.484	363.427	−3.651
5300	58.096	412.968	359.362	284.112	−198.746	374.226	−3.688
5400	58.100	414 054	360.364	289.922	−200.055	385.049	−3.725
5500	58.103	415.120	361.350	295 732	−201.411	395.896	−3.760
5600	58.107	416.167	362.320	301.543	−202.815	406.770	−3.794
5700	58.110	417.195	363.274	307.354	−204.269	417.668	−3.827
5800	58.113	418.206	364.212	313.165	−205.776	428.592	−3.860
5900	58.116	419.199	365.136	318.976	−207.336	439.542	−3.891
6000	58.119	420.176	366.045	324.788	−208.952	450.520	−3.922

PREVIOUS: December 1960 (1 atm) CURRENT· December 1960 (1 bar)

Lithium Perchlorate ($LiClO_4$) **CRYSTAL** **M_r = 106.3916** **Lithium Perchlorate ($LiClO_4$)** **$Cl_1Li_1O_4(cr)$**

$S°(298.15\ K) = [126 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 509\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -380.7 \pm 2.9\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [29.29]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The heats of reaction ($\Delta_r H°$) involving $LiClO_4(cr)$ has been determined by several investigators as follows:

Source	Reaction	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Gilliland and Johnson[1]	$LiClO_4(cr) + KCl(cr) \rightarrow LiCl(cr) + KClO_4(cr)$	−5.86 ± 0.06	−90.34
Markowitz *et al.*[2]	$LiOH(225\ H_2O) + HClO_4(225\ H_2O) \rightarrow LiClO_4\ (451\ H_2O) + H_2O(l)$	−13.54 ± 0.09	−91.7
Birky and Hepler[3]	$LiClO_4(cr) \rightarrow Li^+(aq) + ClO_4(aq)$	−6.31 ± 0.13	−91.11

The adopted value, $\Delta_f H°(298.15\ K) = -91.0\ kcal \cdot mol^{-1}$, for $LiClO_4(cr)$ is the weighted average of the three values listed.

Heat Capacity and Entropy

Heat capacities and $S°(298.15\ K)$ were estimated by comparison with those of $KClO_4(cr)$.

Fusion Data

T_{fus} was obtained from Richards and Willard.[4] The value of $\Delta_{fus} H°(509\ K)$ was estimated by comparison with the value, $\Delta_{fus} H°(528\ K) = 5.4\ kcal \cdot mol^{-1}$, for $NaClO_3(cr)$ reported by Kelley.[5]

References

[1] A. A. Gilliland and W. H. Johnson, J. Res. Nat. Bur. Stand. 65A, 67 (1961).
[2] M. M. Markowitz, R. F. Harris and H. Stewart, Jr., J. Phys. Chem. 63, 1325 (1959).
[3] M. M. Birky and L. G. Hepler, J. Phys. Chem. 64, 686 (1960).
[4] T. W Richards and H. H. Willard, J. Amer. Chem. Soc., 32, 4 (1910).
[5] K. K. Kelley, U. S. Bur. Mines Bull. 584, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	105.018	125.520	125.520	0.	−380.744	−253.911	44.484
300	105.437	126.171	125.522	0.195	−380.735	−253.125	44.073
400	129.704	160.077	129.980	12.039	−379.169	−210.770	27.524
500	143.511	190.659	139.119	25.770	−379.274	−168.682	17.622
509.000	144.340	193.227	140.053	27.065	--- CRYSTAL <--> LIQUID ---		
600	152.716	217.656	150.004	40.591	−375.571	−126.899	11.048
700	160.038	241.758	161.421	56.236	−371.197	−85.791	6.402
800	166.523	263.561	172.847	72.571	−366.282	−45.349	2.961
900	172.067	283.501	184.050	89.506	−360.909	−5.550	0.322
1000	176.983	301.890	194.926	106.963	−355.130	33.628	−1.757
1100	180.972	318.945	205.435	124.861	−349.006	72.210	−3.429
1200	184.933	334.862	215.564	143.157	−342.565	110.221	−4.798
1300	188.866	349.820	225.322	161.847	−335.799	147.680	−5.934
1400	192.771	363.959	234.724	180.929	−328.701	184.607	−6.888
1500	196.648	377.392	243.791	200.400	−321.266	221.014	−7.696

PREVIOUS: June 1963   CURRENT: March 1964

Lithium Perchlorate ($LiClO_4$) **$Cl_1Li_1O_4(cr)$**

Lithium Perchlorate ($LiClO_4$) LIQUID M_r = 106.3916 Lithium Perchlorate ($LiClO_4$) $Cl_1Li_1O_4(l)$

$S°(298.15\ K) = [164.611]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = [-358.355]\ kJ{\cdot}mol^{-1}$

$T_{fus} = 509\ K$ $\Delta_{fus}H° = [29.3]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(LiClO_4, l, 298.15\ K)$ is calculated from $\Delta_fH°(LiClO_4, cr, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(509\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ for $LiClO_4(l)$ was estimated by comparison with that for $NaClO_3(l)$. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting temperature (T_{fus}) was obtained from Richards and Willard.[1] The value of $\Delta_{fus}H°(509\ K)$ was estimated by comparison with the value, $\Delta_{fus}H°(528\ K) = 5.4\ kcal{\cdot}mol^{-1}$, for $NaClO_3(cr)$ reported by Kelley.[2]

References

[1] T. W. Richards and H. H. Willard, J. Amer. Chem. Soc. 32, 4 (1910).
[2] K. K. Kelley, U. S. Bur. Mines Bull. 584, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	161.084	164.611	164.611	0.	−358.355	−243.178	42.604
300	161.084	165.608	164.614	0.298	−358.243	−242.463	42.217
400	161.084	211.949	170.933	16.406	−352.412	−204.763	26.739
500	161.084	247.894	182.864	32.515	−350.140	−168.166	17.568
509.000	161.084	250.767	184.039	33.965	--- CRYSTAL <--> LIQUID ---		
600	161.084	277.263	196.224	48.623	−345.150	−132.242	11.513
700	161.084	302.094	209.620	64.732	−340.312	−97.142	7.249
800	161.084	323.604	222.554	80.840	−335.624	−62.725	4.096
900	161.084	342.577	234.856	96.948	−331.077	−28.887	1.677
1000	161.084	359.549	246.492	113.057	−326.647	4.451	−0.232
1100	161.084	374.901	257.479	129.165	−322.313	37.351	−1.774
1200	161.084	388.918	267.856	145.274	−318.059	69.859	−3.041
1300	161.084	401.811	277.671	161.382	−313.876	102.015	−4.099
1400	161.084	413.749	286.970	177.490	−309.751	133.852	−4.994
1500	161.084	424.862	295.797	193.599	−305.678	165.395	−5.760

PREVIOUS: December 1960 CURRENT: March 1964

Lithium Perchlorate ($LiClO_4$) CRYSTAL-LIQUID

0 to 509 K crystal
above 500 K liquid

Refer to the individual tables for details.

$M_r = 106.3916$ **Lithium Perchlorate ($LiClO_4$)** $Cl_1Li_1O_4(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1}mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	105.018	125.520	125.520	0.	−380.744	−253.911	44.484
300	105.437	126.171	125.522	0.195	−380.735	−253.125	44.073
400	129.704	160.077	129.980	12.039	−379.169	−210.770	27.524
500	143.511	190.659	139.119	25.770	−379.274	−168.682	17.622
509.000	144.340	193.227	140.053	27.065	CRYSTAL <--> LIQUID TRANSITION		
509.000	161.084	250.767	140.053	56.353			
600	161.084	277.263	158.909	71.012	−345.150	−132.242	11.513
700	161.084	302.094	177.636	87.120	−340.312	−97.142	7.249
800	161.084	323.604	194.568	103.229	−335.624	−62.725	4.096
900	161.084	342.577	209.980	119.337	−331.077	−28.887	1.677
1000	161.084	359.549	224.103	135.446	−326.647	4.451	−0.232
1100	161.084	374.901	237.125	151.554	−322.313	37.351	−1.774
1200	161.084	388.918	249.199	167.662	−318.059	69.859	−3.041
1300	161.084	401.811	260.449	183.771	−313.876	102.015	−4.099
1400	161.084	413.749	270.978	199.879	−309.751	133.852	−4.994
1500	161.084	424.862	280.871	215.988	−305.678	165.395	−5.760

PREVIOUS: CURRENT: March 1964

Lithium Perchlorate ($LiClO_4$) $Cl_1Li_1O_4(cr,l)$

Magnesium Chloride (MgCl) IDEAL GAS $M_r = 59.758$ Magnesium Chloride (MgCl) $Cl_1Mg_1(g)$

$S°(298.15\ K) = 233.413\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -43.3 \pm 42\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -43.5 \pm 42\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Sigma$	0	2

$\omega_e = 462.4\ cm^{-1}$ $\quad \omega_e x_e = 2.02\ cm^{-1}$ $\quad \sigma = 1$
$B_e = [0.2417]\ cm^{-1}$ $\quad \alpha_e = [0.0014]\ cm^{-1}$ $\quad r_e = 2.199$ Å

Enthalpy of Formation

The enthalpy of formation is calculated from $D_0^\circ = 3.2$ eV reported by Herzberg.[1] $D_0^\circ = 2.7 \pm 0.7$ eV reported by Gaydon,[2] yields $\Delta_f H°(\text{MgCl, g, 298.15 K}) = 1.0 \pm 16\ kcal{\cdot}mol^{-1}$.

Heat Capacity and Entropy

Spectroscopic constants were reported by Herzberg[1] and adjusted for natural isotopic abundance. The bond length was reported by Morgan and Barrow.[3] B_e and α_e were estimated by the method suggested by Herzberg.[1]

References

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Magnesium Chloride (MgCl) $Cl_1Mg_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.361	−43.287	−43.287	INFINITE
100	29.610	198.431	262.874	−6.444	−42.467	−51.910	27.115
200	32.761	219.902	236.542	−3.328	−42.877	−61.232	15.992
250	33.983	227.351	233.982	−1.658	−43.187	−65.786	13.745
298.15	34.828	233.413	233.413	0.	−43.514	−70.109	12.283
300	34.855	233.628	233.413	0.064	−43.527	−70.274	12.236
350	35.477	239.051	233.840	1.824	−43.889	−74.704	11.149
400	35.930	243.819	234.795	3.609	−44.272	−79.080	10.327
450	36.268	248.071	236.039	5.415	−44.675	−83.407	9.682
500	36.528	251.907	237.437	7.235	−45.098	−87.688	9.161
600	36.898	258.602	240.422	10.908	−46.009	−96.122	8.368
700	37.148	264.309	243.437	14.611	−47.014	−104.396	7.790
800	37.330	269.282	246.364	18.335	−48.128	−112.519	7.347
900	37.472	273.687	249.159	22.075	−49.366	−120.495	6.993
1000	37.587	277.642	251.813	25.828	−59.338	−127.613	6.666
1100	37.685	281.229	254.327	29.592	−60.880	−134.365	6.380
1200	37.772	284.512	256.707	33.365	−62.419	−140.978	6.137
1300	37.849	287.538	258.964	37.146	−63.955	−147.462	5.925
1400	37.921	290.346	261.107	40.935	−192.897	−150.661	5.621
1500	37.988	292.964	263.144	44.730	−193.076	−147.638	5.141
1600	38.051	295.418	265.085	48.532	−193.252	−144.603	4.721
1700	38.112	297.727	266.938	52.340	−193.427	−141.557	4.350
1800	38.170	299.907	268.710	56.154	−193.601	−138.501	4.019
1900	38.227	301.972	270.407	59.974	−193.773	−135.435	3.723
2000	38.282	303.934	272.034	63.800	−193.945	−132.361	3.457
2100	38.336	305.803	273.598	67.631	−194.117	−129.277	3.216
2200	38.390	307.588	275.103	71.467	−194.291	−126.185	2.996
2300	38.442	309.296	276.553	75.308	−194.466	−123.086	2.795
2400	38.494	310.933	277.951	79.155	−194.644	−119.979	2.611
2500	38.545	312.505	279.302	83.007	−194.826	−116.864	2.442
2600	38.596	314.018	280.609	86.864	−195.014	−113.741	2.285
2700	38.647	315.476	281.873	90.727	−195.208	−110.612	2.140
2800	38.697	316.882	283.098	94.594	−195.409	−107.475	2.005
2900	38.747	318.241	284.287	98.466	−195.619	−104.331	1.879
3000	38.796	319.555	285.441	102.343	−195.839	−101.179	1.762
3100	38.846	320.828	286.562	106.225	−196.071	−98.020	1.652
3200	38.895	322.062	287.652	110.112	−196.314	−94.854	1.548
3300	38.944	323.260	288.713	114.004	−196.571	−91.679	1.451
3400	38.992	324.423	289.746	117.901	−196.843	−88.496	1.360
3500	39.041	325.554	290.753	121.803	−197.131	−85.306	1.273
3600	39.090	326.655	291.735	125.709	−197.435	−82.106	1.191
3700	39.138	327.726	292.694	129.621	−197.758	−78.898	1.114
3800	39.186	328.771	293.629	133.537	−198.099	−75.681	1.040
3900	39.235	329.789	294.544	137.458	−198.460	−72.455	0.970
4000	39.283	330.783	295.437	141.384	−198.842	−69.219	0.904
4100	39.331	331.754	296.311	145.314	−199.246	−65.974	0.841
4200	39.379	332.702	297.166	149.250	−199.673	−62.718	0.780
4300	39.427	333.629	298.004	153.190	−200.124	−59.452	0.722
4400	39.475	334.536	298.824	157.135	−200.600	−56.175	0.667
4500	39.523	335.424	299.627	161.085	−201.102	−52.887	0.614
4600	39.571	336.293	300.415	165.040	−201.631	−49.588	0.563
4700	39.618	337.145	301.187	168.999	−202.188	−46.277	0.514
4800	39.666	337.979	301.945	172.964	−202.774	−42.953	0.467
4900	39.714	338.797	302.689	176.933	−203.391	−39.617	0.422
5000	39.762	339.600	303.419	180.906	−204.039	−36.269	0.379
5100	39.809	340.388	304.136	184.885	−204.719	−32.906	0.337
5200	39.857	341.162	304.841	188.868	−205.433	−29.531	0.297
5300	39.904	341.921	305.533	192.856	−206.180	−26.141	0.258
5400	39.952	342.668	306.214	196.849	−206.963	−22.737	0.220
5500	40.000	343.401	306.884	200.847	−207.783	−19.317	0.183
5600	40.047	344.122	307.542	204.849	−208.639	−15.883	0.148
5700	40.095	344.832	308.190	208.856	−209.535	−12.433	0.114
5800	40.142	345.529	308.828	212.868	−210.469	−8.967	0.081
5900	40.190	346.216	309.456	216.884	−211.444	−5.485	0.049
6000	40.237	346.892	310.074	220.906	−212.461	−1.986	0.017

PREVIOUS. March 1966 (1 atm) CURRENT March 1966 (1 bar)

Magnesium Chloride, Ion ($MgCl^+$) IDEAL GAS $M_r = 59.75745$ Magnesium Chloride, Ion ($MgCl^+$) $Cl_1Mg_1^+(g)$

$S°(298.15\ K) = [228.6 \pm 8]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 646.6 \pm 84\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [652.704] \pm 84\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^{+g}$	0	1
$^3\pi_u$	[9000]	6
$^1\pi_u$	[11000]	2
$^3\Sigma_g^-$	[20000]	3
$^1\Delta$	[25000]	2
$^1\Sigma^+$	[30000]	1

$\omega_e = [400]\ cm^{-1}$ $\quad \omega_ex_e = [2]\ cm^{-1}$ $\quad \sigma = 1$
$B_e = [0.2415]\ cm^{-1}$ $\quad \alpha_e = [0.00164]\ cm^{-1}$ $\quad r_e = [2.2]$ Å

Enthalpy of Formation

The ionization potential of MgCl(g) was reported to be 7.2, 7.5 ± 0.5 and 7 ± 1 eV by Krasnov,[1] Hildenbrand,[9] and Beckett and Cassidy,[2] respectively. The corresponding heats of formation at 298 K for $MgCl^+$(g) are derived as 156, 163, and 151 $kcal{\cdot}mol^{-1}$, using $\Delta_fH°$(MgCl, g, 0 K) = $-10.34\ kcal{\cdot}mol^{-1}$ from the JANAF MgCl(g) table (March 31, 1966). The value of $\Delta_fH°$(298.15 K) for $MgCl^+$(g) is tentatively selected as 156 ± 20 $kcal{\cdot}mol^{-1}$ (652.704 ± 84 $kJ{\cdot}mol^{-1}$).

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as NaCl(g) which is esoelectronic with $MgCl^+$(g). The six electronic states are obtained from Fougere.[3] The corresponding electronic levels are estimated by comparison with the isoelectronic molecules BeS,[4] BeO,[5,6] and MgO.[5,7] The bond distance is estimated by the method suggested by Krasnov.[8] The values of ω_e and ω_ex_e are estimated by comparison with those for MgCl(g) and NaCl(g). B_e and α_e are calculated by the method recommended by Herzberg.[5]

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.516	646.579		
100	30.033	192.784	258.681	−6.590			
200	33.588	214.752	231.749	−3.399			
250	34.711	222.375	229.136	−1.690			
298.15	35.446	228.556	228.556	0.	652.704	621.302	−108.849
300	35.470	228.775	228.557	0.066	652.731	621.107	−108.144
350	35.996	234.285	228.991	1.853	653.436	615.780	−91.900
400	36.374	239.117	229.961	3.663	654.116	610.354	−79.704
450	36.655	243.419	231.221	5.489	654.773	604.844	−70.208
500	36.872	247.292	232.638	7.327	655.407	599.262	−62.604
600	37.186	254.045	235.659	11.031	656.606	587.919	−51.183
700	37.405	259.794	238.707	14.761	657.707	576.382	−43.010
800	37.572	264.800	241.662	18.510	658.697	564.696	−36.871
900	37.712	269.234	244.484	22.275	659.561	552.892	−32.089
1000	37.841	273.214	247.161	26.052	651.693	541.712	−28.296
1100	37.977	276.827	249.697	29.843	652.256	530.687	−25.200
1200	38.140	280.138	252.097	33.649	652.828	519.610	−22.618
1300	38.347	283.198	254.373	37.473	653.414	508.485	−20.431
1400	38.618	286.050	256.535	41.320	526.609	500.481	−18.673
1500	38.970	288.726	258.593	45.199	528.592	498.546	−17.361
1600	39.412	291.254	260.556	49.117	530.611	496.478	−16.208
1700	39.954	293.659	262.433	53.085	532.674	494.281	−15.187
1800	40.595	295.961	264.232	57.111	534.792	491.962	−14.276
1900	41.333	298.175	265.961	61.207	536.973	489.523	−13.458
2000	42.158	300.316	267.625	65.381	539.228	486.968	−12.718
2100	43.059	302.394	269.232	69.641	541.564	484.298	−12.046
2200	44.020	304.419	270.785	73.995	543.987	481.515	−11.433
2300	45.025	306.398	272.291	78.447	546.500	478.619	−10.870
2400	46.056	308.336	273.752	83.001	549.108	475.612	−10.351
2500	47.095	310.237	275.174	87.658	551.810	472.495	−9.872
2600	48.124	312.104	276.559	92.419	554.605	469.267	−9.428
2700	49.128	313.940	277.909	97.282	557.490	465.931	−9.014
2800	50.093	315.744	279.228	102.244	560.462	462.485	−8.628
2900	51.007	317.518	280.518	107.299	563.514	458.932	−8.266
3000	51.859	319.262	281.781	112.443	566.639	455.273	−7.927
3100	52.644	320.975	283.017	117.669	569.830	451.509	−7.608
3200	53.354	322.658	284.230	122.969	573.078	447.640	−7.307
3300	53.989	324.309	285.419	128.337	576.376	443.669	−7.023
3400	54.546	325.930	286.587	133.764	579.713	439.598	−6.754
3500	55.026	327.518	287.734	139.244	583.081	435.428	−6.498
3600	55.431	329.074	288.861	144.767	586.473	431.161	−6.256
3700	55.765	330.597	289.968	150.327	589.878	426.800	−6.025
3800	56.030	332.088	291.057	155.918	593.289	422.347	−5.806
3900	56.233	333.546	292.128	161.531	596.700	417.804	−5.596
4000	56.376	334.972	293.181	167.162	600.101	413.174	−5.395
4100	56.467	336.365	294.218	172.805	603.488	408.458	−5.204
4200	56.510	337.727	295.238	178.454	606.853	403.661	−5.020
4300	56.510	339.056	296.241	184.105	610.191	398.784	−4.844
4400	56.472	340.355	297.229	189.755	613.498	393.829	−4.675
4500	56.401	341.624	298.202	195.399	616.769	388.799	−4.513
4600	56.302	342.862	299.159	201.034	619.999	383.698	−4.357
4700	56.179	344.072	300.102	206.658	623.186	378.526	−4.207
4800	56.036	345.253	301.030	212.269	626.325	373.287	−4.062
4900	55.876	346.407	301.945	217.865	629.413	367.984	−3.923
5000	55.702	347.534	302.845	223.444	632.449	362.617	−3.788
5100	55.518	348.635	303.732	229.005	635.430	357.191	−3.658
5200	55.326	349.711	304.606	234.547	638.354	351.707	−3.533
5300	55.128	350.763	305.467	240.070	641.220	346.167	−3.412
5400	54.925	351.792	306.315	245.573	644.025	340.574	−3.294
5500	54.721	352.798	307.151	251.055	646.769	334.929	−3.181
5600	54.516	353.782	307.975	256.517	649.451	329.234	−3.071
5700	54.311	354.745	308.788	261.958	652.068	323.493	−2.964
5800	54.108	355.688	309.588	267.379	654.621	317.706	−2.861
5900	53.907	356.611	310.377	272.780	657.109	311.876	−2.761
6000	53.710	357.516	311.155	278.161	659.531	306.004	−2.664

PREVIOUS: June 1968 (1 atm)   CURRENT: June 1968 (1 bar)

Magnesium Chloride, Ion ($MgCl^+$) $Cl_1Mg_1^+(g)$

Nitrosyl Chloride (ONCl) IDEAL GAS $M_r = 65.4591$ Nitrosyl Chloride (ONCl) $Cl_1N_1O_1(g)$

$\Delta_f H°(0\ K) = 53.622 \pm 0.42\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = 261.680 \pm 0.17\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = 51.714 \pm 0.42\ kJ\cdot mol^{-1}$

Vibrational Frequencies, Degeneracies and Anharmonicity Constants

ν, cm^{-1}	X_{ii}, cm^{-1}	X_{ij}, cm^{-1}
1799.7(1)	$X_{11} = -17.8$	$X_{12} = 0.0$
595.6(1)	$X_{22} = -2.6$	$X_{23} = -4.3$
330.9(1)	$X_{33} = -1.0$	$X_{13} = -0.6$

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: C_s

Bond Distances: O–N = 1.143 ± 0.012 Å; N–Cl = 1.976 ± 0.005 Å

Bond Angle: O–N–Cl = 113.0° ± 0.7°

Rotational Constants: $A_0 = 2.8492\ cm^{-1}$; $B_0 = 0.19034\ cm^{-1}$; $C_0 = 0.17842\ cm^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from $\Delta_r H° = 18.43 \pm 0.06\ kcal\cdot mol^{-1}$ derived by 3rd law analysis of equilibrium data[1] for $2ONCl(g) \rightarrow 2NO(g) + Cl_2(g)$. 2nd law analysis yields $\Delta_r H° = 18.39 \pm 0.07$ and an entropy deviation of $-0.09 \pm 0.16\ cal\cdot K^{-1}\cdot mol^{-1}$ from the 3rd law $\Delta_r S°$. Data analyzed cover a temperature range of 372.7 to 491.3 K and consist of a combination of three runs reported by Beeson and Yost.[1] Combination is justified by the mutual consistency of the three runs, which involved excess NO, excess Cl_2, and roughly the stoichiometric ratio of NO and Cl_2, respectively. Earlier data reviewed by Bichowsky and Rossini[2] are considered less reliable.

Heat Capacity and Entropy

We list structural parameters which approximate the adopted rotational constants[3] obtained from microwave spectra of three isotopic molecules. These structural parameters are minor modifications of those given by Millen and Pannell.[3] Changes are well within the ranges specified by the authors but give improved agreement with rotational constant A_0. Literature values include (O–N) = 1.139 ± 0.012[3], 1.14 ± 0.02[4,7] and 1.17 ± 0.06 Å[5,6] (N–Cl) = 1.975 ± 0.005,[3] 1.95 ± 0.01,[4] 1.95 ± 0.06[5,6] and 1.97 ± 0.01 Å;[7,6] and angle (O–N–Cl) = 113.33° ± 0.67°,[3] 116° ± 2°,[4] 114° ± 3°[5,6] and 113° ± 2°.[7,6] The earlier values[4,5,7] resulted from electron–diffraction data by Ketelaar and Palmer[4] and two separate analyses by Rogers and Williams[5] and Whiffen[7] of older microwave data by Rogers *et al.*[6] Rotational constants are adjusted for the natural isotopic abundance of Cl. A_0 is relatively uncertain.

Observed values and anharmonicity constants are from the gas–phase infrared study of Jones *et al.*,[8] who reviewed earlier spectral data. Values of are adjusted for the natural isotopic abundance of chlorine. The anharmonicity constants differ from, and supersede, earlier values by Landau and Fletcher[9] used by Gordon[10] in calculating thermodynamic functions for ONCl.

New functions have been calculated through the courtesy of McBride,[11] who used the above vibrational and rotational constants with first and second order corrections (method NRRA02) in the NASA–Lewis computer program, McBride and Gordon .[12] We adopt these functions directly for 0 to 298.15 K and reproduce the functions at higher temperatures by integration of $C_p°$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.360	53.622	53.622	INFINITE
100	35.016	218.558	298.546	−7.999	52.623	56.874	−29.708
200	40.756	244.629	265.649	−4.204	51.988	61.406	−16.038
298.15	44.589	261.680	261.680	0.	51.714	66.096	−11.580
300	44.643	261.956	261.681	0.083	51.711	66.185	−11.524
400	47.149	275.162	263.465	4.679	51.629	71.027	−9.275
500	49.079	285.898	266.910	9.494	51.658	75.875	−7.927
600	50.687	294.992	270.852	14.484	51.761	80.709	−7.026
700	52.037	302.910	274.878	19.622	51.915	85.522	−6.382
800	53.166	309.934	278.829	24.884	52.104	90.311	−5.897
900	54.106	316.252	282.642	30.249	52.317	95.074	−5.518
1000	54.892	321.995	286.295	35.700	52.549	99.812	−5.214
1100	55.554	327.258	289.783	41.223	52.794	104.527	−4.964
1200	56.117	332.117	293.111	46.807	53.048	109.219	−4.754
1300	56.603	336.628	296.287	52.444	53.310	113.889	−4.576
1400	57.026	340.839	299.320	58.126	53.578	118.539	−4.423
1500	57.399	344.786	302.221	63.847	53.849	123.170	−4.289
1600	57.733	348.501	304.999	69.604	54.123	127.782	−4.172
1700	58.035	352.011	307.662	75.393	54.399	132.377	−4.067
1800	58.311	355.336	310.219	81.210	54.675	136.956	−3.974
1900	58.566	358.495	312.677	87.054	54.951	141.520	−3.891
2000	58.804	361.506	315.044	92.923	55.225	146.069	−3.815
2100	59.027	364.380	317.325	98.815	55.497	150.605	−3.746
2200	59.240	367.131	319.527	104.728	55.766	155.128	−3.683
2300	59.443	369.769	321.655	110.662	56.031	159.638	−3.625
2400	59.637	372.303	323.713	116.616	56.292	164.137	−3.572
2500	59.826	374.741	325.705	122.589	56.547	168.625	−3.523
2600	60.009	377.091	327.637	128.581	56.797	173.103	−3.478
2700	60.188	379.359	329.511	134.591	57.040	177.572	−3.435
2800	60.363	381.551	331.330	140.619	57.277	182.032	−3.396
2900	60.536	383.673	333.099	146.664	57.508	186.483	−3.359
3000	60.706	385.728	334.819	152.726	57.733	190.927	−3.324
3100	60.875	387.721	336.494	158.805	57.952	195.363	−3.292
3200	61.042	389.656	338.125	164.901	58.167	199.792	−3.261
3300	61.208	391.537	339.715	171.013	58.378	204.214	−3.232
3400	61.374	393.367	341.266	177.142	58.586	208.631	−3.205
3500	61.539	395.148	342.780	183.288	58.792	213.041	−3.179
3600	61.704	396.884	344.259	189.450	58.997	217.445	−3.155
3700	61.870	398.577	345.705	195.629	59.204	221.843	−3.132
3800	62.035	400.229	347.118	201.824	59.414	226.236	−3.110
3900	62.201	401.843	348.500	208.036	59.627	230.624	−3.089
4000	62.368	403.420	349.854	214.264	59.847	235.005	−3.069
4100	62.534	404.962	351.179	220.509	60.074	239.382	−3.050
4200	62.702	406.471	352.478	226.771	60.310	243.752	−3.032
4300	62.871	407.948	353.751	233.050	60.556	248.117	−3.014
4400	63.041	409.395	354.999	239.345	60.815	252.476	−2.997
4500	63.212	410.814	356.223	245.658	61.088	256.828	−2.981
4600	63.384	412.205	357.425	251.988	61.375	261.175	−2.966
4700	63.557	413.570	358.605	258.335	61.678	265.515	−2.951
4800	63.731	414.910	359.765	264.699	61.999	269.849	−2.937
4900	63.907	416.226	360.903	271.081	62.338	274.176	−2.923
5000	64.084	417.519	362.023	277.481	62.696	278.495	−2.909
5100	64.262	418.790	363.123	283.898	63.073	282.808	−2.897
5200	64.442	420.039	364.206	290.333	63.471	287.112	−2.884
5300	64.623	421.269	365.271	296.786	63.891	291.409	−2.872
5400	64.806	422.478	366.319	303.258	64.332	295.698	−2.860
5500	64.990	423.669	367.351	309.748	64.794	299.978	−2.849
5600	65.176	424.842	368.367	316.256	65.279	304.250	−2.838
5700	65.363	425.997	369.368	322.783	65.785	308.513	−2.827
5800	65.552	427.135	370.355	329.329	66.313	312.767	−2.817
5900	65.743	428.258	371.326	335.893	66.863	317.011	−2.807
6000	65.935	429.364	372.285	342.477	67.434	321.246	−2.797

PREVIOUS December 1972 (1 atm) CURRENT. December 1972 (1 bar)

Nitryl Chloride (NO_2Cl) IDEAL GAS $M_r = 81.4585$ Nitryl Chloride (NO_2Cl) $Cl_1N_1O_2(g)$

$S°(298.15\ K) = 272.187\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 17.54 \pm 1.7\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 12.13 \pm 1.7\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
1293(1)	1685(1)
794(1)	411(1)
367(1)	651(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: N–Cl = 1.83 Å; N–O = 1.21 Å
Bond Angles: O–N–O = 129.5°; O–N–Cl = 115.25°
Product of the Moments of Inertia: $I_A I_B I_C = 2.36673 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

The selected enthalpy of formation was obtained from the recalculation of the heat of reaction $ClNO_2 + NO = ClNO + NO_2$ which has been measured calorimetrically as $-9.27\ kcal \cdot mol^{-1}$ by Ray and Ogg.[1] Not only the thermal effects of $2NO_2 = N_2O_4$ but also $NO + NO_2 = N_2O_3$ (a minor one) have been considered in calculation. Using all JANAF auxiliary data for ClNO, NO, NO_2, N_2O_3 and N_2O_4, the recalculation gives $\Delta_f H°(298.15\ K) = 2.90 \pm 0.4\ kcal \cdot mol^{-1}$ for $NO_2Cl(g)$. For the reaction $ClNO + N_2O_5 = ClNO_2 + 2NO_2$ also measured by Ray and Ogg,[1] the recalculation gives $\Delta_f H°(NO_2Cl,\ g,\ 298.15\ K) = 2.56 \pm 0.4\ kcal \cdot mol^{-1}$.

Martin and Koehlein[2] have determined kinetically the heat of reaction, $\Delta_r H°(273.15\ K) = 3.10\ kcal \cdot mol^{-1}$ for the reaction $NO_2 + NOCl = NO + NO_2Cl$ which gives $\Delta_f H°(298.15\ K) = 1.90 \pm 1\ kcal \cdot mol^{-1}$ for $NO_2Cl(g)$. Cordes and Johnston[3] have also determined kinetically the $\Delta_r H°(0\ K) = 29.5\ kcal \cdot mol^{-1}$ for the reaction $NO_2Cl = NO_2 + Cl$ which gives $\Delta_f H°(298.15\ K) = 6.3 \pm 0.3\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The selected bond distances and bond angles were obtained from microwave spectrum studies by Clayton *et al.*[4] Millen and Sinnott,[5] reported bond distance N–Cl = 1.840 Å, N–O = 1.202 Å and angle ONO = 130° 35' from the microwave measurement. These two are in good agreement.

The selected vibrational frequencies were obtained from infrared and Raman spectrum measurements by Ryason and Wilson.[6] However, the assignment of the fundamental frequencies has been revised by Dodd *et al.*[7] and Morino and Tanaka.[8] Morino and Tanaka's assignment was adopted. The principal moments of inertia are $I_A = 6.3641 \times 10^{-39}$, $I_B = 16.3632 \times 10^{-39}$ and $I_C = 22.7272 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	-12.199	17.544	17.544	INFINITE
100	35.314	225.280	313.645	-8.837	15.094	27.338	-14.280
200	44.951	252.629	276.802	-4.835	13.211	40.377	-10.545
250	49.431	263.152	273.042	-2.473	12.578	47.246	-9.871
298.15	53.187	272.187	272.187	0.	12.134	53.965	-9.454
300	53.321	272.517	272.188	0.099	12.119	54.225	-9.441
350	56.696	280.995	272.850	2.851	11.807	61.269	-9.144
400	59.639	288.763	274.360	5.761	11.617	68.349	-8.925
450	62.214	295.939	276.364	8.809	11.527	75.447	-8.758
500	64.467	302.613	278.659	11.977	11.519	82.551	-8.624
600	68.161	314.709	283.681	18.617	11.691	96.744	-8.422
700	70.985	325.438	288.894	25.580	12.043	110.894	-8.275
800	73.153	335.064	294.074	32.792	12.513	124.985	-8.161
900	74.831	343.781	299.121	40.195	13.062	139.011	-8.068
1000	76.145	351.736	303.990	47.746	13.663	152.974	-7.991
1100	77.185	359.044	308.668	55.415	14.299	166.874	-7.924
1200	78.020	365.798	313.151	63.176	14.956	180.716	-7.866
1300	78.697	372.070	317.445	71.013	15.627	194.502	-7.815
1400	79.252	377.923	321.558	78.912	16.304	208.236	-7.769
1500	79.712	383.407	325.500	86.860	16.982	221.922	-7.728
1600	80.097	388.564	329.282	94.851	17.657	235.563	-7.690
1700	80.422	393.430	332.914	102.878	18.324	249.161	-7.656
1800	80.699	398.035	336.405	110.934	18.981	262.721	-7.624
1900	80.936	402.405	339.764	119.016	19.626	276.244	-7.594
2000	81.141	406.561	343.001	127.120	20.254	289.734	-7.567
2100	81.319	410.525	346.123	135.244	20.865	303.193	-7.542
2200	81.475	414.311	349.137	143.384	21.457	316.624	-7.518
2300	81.612	417.936	352.050	151.538	22.027	330.027	-7.495
2400	81.732	421.412	354.868	159.705	22.574	343.406	-7.474
2500	81.840	424.751	357.597	167.884	23.097	356.764	-7.454
2600	81.935	427.963	360.242	176.073	23.596	370.101	-7.435
2700	82.021	431.056	362.808	184.271	24.068	383.419	-7.418
2800	82.097	434.041	365.299	192.477	24.515	396.720	-7.401
2900	82.167	436.923	367.719	200.690	24.935	410.005	-7.385
3000	82.229	439.710	370.073	208.910	25.329	423.277	-7.370
3100	82.286	442.407	372.363	217.136	25.698	436.536	-7.356
3200	82.338	445.020	374.593	225.367	26.041	449.783	-7.342
3300	82.385	447.554	376.766	233.603	26.360	463.019	-7.329
3400	82.428	450.015	378.884	241.844	26.656	476.247	-7.317
3500	82.468	452.405	380.951	250.089	26.929	489.466	-7.305
3600	82.505	454.728	382.968	258.337	27.182	502.678	-7.294
3700	82.538	456.989	384.938	266.589	27.415	515.883	-7.283
3800	82.569	459.191	386.863	274.845	27.630	529.083	-7.273
3900	82.598	461.336	388.745	283.103	27.829	542.276	-7.263
4000	82.625	463.428	390.586	291.364	28.014	555.464	-7.254
4100	82.649	465.468	392.388	299.628	28.185	568.649	-7.245
4200	82.672	467.460	394.152	307.894	28.345	581.829	-7.236
4300	82.694	469.406	395.879	316.162	28.494	595.006	-7.228
4400	82.714	471.307	397.572	324.433	28.635	608.178	-7.220
4500	82.733	473.166	399.231	332.705	28.768	621.347	-7.212
4600	82.750	474.984	400.859	340.979	28.894	634.514	-7.205
4700	82.766	476.764	402.455	349.255	29.015	647.679	-7.198
4800	82.782	478.507	404.021	357.533	29.131	660.841	-7.191
4900	82.796	480.214	405.559	365.811	29.243	674.001	-7.185
5000	82.810	481.887	407.068	374.092	29.352	687.158	-7.179
5100	82.823	483.527	408.552	382.373	29.456	700.313	-7.173
5200	82.835	485.135	410.009	390.656	29.558	713.465	-7.167
5300	82.847	486.713	411.441	398.940	29.657	726.617	-7.161
5400	82.857	488.262	412.850	407.226	29.752	739.766	-7.156
5500	82.868	489.782	414.235	415.512	29.844	752.913	-7.151
5600	82.877	491.276	415.597	423.799	29.932	766.060	-7.146
5700	82.887	492.743	416.938	432.087	30.015	779.204	-7.141
5800	82.895	494.184	418.257	440.376	30.093	792.348	-7.136
5900	82.904	495.601	419.556	448.666	30.164	805.488	-7.131
6000	82.912	496.995	420.835	456.957	30.228	818.629	-7.127

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

Sodium Chloride (NaCl) CRYSTAL $M_r = 58.44277$ Sodium Chloride (NaCl) $Cl_1Na_1(cr)$

$\Delta_f H°(0\ K) = -410.693 \pm 0.34\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 72.115 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -411.120 \pm 0.34\ kJ \cdot mol^{-1}$

$T_{fus} = 1073.8 \pm 1.0\ K$ $\Delta_{fus} H° = 28.158 \pm 0.17\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is based on $\Delta_f H°(298.15\ K) = -57.39$ and $-39.95\ kcal \cdot mol^{-1}$ for $Na^+(aq,\infty)$ and $Cl^-(aq,\infty)$, respectively, and on the enthalpy of solution, $\Delta_{sln} H°(298.15\ K) = 0.922\ kcal \cdot mol^{-1}$ for NaCl. These values were reported in a personal communication from Wagman.[1]

Heat Capacity and Entropy

The low temperature values are based on the heat capacities (3–266 K) reported by Barron *et al.*[2] The earlier work of Clusius *et al.*,[3] results in a slightly higher entropy, $S°(298.15\ K) = 17.33\ cal \cdot K^{-1} \cdot mol^{-1}$, but a lower heat capacity at room temperature, $C_p°(298.15\ K) = 11.9\ cal \cdot K^{-1} \cdot mol^{-1}$. The high temperature values have been obtained by re-analysis of the enthalpies (672–1279 K) of Dawson *et al.*,[4] using the new value for $C_p°(298.15\ K)$. The resulting tables agree within $\pm$ 0.1 $kcal \cdot mol^{-1}$ with the enthalpies (812–1058 K) of Roth and Bertram.[5] The enthalpies (540–1037 K) of Magnus[6] agree well at the lower temperatures but are about 0.3 $kcal \cdot mol^{-1}$ smaller near the melting point.

Fusion Data

The melting temperature was taken from Dawson *et al.*[4] and the heat of melting was obtained by re-analysis of their crystal and liquid enthalpies. Values of $T_{fus} = 1073$ K and $\Delta_{fus} H° = 6.69 \pm 0.06\ kcal \cdot mol^{-1}$ were reported by Dworkin and Bredig.[7]

Sublimation Data

The vapor in equilibrium with NaCl contains both monomeric and polymeric forms (for details, see the tables for NaCl gases).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.611	−410.693	−410.693	INFINITE
100	34.932	23.723	114.140	−9.042	−411.920	−402.460	210.224
200	46.873	52.605	76.643	−4.807	−411.660	−393.046	102.653
298.15	50.509	72.115	72.115	0.	−411.120	−384.024	67.279
300	50.543	72.428	72.116	0.093	−411.110	−383.856	66.835
400	52.350	87.226	74.122	5.242	−413.318	−374.636	48.922
500	53.940	99.080	77.966	10.557	−412.890	−365.010	38.132
600	55.476	109.050	82.337	16.028	−412.252	−355.491	30.948
700	57.204	117.727	86.786	21.659	−411.408	−346.095	25.826
800	59.312	125.498	91.147	27.481	−410.346	−336.834	21.993
900	61.869	132.627	95.365	33.536	−409.038	−327.721	19.020
1000	64.865	139.296	99.428	39.868	−407.461	−318.768	16.651
1073.800	67.371	144.002	102.330	44.747	--- CRYSTAL <--> LIQUID ---		
1100	68.325	145.637	103.343	46.524	−405.588	−309.986	14.720
1200	71.965	151.742	107.123	53.542	−500.162	−298.950	13.013
1300	75.145	157.633	110.783	60.905	−496.764	−282.318	11.344
1400	77.530	163.293	114.333	68.544	−493.094	−265.958	9.923
1500	79.245	168.704	117.779	76.388	−489.224	−249.868	8.701

PREVIOUS: December 1960 CURRENT: September 1964

Sodium Chloride (NaCl) LIQUID $M_r = 58.44277$ Sodium Chloride (NaCl) $Cl_1Na_1(l)$

$S°(298.15\ K) = [95.055]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1073.8 \pm 1.0\ K$

$\Delta_f H°(298.15\ K) = [-385.923]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 28.158 \pm 0.17\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(NaCl, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1073.8\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

These were obtained by analysis of the enthalpies (1076–1279 K) of Dawson *et al.*[1] The heat capacity was extrapolated to a constant value of 16.0 at the higher temperatures. A glass transition was assumed at 800 K and below this temperature $C_p°$ was taken to that of the crystal.

$S°(298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

The melting temperature was taken from Dawson *et al.*[1] and the heat of melting was obtained by reanalysis of their crystal and liquid enthalpies. Values of $T_{fus} = 1073$ K and $\Delta_{fus}H° = 6.69 \pm 0.06\ kcal \cdot mol^{-1}$ were reported by Dworkin and Bredig.[2]

Sublimation Data

The vapor in equilibrium with NaCl contains both monomeric and polymric forms (for details refer to the tables for NaCl gases).

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
0							
100							
200							
298.15	50.509	95.055	95.055	0.	−385.923	−365.667	64.063
300	50.543	95.367	95 055	0.093	−385.913	−365.541	63.646
400	52.350	110.165	97.061	5.242	−388.121	−358.615	46.830
500	53.940	122.019	100.905	10.557	−387.693	−351.283	36.698
600	55.476	131.989	105.276	16.028	−387.055	−344.058	29.953
700	57.204	140.666	109.725	21.659	−386.212	−336.955	25.144
800	59.312	148.437	114.086	27.481	−385.149	−329.988	21.546
800.000	59.312	148.437	114.086	27.481	GLASS <--> LIQUID TRANSITION		
800.000	76.400	148.437	114.086	27.481			
900	74.852	157.354	118.410	35.050	−382.327	−323.264	18.762
1000	72.509	165.127	122.702	42.425	−379.707	−316.845	16.550
1073.800	70.668	170.225	125.796	47.708	--- CRYSTAL <--> LIQUID ---		
1100	70.082	171.921	126.874	49.552	−377.364	−310.674	14.753
1200	68.325	177.937	130.883	56.464	−472.043	−302.265	13.157
1300	67.446	183.367	134 715	63.248	−469.224	−288.232	11.581
1400	67.070	188.351	138.371	69.972	−466.469	−274 413	10.238
1500	66.944	192.973	141.858	76.672	−463.744	−260.790	9.082
1600	66.944	197.293	145.190	83.366	−461.028	−247.349	8.075
1700	66.944	201.352	148.375	90.061	−458.317	−234 077	7.192
1800	66.944	205.178	151.426	96.755	−455.610	−220.964	6.412
1900	66.944	208.798	154.351	103.449	−452.909	−208.002	5.718
2000	66.944	212.232	157.160	110.144	−450.213	−195.182	5.098
2100	66.944	215.498	159.861	116.838	−447.524	−182.497	4.539
2200	66.944	218.612	162.461	123.533	−444.842	−169.939	4.035
2300	66.944	221.588	164.967	130.227	−442.169	−157.503	3.577
2400	66.944	224.437	167.386	136.921	−439.506	−145.184	3.160
2500	66.944	227.170	169.723	143.616	−436.855	−132.975	2.778

PREVIOUS: December 1960 CURRENT· September 1964

Sodium Chloride (NaCl) CRYSTAL-LIQUID

0 to 1073.8 K crystal
above 1073.8 K liquid

Refer to the individual tables for details.

M_r = 58.44277 Sodium Chloride (NaCl) $Cl_1Na_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−10.611	−410.693	−410.693	INFINITE
100	34.932	23.723	114.140	−9.042	−411.920	−402.460	210.224
200	46.873	52.605	76.643	−4.807	−411.660	−393.046	102.653
298.15	50.509	72.115	72.115	0.	−411.120	−384.024	67.279
300	50.543	72.428	72.116	0.093	−411.110	−383.856	66.835
400	52.350	87.226	74.122	5.242	−413.318	−374.636	48.922
500	53.940	99.080	77.966	10.557	−412.890	−365.010	38.132
600	55.476	109.050	82.337	16.028	−412.252	−355.491	30.948
700	57.204	117.727	86.786	21.659	−411.408	−346.095	25.826
800	59.312	125.498	91.147	27.481	−410.346	−336.834	21.993
900	61.869	132.627	95.365	33.536	−409.038	−327.721	19.020
1000	64.865	139.296	99.428	39.868	−407.461	−318.768	16.651
1073.800	67.371	144.002	102.330	44.747	CRYSTAL <--> LIQUID		
1073.800	70.668	170.225	102.330	72.905	TRANSITION		
1100	70.082	171.921	103.968	74.748	−377.364	−310.674	14.753
1200	68.325	177.937	109.886	81.661	−472.043	−302.265	13.157
1300	67.446	183.367	115.333	88.445	−469.224	−288.232	11.581
1400	67.070	188.351	120.373	95.169	−466.469	−274.413	10.238
1500	66.944	192.973	125.061	101.869	−463.744	−260.790	9.082
1600	66.944	197.293	129.442	108.563	−461.028	−247.349	8.075
1700	66.944	201.352	133.553	115.257	−458.317	−234.077	7.192
1800	66.944	205.178	137.427	121.952	−455.610	−220.964	6.412
1900	66.944	208.798	141.089	128.646	−452.909	−208.002	5.718
2000	66.944	212.232	144.561	135.341	−450.213	−195.182	5.098
2100	66.944	215.498	147.862	142.035	−447.524	−182.497	4.539
2200	66.944	218.612	151.008	148.729	−444.842	−169.939	4.035
2300	66.944	221.588	154.012	155.424	−442.169	−157.503	3.577
2400	66.944	224.437	156.888	162.118	−439.506	−145.184	3.160
2500	66.944	227.170	159.645	168.813	−436.855	−132.975	2.778

PREVIOUS: CURRENT. September 1964

Sodium Chloride (NaCl) IDEAL GAS $M_r = 58.44277$ Sodium Chloride (NaCl) $Cl_1Na_1(g)$

$S°(298.15\ K) = 229.793\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -180.00 \pm 2.1\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -181.42 \pm 2.1\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 363.62\ cm^{-1}$ $\omega_e x_e = 1.72\ cm^{-1}$ $\sigma = 1$
$B_e = 0.21691\ cm^{-1}$ $\alpha_e = 0.001598\ cm^{-1}$ $r_e = 2.3606\ Å$

Enthalpy of Formation

The enthalpy of formation is based on a enthalpy of sublimation $\Delta_{sub}H°(298.15\ K) = 54\ 9\ kcal{\cdot}mol^{-1}$ obtained from the more consistent sets of vapor pressure data by correction for the presence of dimer. Observed vapor pressures were converted to monomer pressures by use of dimer–monomer ratios calculated from JANAF Gibbs energy functions and $\Delta_r H°(298.15\ K) = 48.6\ kcal{\cdot}mol^{-1}$ for the reaction $(NaCl)_2(g) \rightarrow 2\ NaCl(g)$. Higher polymeric species were neglected. Analyses of the resulting monomer pressures are summarized below.

Source	T/K	$\Delta_{sub}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	 3rd law
Nesmeyanov and Sazonov[1]	743 - 948*	54.35	54.94
Zimm and Mayer[2]	760 - 897*	55.15	54.91
Mayer and Wintner[3]	890 - 944*	49.6	55.37
Niwa[4]	883 - 973*	52.6	55.03
Barton and Bloom[5]	1340 - 1540**	56.67	54.68
Flock and Rodebush[6]	1250 - 1428**	55.65	54.98
Wartenberg and Albrecht[7]	1429 - 1720**	60.0	54.45
Ruff and Mugden[8]	1433 - 1723**	59.5	54.44

*Knudsen effusion measurements over crystal **total pressures over liquid

Heat Capacity and Entropy

The molecular constants are based on molecular beam studies of the rotational spectra by Clouser and Gordy[9] and on microwave studies by Honig *et al.*[10] The infrared spectra of Rice and Klemperer[11] give a frequency in close agreement (366 cm^{-1}).

References

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[2] B. H. Zimm and J. E. Mayer, J. Chem. Phys. **12**, 362 (1944).
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[10] Honig, Mandel, Stitch and Townes, Phys. Rev. **96**, 629 (1954).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}mol^{-1}	$S°$ J·K^{-1}mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−9.616	−179.997	−179.997	INFINITE
100	30.394	193.507	260.320	−6.681	−179.858	−187.377	97.876
200	34 090	215.819	233.022	−3.440	−180.592	−194.620	50.829
250	35.125	223.546	230.379	−1.708	−180.993	−198.081	41.387
298.15	35.786	229.793	229.793	0.	−181.418	−201.334	35.273
300	35.806	230.014	229.794	0.066	−181.436	−201.458	35.077
350	36.272	235.571	230.231	1.869	−181.945	−204.756	30.558
400	36.604	240.437	231.209	3.691	−185.167	−207.769	27.132
450	36.852	244.764	232.479	5.528	−185.781	−210.557	24.441
500	37.044	248.657	233.906	7.375	−186.370	−213.279	22.281
600	37.324	255.437	236.946	11.095	−187.483	−218.555	19.027
700	37.524	261.206	240.010	14.838	−188.528	−223.650	16.689
800	37.680	266.228	242.980	18.598	−189.526	−228.599	14.926
900	37.809	270.673	245.815	22.373	−190.499	−233.424	13.548
1000	37.921	274.663	248.503	26 159	−191.468	−238.142	12.439
1100	38.022	278.282	251.049	29.957	−192.454	−242.761	11.528
1200	38.116	281.594	253.458	33.764	−290.239	−244.850	10.658
1300	38.205	284.649	255.741	37.580	−290.387	−241.062	9.686
1400	38.289	287.483	257.909	41.404	−290.532	−237.262	8.852
1500	38.371	290.128	259.969	45.237	−290.673	−233.452	8.130
1600	38.450	292.607	261.933	49.079	−290.811	−229.633	7.497
1700	38.528	294.940	263.806	52.927	−290.945	−225.805	6.938
1800	38 604	297.144	265.598	56.784	−291.076	−221.969	6.441
1900	38.679	299.234	267.313	60.648	−291.205	−218.127	5.997
2000	38.754	301.219	268.959	64.520	−291.332	−214.277	5.596
2100	38.828	303.112	270.541	68.399	−291.458	−210.421	5.234
2200	38.901	304.920	272.063	72.285	−291.585	−206.559	4.904
2300	38.973	306.651	273.529	76.179	−291.712	−202.692	4.603
2400	39.045	308.311	274.944	80.080	−291.843	−198.818	4.327
2500	39.117	309.906	276.311	83.988	−291.978	−194.940	4.073
2600	39.189	311.442	277.633	87.903	−292.118	−191.055	3.838
2700	39.260	312.922	278.913	91.826	−292.266	−187.165	3.621
2800	39.331	314.351	280.153	95.756	−292.422	−183.270	3.419
2900	39.402	315.733	281.356	99.692	−292.589	−179.369	3.231
3000	39.473	317.070	282.524	103.636	−292.768	−175.462	3.055
3100	39.544	318.365	283.660	107.587	−292.960	−171.548	2.891
3200	39.614	319.622	284.764	111.545	−293.167	−167.629	2.736
3300	39.685	320.842	285.839	115.510	−293.389	−163.702	2.591
3400	39.755	322.028	286.886	119.482	−293.629	−159.769	2.455
3500	39.825	323.181	287.907	123.461	−293.886	−155.828	2.326
3600	39.895	324.304	288.902	127.447	−294.162	−151.879	2.204
3700	39.965	325.398	289.874	131.440	−294.459	−147.923	2.088
3800	40.035	326.465	290.823	135.440	−294.777	−143.959	1.979
3900	40.105	327.506	291.750	139.447	−295.116	−139.985	1.875
4000	40.175	328.522	292.657	143.461	−295.480	−136.003	1.776
4100	40.245	329.515	293.544	147.482	−295.868	−132.011	1.682
4200	40.315	330.485	294.412	151.510	−296.280	−128.010	1.592
4300	40.385	331.435	295.262	155.545	−296.721	−123.998	1.506
4400	40.455	332.364	296.094	159.587	−297.148	−119.980	1.424
4500	40.524	333.274	296.911	163.636	−297.625	−115.949	1.346
4600	40.594	334.165	297.711	167.692	−298.139	−111.906	1.271
4700	40.664	335.039	298.496	171.755	−298.684	−107.851	1.199
4800	40.733	335.896	299.266	175.825	−299.260	−103.785	1.129
4900	40.803	336.737	300.022	179.901	−299.871	−99.706	1.063
5000	40.873	337.562	300.765	183.985	−300.509	−95.616	0.999
5100	40.942	338.372	301.494	188.076	−301.191	−91.511	0.937
5200	41.012	339.168	302.211	192.174	−301.912	−87.393	0.878
5300	41.082	339.949	302.916	196.278	−302.674	−83.260	0.821
5400	41.151	340.718	303.609	200.390	−303.479	−79.113	0.765
5500	41.221	341.474	304.290	204.509	−304.329	−74.950	0.712
5600	41.290	342.217	304.961	208.634	−305.227	−70 771	0.660
5700	41.360	342.948	305.621	212.767	−306.173	−66.576	0.610
5800	41.429	343.668	306.271	216.906	−307.170	−62.364	0.562
5900	41.499	344.377	306.911	221.052	−308.220	−58.135	0.515
6000	41.568	345.075	307.541	225.206	−309.167	−53.905	0.469

PREVIOUS December 1964 (1 atm) CURRENT December 1964 (1 bar)

Sodium Perchlorate ($NaClO_4$) CRYSTAL M_r = 122.44037 Sodium Perchlorate ($NaClO_4$) $Cl_1Na_1O_4(cr)$

$S°(298.15\ K)$ = [142.256] J·K⁻¹·mol⁻¹
T_{trs} = 581 K
T_{fus} = 755 K

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -382.752 \pm 0.92$ kJ·mol⁻¹
$\Delta_{trs}H°$ = [13.98] kJ·mol⁻¹
$\Delta_{fus}H°$ = Unknown

Enthalpy of Formation

Gilliland and Johnson[1] measured the enthalpy of solution of $NaClO_4(cr)$ and gave $\Delta_f H°(298.15\ K) = -92.48 \pm 0.22$ kcal·mol⁻¹ for $NaClO_4(cr)$. The enthalpy of dilution of $NaClO_4(cr)$ was measured by Vanderzee and Swanson.[2] The data led to $\Delta_f H°(298.15\ K) = -91.464$ kcal·mol⁻¹ which agrees very well with the data reported by Gilliland and Johnson.[1] The value of $\Delta_f H°(298.15\ K)$ was reported to be −92.18 kcal·mol⁻¹,[3] based upon the data prior to 1950. Vorob'ev *et al.*[4] measured the enthalpy of decomposition of $NaClO_4(cr)$ into $NaCl(cr)$ and $O_2(g)$ and gave $\Delta_f H°(298.15\ K) = -90.68 \pm 0.3$ kcal·mol⁻¹ for $NaClO_4(cr)$. The value reported by Gilliland and Johnson[1] was used.

Heat Capacity and Entropy

Heat capacities and $S°(298.15\ K)$ wee estimated by comparison with those for $NaClO_3(cr)$ and $KClO_4(cr)$, respectively.

Transition Data

T_{trs} was reported in.[3] $\Delta_{trs}H°$ was estimated from that for $KClO_4(cr)$.

Fusion Data

T_{fus} was obtained from.[5]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	111.294	142.256	142.256	0.	−382.752	−254.240	44.542
300	111.713	142.946	142.258	0.206	−382.738	−253.443	44.128
400	135.980	178.647	146.961	12.675	−383.569	−210.358	27.470
500	150.206	210.598	156.559	27.020	−380.228	−167.415	17.490
581.000	158.574	233.798	165.736	39.544		I <−−> II	
581.000	158.574	257.836	165.736	53.511		TRANSITION	
600	160.247	262.966	168.734	56.539	−361.860	−125.708	10.944
700	168.511	288.302	184.037	72.986	−356.711	−86.747	6.473
800	175.728	311.286	198.528	90.207	−350.923	−48.569	3.171
900	181.586	332.327	212.242	108.076	−344.612	−11.149	0.647
1000	187.025	351.744	225.234	126.510	−337.858	25.544	−1.334
1100	191.962	369.803	237.565	145.461	−330.708	61.542	−2.922
1200	196.648	386.708	249.297	164.894	−419.964	99.312	−4.323
1300	201.083	402.625	260.485	184.782	−411.207	142.232	−5.715
1400	205.267	417.682	271.180	205.102	−402.083	184.465	−6.882
1500	209.200	431.979	281.428	225.828	−392.615	226.032	−7.871

PREVIOUS: CURRENT: June 1963

$S°(298.15\ K) = [251.9 \pm 13]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 181.92 \pm 4.2\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = 182.00 \pm 4.2\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[6]	[23108]	[6]
[1507]	[4]	[23796]	[4]
[8394]	[10]	[24788]	[4]
[9330]	[8]	[24836]	[2]
[10116]	[6]	[25036]	[6]
[10664]	[4]	[29071]	[4]
[13550]	[8]	[29593]	[2]
[14996]	[6]	[32500]	[10]
		[32524]	[8]

$\omega_e = [424]\ cm^{-1}$ $\omega_ex_e = [2]\ cm^{-1}$ $\sigma = 1$
$B_e = [10.167]\ cm^{-1}$ $\alpha_e = [0.002]\ cm^{-1}$ $r_e = [2.137]$ Å

Enthalpy of Formation

The adopted value of $\Delta_fH°(298.15\ K)$, is based on our third law analysis of unpublished mass spectrometry data (7 points, 1400–1540 K) of Hildenbrand[1] for the reaction $Ni(g) + NiCl_2(g) = 2NiCl(g)$. Our analysis of this data yields 2nd and 3rd law values for $\Delta_fH°(298.15\ K)$ of 43.0 ± 1.3 kcal·mol^{-1} and 43.5 ± 1.0 kcal·mol^{-1}, respectively, with a drift of 0.64 ± 1.17 cal·K^{-1}·mol^{-1}. These values are in good agreement with a value of $\Delta_fH°(298.15\ K) = 42.9 \pm 5.4$ kcal·mol^{-1} based on the dissociation energy of 88 ± 5 kcal·mol^{-1} reported by Bulewicz *et al.*[2] using flame photometry. Additional studies include an analysis by Rao and Dadape[3] of the equilibrium $NiCl_2(g) + Ni(cr) \rightarrow 2NiCl(g)$ by the flow method. Our analysis of their data (10 points, 1243–1298 K) using auxiliary JANAF data[4] yields the following values for $\Delta_fH°(298.15\ K)$; 36.9 ± 1.6 kcal·mol^{-1} (2nd law) and 28.5 ± 0.8 kcal·mol^{-1} (3rd law) with a very large drift of -12.85 ± 2.42 cal·K^{-1}·mol^{-1}. The large drift probably indicates an experimental problem such as lack of equilibrium or the presence of side reactions. Other studies on the enthalpy of formation are summarized by Rao and Dadape[3] and are not considered here since the uncertainties in these studies are very large.

Heat Capacity and Entropy

The 18 observed band systems of NiCl(g) are adequately summarized by Suchard.[5] All of these systems have been observed in emission only and the electronic states giving rise to these transitions have not been assigned. The only rotational analysis by Rao and Rao[6] indicates that the upper and lower states are $^2\Delta_{5/2}$ states but the lower state is not definitely identified with the ground state. In view of these difficulties we have chosen to use the electronic energy levels and quantum weights of $Ni^+(g)$[7] as an approximation to those of NiCl(g). This approximation generally gives upper limit values for the thermal functions, we estimate an uncertainty of ± 3 cal·K^{-1}·mol^{-1} for $S°(298.15\ K)$.

Molecular constant data for the ground state are assigned assuming that the lower state of the G band system represents the ground state.[5,6] While this assignment is not certain, the molecular constant data for most of the observed systems are fairly similar[5] so no gross errors will be introduced if this assignment proves incorrect. On this basis the adopted values of B_e and ω_e are from Rao and Rao[6] and Rao *et al.*,[8] respectively, while ω_ex_e and α_e are our best estimates.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.465	181.915	181.915	INFINITE
100	29.843	216.385	281.814	−6.543	182.874	171.431	−89.546
200	33.290	238.153	255.063	−3.382	182.626	160.032	−41.796
250	34.524	245.720	252.461	−1.685	182.340	154.415	−32.263
298.15	35.443	251.883	251.883	0.	182.004	149.067	−26.116
300	35.475	252.102	251.883	0.066	181.990	148.862	−25.919
350	36.268	257.632	252.318	1.860	181.592	143 372	−21.397
400	36.964	262.521	253.294	3.691	181.152	137.941	−18.013
450	37.586	266.911	254.567	5.555	180.676	132.568	−15.388
500	38.136	270.900	256 004	7.448	180 157	127.250	−13.294
600	39.023	277.936	259.089	11.308	178.923	116.780	−10.167
700	39.645	284.001	262.224	15.244	177.700	106.530	−7.949
800	40.049	289.324	265.286	19.230	176.750	96.427	−6.296
900	40.291	294.056	268.225	23.248	175.778	86.445	−5.017
1000	40.425	298.309	271.024	27.285	174.757	76.573	−4.000
1100	40.496	302.166	273.683	31.331	173.671	66.807	−3.172
1200	40.540	305.691	276.205	35.383	172.512	57.142	−2.487
1300	40.583	308.938	278.600	39.439	171.273	47.578	−1.912
1400	40.646	311.947	280.876	43.500	169.948	38.112	−1.422
1500	40.744	314.755	283.042	47.570	168.536	28.744	−1.001
1600	40.885	317.389	285.107	51.651	167.038	19.473	−0.636
1700	41 076	319.873	287.080	55.748	165.451	10.298	−0.316
1800	41.317	322.227	288.967	59.868	146.630	1.934	−0.056
1900	41.608	324 469	290.777	64.013	144.972	−6.059	0.167
2000	41.945	326.611	292.516	68.191	143.339	−13.966	0.365
2100	42.324	328.667	294.189	72.404	141.737	−21.791	0.542
2200	42.739	330.645	295.801	76.657	140.168	−29.542	0.701
2300	43.183	332.555	297.358	80.952	138.636	−37.221	0.845
2400	43.650	334.402	298.863	85.294	137.142	−44.835	0.976
2500	44.134	336.194	300.321	89.683	135.687	−52.387	1.095
2600	44.627	337.934	301.734	94.121	134.273	−59.882	1.203
2700	45.124	339.628	303.106	98.609	132.900	−67.324	1.302
2800	45.619	341.278	304.440	103.146	131.566	−74.715	1.394
2900	46.107	342.887	305.738	107.732	130.272	−82.059	1.478
3000	46.584	344.458	307.003	112.367	129.017	−89.359	1.556
3100	47.047	345.994	308.236	117.049	127.799	−96.618	1.628
3200	47.491	347.494	309.439	121.776	−250.218	−98.650	1.610
3300	47.916	348.962	310.615	126.546	−249.712	−93.921	1.487
3400	48.318	350.399	311.764	131.358	−249.172	−89.209	1.371
3500	48.698	351.805	312.888	136.209	−248.601	−84.512	1.261
3600	49.053	353.182	313.988	141.097	−248.000	−79.832	1.158
3700	49.384	354.530	315.066	146.019	−247.371	−75.169	1.061
3800	49.690	355.851	316.122	150.973	−246.717	−70.524	0.969
3900	49.973	357.146	317.157	155.956	−246.041	−65.896	0.883
4000	50.232	358.414	318.173	160.967	−245.342	−61.286	0.800
4100	50.468	359.658	319.169	166.002	−244.625	−56.693	0.722
4200	50.683	360.876	320.148	171.059	−243.890	−52.118	0.648
4300	50.877	362.071	321.109	176.138	−243.139	−47.561	0.578
4400	51.051	363.243	322.053	181.234	−242.374	−43.022	0.511
4500	51.207	364.392	322.982	186.347	−241.597	−38.500	0.447
4600	51.346	365.519	323.894	191.475	−240.809	−33.995	0.386
4700	51.469	366.625	324.792	196.616	−240.011	−29.508	0.328
4800	51.578	367.710	325.674	201.768	−239.205	−25.037	0.272
4900	51.672	368.774	326.543	206.931	−238.393	−20.584	0.219
5000	51.755	369.819	327.398	212.103	−237.576	−16.147	0.169
5100	51.826	370.844	328.240	217.282	−236.755	−11.727	0.120
5200	51.887	371.851	329.069	222.467	−235.933	−7.323	0.074
5300	51.939	372.840	329.886	227.659	−235.110	−2.934	0.029
5400	51.983	373.811	330.690	232.855	−234.287	1.439	−0.014
5500	52.019	374.766	331.483	238.055	−233.468	5.797	−0.055
5600	52.048	375.703	332.264	243.258	−232.652	10.140	−0.095
5700	52.072	376.625	333.034	248.465	−231.842	14.468	−0.133
5800	52.090	377.530	333.794	253.673	−231.040	18.782	−0.169
5900	52.104	378.421	334.543	258.882	−230.246	23.083	−0.204
6000	52.114	379.297	335.281	264.093	−229.463	27.370	−0.238

PREVIOUS· September 1977 (1 atm) CURRENT September 1977 (1 bar)

Chlorine Oxide (ClO) IDEAL GAS $M_r = 51.452$ Chlorine Oxide (ClO) $Cl_1O_1(g)$

$D_0^\circ = 22184 \pm 3\ cm^{-1}$
$S^\circ(298.15\ K) = 225.07 \pm 0.5\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H^\circ(0\ K) = 101.05 \pm 0.1\ kJ{\cdot}mol^{-1}$
$\Delta_f H^\circ(298.15\ K) = 101.63 \pm 0.1\ kJ{\cdot}mol^{-1}$

	Electronic States and Molecular Constants ($^{35}Cl^{16}O$), cm^{-1};				Point Group: $C_{\infty v}$	$\sigma = 1$	
State	ϵ_i	g_i	B_e	α_e	ω_e	$\omega_e x_e$	r_e/Å
$X^2\Pi_{3/2}$	0	2	0.62347334	0.005935	853.72446	5.579573	1.56970
$X^2\Pi_{1/2}$	320.31	2	0.62347334	0.005935	853.72446	5.579573	1.56970
$A^2\Pi_{3/2}$	31650	2	0.4450	0.006	519.5	7.2	1.858
$A^2\Pi_{1/2}$	32169	2	0.4450	0.006	519.5	7.2	1.858

Enthalpy of Formation

The dissociation energy of ClO was measured by Coxon and Ramsay[1] from the convergence limit of the A←X subbands. With respect to this study, the first bound excited state, $A^2\Pi$, dissociates to $Cl(^2P_{3/2}) + O(^1D_2)$. The ground dissociation energy, $D_0^\circ = 22184 \pm 3\ cm^{-1}$ (265.380 ± 0.036 kJ·mol), gives the value $\Delta_f H^\circ(0\ K) = 101.035 \pm 0.11$ kJ·mol. Additional data needed for the calculations presented here, e. g. thermal functions for the Cl(g) and Cl_2(ref), O(g) and O_2(ref), are taken from JANAF Thermochemical Tables.[2] An earlier study by Durie and Ramsay[3] yielded a dissociation energy of $22152 \pm 10\ cm^{-1}$ which is in agreement with our adopted value.

Heat Capacity and Entropy

The spectroscopic results given above are for the $^{35}Cl^{16}O$ isotopic species. Isotopic relationships[4] are used to convert the above constants to those for the normally occuring, i.e. natural abundance, species. The latter values are then used in the calculation of the thermal functions. Only the X and A states are included in the calculation of the thermal functions; a sum-over-states technique is used.

The high resolution gas phase infrared spectrum of the fundamental of ClO has been measured using laser diode and Fourier transfer infrared spectroscopy.[5–9] The observed spectrum is in agreement with the inertial parameters obtained from the microwave spectrum.[10–14] The spectroscopic parameters for the X states are taken from Burkholder *et al.*[5] These authors utilized their results, microwave results and the results of laser magnetic resonance studies of the vibrational overtone of both $^{35}Cl^{16}O$ and $^{37}Cl^{16}O$[13], to obtain precise spectroscopic constants for the X states.[13] These authors also give higher order terms in the rotational vibrational Hamiltonian.

The splitting of the X state, A, is the actual splitting corrected for the lowest lying populated rotational state for both the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ components of the X state. The rotational constants given for the X state are B_0 and α_0 values, since they are based on microwave results and results for the first and second vibrational level. Burkholder *et al.*[5] utilized the microwave results, which have been refined by Cohen *et al.*[10] using all available microwave data. The ESR spectrum has been measured.[16,17] Uehara *et al.*[17] interpreted the ESR spectrum including centrifugal distortion effects giving values of the ground state splitting constant, in agreement with the value chosen by Cohen *et al.*,[10] that was obtained from the electronic spectrum by Coxon.[20]

The electronic spectrum has been measured by several workers[18–21] giving electronic levels, including the ground state splitting, vibration and rotation constants and dissociation energies of the ground and first excited state. The dissociation energy, anharmonicity constants and spectroscopic constants for the excited states are obtained from the electronic spectra. Inclusion of the A state increases the entropy 0.1 J mol-1 K^{-1} at temperatures approaching 6000 K. The most recent measurements by Lang *et al.*[22] are in agreement with those of Burkholder *et al.*[5] Results of previous studies are summarized in two references.[5 22] The other electronic states, which lie about 50,000 cm^{-1}, are not included in the calculations.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.000	0.000	INFINITE	−9.517	101.045	101.045	INFINITE
100	30.834	189.125	254.946	− 6.582	101.072	100.275	− 52.377
200	33.479	211.506	228.195	− 3.338	101.342	99.386	− 25.956
250	34.030	219.038	225.637	− 1.650	101.492	98.879	− 20.659
298.15	34.479	225.071	225.071	0.000	101.630	98.363	− 17.232
300	34.496	225.285	225.072	0.064	101.635	98.343	− 17.123
350	34.919	230.635	225.494	1.799	101.773	97.783	− 14.593
400	35.297	235.323	226.435	3.555	101.906	97.204	− 12.693
450	35.626	239.499	227.659	5.328	102.032	96.609	− 11.214
500	35.909	243.268	229.034	7.117	102.153	96.000	− 10.029
600	36.357	249.857	231.971	10.731	102.371	94.747	− 8.248
700	36.688	255.487	234.938	14.384	102.561	93.461	− 6.974
800	36.941	260.403	237.821	18.066	102.725	92.150	− 6.017
900	37.139	264.766	240.577	21.771	102.866	90.819	− 5.271
1000	37.302	268.688	243.195	25.493	102.989	89.474	− 4.674
1100	37.439	272.250	245.677	29.230	103.097	88.117	− 4.184
1200	37.558	275.513	248.029	32.980	103.191	86.751	− 3.776
1300	37.665	278.523	250.261	36.741	103.275	85.378	− 3.430
1400	37.762	281.318	252.380	40.513	103.349	83.999	− 3.134
1500	37.854	283.927	254.398	44.294	103.413	82.614	− 2.877
1600	37.940	286.372	256.320	48.083	103.470	81.225	− 2.652
1700	38.024	288.675	258.156	51.882	103.518	79.833	− 2.453
1800	38.106	290.851	259.913	55.688	103.558	78.439	− 2.276
1900	38.185	292.913	261.596	59.503	103.589	77.042	− 2.118
2000	38.263	294.874	263.211	63.325	103.612	75.645	− 1.976
2100	38.340	296.742	264.765	67.155	103.624	74.245	− 1.847
2200	38.414	298.528	266.258	70.993	103.627	72.847	− 1.730
2300	38.486	300.237	267.699	74.838	103.620	71.448	− 1.623
2400	38.553	301.876	269.089	78.690	103.601	70.049	− 1.525
2500	38.616	303.451	270.432	82.548	103.570	68.651	− 1.434
2600	38.672	304.967	271.731	86.413	103.525	67.256	− 1.351
2700	38.719	306.427	272.990	90.282	103.466	65.862	− 1.274
2800	38.758	307.836	274.209	94.156	103.392	64.470	− 1.203
2900	38.785	309.197	275.392	98.034	103.302	63.081	− 1.136
3000	38.801	310.512	276.541	101.913	103.194	61.697	− 1.074
3100	38.803	311.784	277.658	105.793	103.067	60.316	− 1.016
3200	38.790	313.016	278.743	109.673	102.922	58.938	− 0.962
3300	38.763	314.209	279.800	113.551	102.757	57.567	− 0.911
3400	38.719	315.366	280.829	117.425	102.572	56.200	− 0.863
3500	38.660	316.488	281.832	121.294	102.367	54.840	− 0.818
3600	38.585	317.576	282.810	125.157	102.140	53.486	− 0.776
3700	38.494	318.632	283.764	129.011	101.892	52.136	− 0.736
3800	38.388	319.657	284.695	132.855	101.623	50.796	− 0.698
3900	38.267	320.652	285.604	136.688	101.332	49.463	− 0.663
4000	38.131	321.620	286.493	140.508	101.019	48.136	− 0.629
4100	37.981	322.559	287.361	144.313	100.685	46.818	− 0.596
4200	37.819	323.473	288.210	148.104	100.330	45.508	− 0.566
4300	37.645	324.361	289.040	151.877	99.954	44.207	− 0.537
4400	37.461	325.224	289.853	155.632	99.557	42.915	− 0.510
4500	37.266	326.064	290.648	159.369	99.139	41.633	− 0.483
4600	37.063	326.880	291.427	163.085	98.701	40.360	− 0.458
4700	36.852	327.675	292.190	166.781	98.243	39.095	− 0.435
4800	36.635	328.449	292.937	170.455	97.764	37.842	− 0.412
4900	36.412	329.202	293.670	174.108	97.267	36.601	− 0.390
5000	36.184	329.935	294.388	177.738	96.750	35.369	− 0.370
5100	35.952	330.650	295.092	181.344	96.213	34.145	− 0.350
5200	35.718	331.345	295.782	184.928	95.659	32.931	− 0.331
5300	35.481	332.024	296.460	188.488	95.084	31.732	− 0.313
5400	35.243	332.685	297.125	192.024	94.491	30.542	− 0.295
5500	35.004	333.329	297.777	195.537	93.880	29.363	− 0.279
5600	34.765	333.958	298.417	199.025	93.249	28.195	− 0.263
5700	34.526	334.571	299.046	202.490	92.600	27.038	− 0.248
5800	34.289	335.169	299.664	205.930	91.931	25.894	− 0.233
5900	34.053	335.753	300.271	209.347	91.244	24.764	− 0.219
6000	33.819	336.324	300.867	212.741	90.538	23.643	− 0.206

PREVIOUS: June 1961 (1 bar) CURRENT: December 1992 (1 bar)

Titanium Chloride Oxide (OTiCl) IDEAL GAS $M_r = 99.3324$

$S°(298.15\ K) = [263.661]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [-242.642]\ kJ{\cdot}mol^{-1}$

$\Delta_f H°(298.15\ K) = [-244.262]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[880](1)
[230](2)
[490](1)

Ground State Quantum Weight: [2] $\sigma = 1$
Point Group. [$C_{\infty v}$]
Bond Distances: O–Ti = [1.62] Å; Ti–Cl = [2.17] Å
Bond Angle: O–Ti–Cl = [180]°
Rotational Constant: $B_0 = [0.092252]\ cm^{-1}$

Enthalpy of Formation

$\Delta_f H°$(TiOCl, g, 298.15 K) is calculated from an estimated value of $\Delta_f H°$((TiOCl, g, 0 K) = −58 kcal·mol^{-1}.[1]

Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1]

Reference

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Titanium Chloride Oxide (OTiCl) $Cl_1O_1Ti_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.142	−242.642	−242.642	INFINITE
100	36.633	215.420	305.606	−9.019	−242.987	−245.587	128.282
200	46.229	244.103	268.229	−4.825	−243.685	−247.916	64.749
250	49.321	254.766	264.499	−2.433	−243.995	−248.937	52.012
298.15	51.654	263.661	263.661	0.	−244.262	−249.864	43.775
300	51.733	263.980	263.662	0.096	−244.272	−249.898	43.511
350	53.622	272.103	264.299	2.731	−244.521	−250.816	37.432
400	55.104	279.364	265.736	5.451	−244.750	−251.700	32.869
450	56.272	285.924	267.621	8.237	−244.969	−252.555	29.316
500	57.200	291.903	269.754	11.074	−245.182	−253.387	26.471
600	58.546	302.459	274.349	16.866	−245.612	−254.987	22.199
700	59.444	311.556	279.029	22.769	−246.061	−256.515	19.141
800	60.067	319.537	283.604	28.746	−246.526	−257.977	16.844
900	60.514	326.639	287.998	34.776	−247.050	−259.377	15.054
1000	60.844	333.032	292.187	40.845	−247.702	−260.714	13.618
1100	61.094	338.844	296.169	46.942	−248.549	−261.976	12.440
1200	61.288	344.168	299.950	53.062	−253.579	−263.032	11.449
1300	61.441	349.080	303.543	59.199	−254.101	−263.799	10.600
1400	61.563	353.638	306.960	65.349	−254.707	−264.522	9.869
1500	61.663	357.889	310.215	71.510	−255.412	−265.200	9.235
1600	61.745	361.871	313.321	77.681	−256.230	−265.826	8.678
1700	61.814	365.617	316.288	83.859	−257.174	−266.398	8.185
1800	61.871	369.152	319.127	90.043	−258.260	−266.910	7.746
1900	61.920	372.498	321.849	96.233	−259.502	−267.357	7.350
2000	61.962	375.675	324.462	102.427	−275.600	−267.281	6.981
2100	61.999	378.699	326.973	108.625	−277.943	−266.808	6.636
2200	62.030	381.584	329.390	114.827	−280.299	−266.222	6.321
2300	62.058	384.342	331.720	121.031	−282.671	−265.529	6.030
2400	62.082	386.984	333.968	127.238	−285.059	−264.733	5.762
2500	62.103	389.519	336.140	133.447	−287.463	−263.837	5.513
2600	62.123	391.955	338.240	139.659	−289.884	−262.844	5.281
2700	62.139	394.300	340.273	145.872	−292.324	−261.757	5.064
2800	62.155	396.560	342.243	152.087	−294.781	−260.580	4.861
2900	62.168	398.741	344.154	158.303	−297.256	−259.316	4 671
3000	62.181	400.849	346.009	164.520	−299.750	−257.965	4.492
3100	62.192	402.888	347.811	170.739	−302.262	−256.530	4.323
3200	62.202	404.863	349.563	176.959	−304.790	−255.015	4.163
3300	62.211	406.777	351.268	183.179	−307.336	−253.421	4.011
3400	62.220	408.634	352.928	189.401	−309.897	−251.748	3.868
3500	62.228	410.438	354.546	195.623	−312.473	−250.001	3.731
3600	62.235	412.191	356.123	201.846	−315.063	−248.179	3.601
3700	62.241	413.896	357.661	208.070	−726.763	−238.497	3.367
3800	62.247	415.556	359.163	214.295	−728.142	−225.282	3.097
3900	62.253	417.173	360.630	220.520	−729.586	−212.030	2.840
4000	62.258	418.749	362.063	226.745	−731.091	−198.741	2.595
4100	62.263	420.287	363.465	232.971	−732.657	−185.412	2.362
4200	62.267	421.787	364.835	239.198	−734.278	−172.046	2.140
4300	62.271	423.252	366.177	245.425	−735.952	−158.639	1.927
4400	62.275	424.684	367.490	251.652	−737.677	−145.194	1.724
4500	62.279	426.084	368.777	257.880	−739.448	−131.709	1.529
4600	62.282	427.452	370.038	264.108	−741.263	−118.183	1.342
4700	62.286	428.792	371.274	270.336	−743.119	−104.618	1.163
4800	62.289	430.103	372.486	276.565	−745.013	−91.013	0.990
4900	62.291	431.388	373.675	282.794	−746.942	−77.368	0.825
5000	62.294	432.646	374.842	289.023	−748.903	−63.683	0.665
5100	62.296	433.880	375.987	295.253	−750.893	−49.959	0.512
5200	62.299	435.089	377.112	301.482	−752.911	−36.196	0.364
5300	62.301	436.276	378.217	307.712	−754.954	−22.393	0.221
5400	62.303	437.441	379.303	313.943	−757.019	−8.552	0.083
5500	62.305	438.584	380.371	320.173	−759.105	5.327	−0.051
5600	62.307	439.707	381.420	326.404	−761.210	19.245	−0.180
5700	62.309	440.809	382.453	332.634	−763.331	33.201	−0.304
5800	62.310	441.893	383.468	338.865	−765.468	47.194	−0.425
5900	62.312	442.958	384.467	345.096	−767.619	61.223	−0.542
6000	62.314	444.006	385.451	351.328	−769.783	75.290	−0.655

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

Titanium Chloride Oxide (OTiCl) $Cl_1O_1Ti_1(g)$

$\Delta_a H°(0\ K) = 540.4 \pm 8\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = 256.84 \pm 0.1\ J \cdot mol^{-1} \cdot K^{-1}$

$\Delta_f H°(0\ K) = 99 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 97 \pm 8\ kJ \cdot mol^{-1}$

Electronic Levels and Molecular Constants, cm^{-1}

State	ϵ_i	g_i	ν_1	ν_2	ν_3	$r_e/(Å)$	<°	$I_AI_BI_C(gm^3cm^6)$
X^2B_1	0	2	945.580	447.675	1110.1054	1.471	117.6	$1.368837 \times 10^{-115}$
A^2A_2	21013.9	2	708.30	289.56	791.60	1.6270	106°18'	$2.793762 \times 10^{-115}$

Point Group: C_{2v} $\sigma = 2$

Enthalpy of Formation

Clyne and Watson[1] recommended $\Delta_f H°(298.15\ K) = 101.5 \pm 3.1\ kJ \cdot mol^{-1}$, using the techniques of mass spectrometry based on measurements of the equilibrium constant of the gas phase reaction:

$$OClO(g) + Br(g) = BrO(g) + ClO(g)$$

Alqasmi *et al.*[2] obtained $\Delta_f H°(298.15\ K) = 92.9 \pm 2.1\ kJ \cdot mol^{-1}$, from measurements of the enthalpy of the reaction:

$$2ClNO(g) + ClO_2(g) \rightarrow ClNO_2(g) + NO_2(g) + Cl_2(g)$$

The value is calculated using auxiliary data from JANAF.[3] Alqasmi *et al.*[2] summarized the available thermochemical data for this species including the work of Clyne and Watson.[1]

A value of $97 \pm 8\ kJ \cdot mol^{-1}$ is chosen. Within the experimental uncertainty, the values of $\Delta_f H°$ for OClO(g) and ClOO(g) are the same.

Heat Capacity and Entropy

The microwave spectrum of ClO_2 has been investigated in a series of papers by Curl *et al.*[4-9] They have determined the inertial parameters for both chlorine isotopic species in the ground and some excited vibrational states and have identified the ground electronic state as a $^2B_1$ state.[4-9] The results of these studies have been used to compute the moments of inertia for the normally occurring isotopic species from which the structure was derived. The principle moments of inertia in ($g \cdot cm^2$) are: $I_A = 1.6217 \times 10^{-39}$, $I_B = 8.4128 \times 10^{-39}$, $I_C = 10.0339 \times 10^{-39}$ for the X^2B_1 state and $I_A = 2.6590 \times 10^{-39}$, $I_B = 9.0067 \times 10^{-39}$, $I_C = 11.6657 \times 10^{-39}$ for the A^2A_2 state.

More recent microwave studies have characterized the higher order terms in the rotational Hamiltonian for the ground vibrational state[10] and for the all the vibrational fundamentals and $2\upsilon_2$.[11] The ground state vibrational fundamentals, υ_1 and υ_2, have been determined using high resolution laser diode and Fourier transform spectroscopy.[11 12] The antisymmetric stretching mode, ν_3, has been determined by IR-microwave double resonance measurements.[13] The electronic spectrum of ClO_2 has been investigated by many workers. The vibrational and rotational constants have been determined for both the ground and excited electronic states.[14-16] Richardson *et al.*[17] have also observed the infrared spectrum for many vibrational levels of the ground electronic state References to earlier works can be found in the above papers. Fluorescence measurements using a variety of argon ion laser lines have been observed by Curl *et al.*[18] and Sakurai *et al.*[19] Recently Richard *et al.*[20] have observed the fluorescence spectrum of ClO_2 cooled in a supersonic jet. This will probably lead to more accurate spectroscopic constants for this species.[20,21] Wahner *et al.*[22] have measured cross sections for this species as a function of temperature in the wavelength range of 240-480 nm.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−10.796	99.478	99.478	INFINITE
100	33.812	216.512	291.127	−7.462	98.452	103.582	−54.105
200	37.603	241.016	260.538	−3.904	97.579	109.069	−28.486
250	39.822	249.644	257.520	−1.969	97.247	111.982	−23.397
298.15	41.953	256.841	256.841	.000	97.000	114.843	−20.120
300	42.033	257.101	256.842	.078	96.992	114.954	−20.015
350	44.104	263.738	257.361	2.232	96.810	117.963	−17.605
400	45 956	269.751	258.540	4.484	96.693	120.993	−15.800
450	47.563	275.259	260.096	6.823	96.626	124.035	−14.398
500	48.936	280.343	261.870	9.237	96.600	127.082	−13.276
600	51.082	289.466	265.727	14.244	96 632	133.177	−11.594
700	52.619	297.462	269.701	19.433	96.730	139.261	−10.392
800	53.735	304.565	273.623	24.753	96.864	145.328	−9.489
900	54.561	310.944	277.422	30.170	97.015	151.377	−8.786
1000	55.185	316.727	281.068	35.659	97.174	157.409	−8.222
1100	55.666	322.010	284.553	41.202	97.333	163.425	−7.760
1200	56.043	326.870	287.880	46.789	97.490	169.426	−7.375
1300	56.343	331.368	291.054	52.409	97.640	175.415	−7.048
1400	56.586	335.553	294.085	58.055	97.783	181.392	−6.768
1500	56.785	339.464	296.981	63.724	97.915	187.359	−6.524
1600	56.950	343.134	299.752	69.411	98.035	193.318	−6.311
1700	57.088	346.591	302.407	75.113	98.141	199.270	−6.123
1800	57.204	349.858	304.953	80.828	98.231	205.216	−5.955
1900	57.304	352.953	307.399	86.554	98.303	211.158	−5.805
2000	57.390	355.895	309.751	92.288	98.357	217.096	−5.670
2100	57.466	358.697	312.015	98.031	98.390	223.032	−5.548
2200	57.532	361.372	314.198	103.781	98.401	228.968	−5.436
2300	57.593	363.930	316.305	109.538	98.390	234.902	−5.335
2400	57.648	366.383	318.341	115.300	98.355	240.838	−5.242
2500	57.700	368.737	320.310	121.067	98.295	246.776	−5.156
2600	57.751	371.001	322.217	126.840	98.210	252.717	−5.077
2700	57.801	373.182	324.064	132.617	98.101	258.662	−5 004
2800	57.853	375.285	325.856	138.400	97.966	264.611	−4.936
2900	57.906	377.316	327.596	144.188	97.807	270.564	−4.873
3000	57.964	379.280	329.286	149.981	97.625	276.525	−4.815
3100	58.026	381.181	330.929	155.781	97.420	282.492	−4.760
3200	58.093	383.025	332.529	161.587	97.194	288.465	−4.709
3300	58.167	384.813	334.086	167.400	96.949	294.446	−4.661
3400	58.249	386.551	335.604	173.220	96.687	300.435	−4.616
3500	58.339	388.241	337.084	179.050	96.410	306.431	−4.573
3600	58.437	389.886	338.528	184.888	96.120	312.436	−4.533
3700	58.545	391.488	339.937	190.737	95.820	318 448	−4.496
3800	58.662	393.051	341.315	196.598	95.512	324.470	−4.460
3900	58.789	394.576	342.661	202.470	95.199	330.500	−4.427
4000	58.926	396.066	343.977	208.356	94.885	336.537	−4.395
4100	59 072	397.523	345.266	214.256	94.571	342.582	−4.365
4200	59.229	398.949	346.527	220.171	94.260	348.635	−4.336
4300	59.395	400.344	347.762	226.102	93.954	354 695	−4.309
4400	59.571	401.712	348.973	232.050	93.657	360.762	−4.283
4500	59.756	403.052	350.160	238.016	93.370	366.835	−4.258
4600	59.949	404.368	351.324	244.001	93.096	372.915	−4.235
4700	60 151	405.659	352.467	250.006	92.835	379.001	−4.212
4800	60.360	406.928	353.588	256.032	92.591	385.093	−4.191
4900	60.577	408.175	354.689	262.079	92.364	391.190	−4.170
5000	60.800	409.401	355.771	268.147	92.155	397.290	−4.150
5100	61.028	410.607	356.835	274.239	91.966	403.395	−4.132
5200	61.262	411.794	357.880	280.353	91.798	409.502	−4.113
5300	61.500	412.964	358.909	286.491	91.650	415.614	−4.096
5400	61.741	414.115	359.920	292.653	91.524	421.727	−4.079
5500	61.986	415.250	360.916	298.840	91.419	427.843	−4.063
5600	62.233	416.370	361.896	305.051	91.335	433.961	−4.048
5700	62.481	417.473	362.862	311.286	91.272	440.080	−4.033
5800	62.730	418.562	363.813	317.547	91.230	446.200	−4.018
5900	62.980	419.637	364.750	323.832	91.208	452.319	−4.005
6000	63.229	420.697	365.673	330.143	91.204	458.441	−3.991

PREVIOUS, March 1961 (1 bar) CURRENT December 1992 (1 bar)

Chlorine Oxide (ClOO) IDEAL GAS $M_r = 67.4515$ Chlorine Oxide (ClOO) $Cl_1O_2(g)$

$S°(298.15\ K) = 269.32 \pm 0.5\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 99.7 \pm 3.0\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 98.0 \pm 4.0\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight State	ϵ_i, cm^{-1}	g_i
X^2A''	0.0	2

Vibrational Levels and Degeneracies ν, cm^{-1}
1442.8 (1)
408.3 (1)
192.4 (1)

Point Group: C_s $\sigma = 1$
Bond Distances: Cl-O = [1.83]Å; O-O = [1.23] Å
Bond Angle: Cl-O-O = [110]°
Product of the Moments of Inertia: $I_A I_B I_C = [2.418103 \times 10^{-115}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(ClOO, g), has been estimated, calculated and determined experimentally. The reported values are listed below.

Source	Technique (T/K)	Reaction	$\Delta_f H°$(ClOO,g,0 K)
Benson and Buss[4]	$D_0° = 33.5 \pm 8.4$; 0	ClOO = Cl + O_2	[86.1]
Clyne and Coxon[3]			
Clyne *et al.*[1]	mass spectrometry, 298	ClO + ClO ↔ Cl + ClOO	89.8
Clyne and Watson[2]	mass spectrometry, 298	BrO + ClO ↔ Br + ClOO	91.7
Baer *et al.*[11]	laser flash photolysis, 160-300	Cl + O_2 + M = ClOO + M	99.128
Nicovich *et al.*[5]	laser flash photolysis, 181-200	Cl + O_2 + M = ClOO + M	99.7
Mauldin *et al.*[12]	pulse photolysis, 191-250	Cl + O_2 + M = ClOO + M	100.4
Rathman and Schindler[16]	G1 direct isodesmic theory, 0		[121.3]

Based on the above experimental studies we adopt $\Delta_f H°$(ClOO,g,0 K) = 99.7 ± 3 kJ·mol. This corresponds $D_0°$(Cl-OO) = 20 ± 2 kJ·mol. Within the experimental uncertainty, the values of $\Delta_f H°$ for OClO(g) and ClOO(g) are the same.

Heat Capacity and Entropy

Jacox[6] has summarized the IR studies on the three fundamental frequencies (1443, 373, 407)[7-9] and unstructured gas phase absorption[9-12] between 225 and 270 nm. Since her review, there have been two matrix isolation studies which have redefined (reversed the assignment of) ν_2 and ν_3. We adopt the values recommended by Johnston *et al.*[9] (for ν_1) and Johnsson *et al.*[13] (Ar matrix) and Mueller and Willmer[14] (Ne and Ar matrices) for ν_2 and ν_3.

The infrared spectrum of all the fundamentals of ClOO in an argon matrix has been observed by Arkell and Schwager.[8] They observed spectra for the ^{18}O species as well as the ^{16}O species. They did not observe any chlorine isotopic species. Rochkind and Pimentel[7] have observed the stretching fundamentals in a nitrogen matrix isolated infrared spectrum in agreement with Arkell and Schwager.[8] Johnston *et al.*[9] have observed a low resolution gas phase spectrum of the ν_1 fundamental in agreement with Arkell and Schwager's value.[8]

The bond distances and bond angle are from the estimate Arkell and Schwager[8] used in their normal coordinate analysis. Moments of inertia are calculated for the naturally occuring isotopic species. The EPR spectrum has been observed in a Zeolite matrix by Raghunathan and Sur.[15] The spectrum is consistent with a $^2A''$ ground state for the ClOO species. The principle moments of inertia (in g·cm²) are: $I_A = [1.2458 \times 10^{-39}]$, $I_B = [13.3231 \times 10^{-39}]$, $I_C = [14.5689 \times 10^{-39}]$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−11.610	99.700	99.700	INFINITE
100	35.208	224.953	307.450	−8.250	98.700	102.986	−53.794
200	42.256	251.656	273.434	−4.356	98.165	107.527	−28.083
250	44.507	261.341	270.075	−2.183	98.070	109.880	−22.958
298.15	46.119	269.324	269.324	.000	98.037	112.158	−19.650
300	46.174	269.609	269.325	.085	98.037	112.246	−19.544
350	47.518	276.831	269.892	2.429	98.044	114.614	−17.105
400	48.668	283.253	271.168	4.834	98.079	116.979	−15.276
450	49.678	289.045	272.838	7.293	98.133	119.338	−13.852
500	50.572	294.326	274.726	9.800	98.200	121.691	−12.713
600	52.059	303.684	278.793	14.934	98.359	126.375	−11.002
700	53.211	311.799	282.941	20.200	98.535	131.030	−9.778
800	54.101	318.965	287.005	25.568	98.716	135.660	−8.858
900	54.792	325.379	290.919	31.014	98.896	140.267	−8.141
1000	55.333	331.181	294.659	36.521	99.073	144.854	−7.566
1100	55.761	336.475	298.224	42.077	99.244	149.424	−7.096
1200	56.104	341.342	301.617	47.671	99.409	153.979	−6.703
1300	56.383	345.845	304.848	53.296	99.564	158.520	−6.369
1400	56.611	350.032	307.928	58.946	99.710	163.049	−6.083
1500	56.799	353.944	310.866	64.616	99.844	167.569	−5.835
1600	56.957	357.615	313.675	70.304	99.965	172.080	−5.618
1700	57.090	361.072	316.362	76.007	100.071	176.583	−5.426
1800	57.204	364.338	318.937	81.722	100.162	181.081	−5.255
1900	57.301	367.434	321.409	87.447	100.234	185.575	−5.102
2000	57.385	370.375	323.784	93.182	100.287	190.065	−4.964
2100	57.457	373.177	326.070	98.924	100.320	194.553	−4.839
2200	57.521	375.851	328.273	104.673	100.330	199.041	−4.726
2300	57.577	378.409	330.397	110.428	100.317	203.527	−4.622
2400	57.626	380.861	332.449	116.188	100.280	208.015	−4.527
2500	57.670	383.214	334.433	121.953	100.218	212.505	−4.440
2600	57.709	385.477	336.353	127.722	100.129	216.998	−4.360
2700	57.744	387.656	338.213	133.495	100.015	221.496	−4.285
2800	57.775	389.756	340.017	139.270	99.874	225.998	−4.216
2900	57.803	391.784	341.767	145.049	99.706	230.504	−4.152
3000	57.829	393.744	343.467	150.831	99.512	235.018	−4.092
3100	57.852	395.641	345.120	156.615	99.291	239.539	−4.036
3200	57.873	397.478	346.727	162.401	99.046	244.066	−3.984
3300	57.893	399.259	348.292	168.190	98.776	248.602	−3.935
3400	57.910	400.987	349.817	173.980	98.484	253.147	−3.889
3500	57.926	402.666	351.303	179.772	98.169	257.700	−3.846
3600	57.941	404.298	352.753	185.565	97.833	262.263	−3.805
3700	57.955	405.886	354.167	191.360	97.479	266.835	−3.767
3800	57.968	407.432	355.549	197.156	97.107	271.418	−3.731
3900	57.979	408.938	356.898	202.953	96.720	276.011	−3.697
4000	57.990	410.406	358.218	208.752	96.318	280.612	−3.664
4100	58.000	411.838	359.508	214.551	95.904	285.225	−3.634
4200	58.010	413.236	360.771	220.352	95.478	289.847	−3.605
4300	58.018	414.601	362.007	226.153	95.043	294.481	−3.577
4400	58.026	415.935	363.217	231.956	94.600	299.124	−3.551
4500	58.034	417.239	364.404	237.759	94.150	303.776	−3.526
4600	58.041	418.514	365.566	243.562	93.694	308.440	−3.502
4700	58.048	419.763	366.706	249.367	93.233	313.113	−3.480
4800	58.054	420.985	367.824	255.172	92.768	317.796	−3.458
4900	58.060	422.182	368.921	260.978	92.299	322.490	−3.438
5000	58.066	423.355	369.998	266.784	91.828	327.193	−3.418
5100	58.071	424.505	371.056	272.591	91.355	331.905	−3.399
5200	58.076	425.633	372.094	278.398	90.879	336.625	−3.381
5300	58.081	426.739	373.115	284.206	90.402	341.357	−3.364
5400	58.085	427.825	374.118	290.014	89.922	346.095	−3.348
5500	58.089	428.890	375.104	295.823	89.439	350.843	−3.332
5600	58.093	429.937	376.074	301.632	88.954	355.602	−3.317
5700	58.097	430.965	377.028	307.442	88.465	360.367	−3.302
5800	58.100	431.976	377.967	313.251	87.972	365.142	−3.288
5900	58.104	432.969	378.891	319.062	87.474	369.924	−3.275
6000	58.107	433.946	379.800	324.872	86.971	374.716	−3.262

PREVIOUS: CURRENT; December 1992 (1bar)

Chlorine Oxide (ClOO) $Cl_1O_2(g)$

Chlorine Oxide (ClO_3) IDEAL GAS $M_r = 83.4509$ Chlorine Oxide (ClO_3) $Cl_1O_3(g)$

$\Delta_f H°(0\ K) = 200 \pm 10\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 194 \pm 12\ kJ \cdot mol^{-1}$

$S°(28{=}98.15\ K) = 270.75 \pm 0.5\ J \cdot K^{-1} \cdot mol^{-1}$

Electronic Level and Quantum Weight State	ϵ_n, cm^{-1}	g_i
$^2A_1$	0.0	2

Vibrational Levels and Degeneracies ν, cm^{-1}
905.0 (1)
566.6 (1)
1081.3 (2)
475.8 (2)

Point Group: C_{3v} $\sigma = 3$
Bond Distance: Cl-O = 1.50 ± 0.01 Å
Bond Angle: O-Cl-O = 113.5 ± 2°
Product of the Moments of Inertia: $I_A I_B I_C = 13.174066 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(0\ K) = 200 \pm 10$ kJ·mol for $ClO_3(g)$ based on kinetic studies of Colussi et al.[3 4,7] and the quantum mechanical calculations of Rathman and Schindler[6] and Rauk *et al.*[8] Early recommended values for the enthalpy of formation of $ClO_3(g)$, 155 kJ·mol^{-1}, were based on a calorimetrically determined value of Goodeve and Marsh[1]. This value is now known to be erroneous. The recent determined values are listed in the table below.

Source	Technique	T/K	$\Delta_f H°$(kJ·mol)
Colussi[3]	laser flash photolysis and unimolecular reaction theory	0	238
Colussi *et al.*[4]	second-order rate constants	0	217.1 ± 20.9
Rathman and Schindler[5]	G1 direct isodesmic theory	0	201
Rathman and Schindler(2)[6]	G1 direct isodesmic theory	0	201
Colussi and Grela[7]	adopted value of Rathman and Schindler	0	200.8
Rauk *et al.*[8]	G2 energy calculations	0	197.68

Heat Capacity and Entropy

Jacox[9] has examined the literature pertaining to the structure, vibrational frequencies, and electronic transitions of $ClO_3(g)$. She has recommended a structure and the four vibrational frequencies as derived from the IR study of Grothe and Willner.[10] We adopt her recommendations.

The vibrational frequencies adopted in this calculation are from the experimental study of Grothe and Willner[10] The authors measured the IR bands of four isotopemers of ^{18}O-enriched ClO_3. From this spectroscopic data, a C_{3v} structure was derived with r(C-lO) = 1.50 ± 0.01 Å and a bond angle of 113.5 ± 2°. The principal moments of inertia are (in g·cm²): $I_A = I_B = 8.8757 \times 10^{-39}$ and $I_C = 16.7229 \times 10^{-39}$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−11.941	200.000	200.000	INFINITE
100	34.252	225.267	311.275	−8.601	197.527	210.447	−109.926
200	43.422	251.511	275.317	−4.761	195.481	224.220	−58.560
250	48.673	261.770	271.600	−2.458	194.788	231.490	−48.367
298.15	53.328	270.748	270.748	.000	194.325	238.604	−41.802
300	53.496	271.078	270.749	.099	194.311	238.879	−41.592
350	57.731	279.651	271.416	2.882	194.020	246.332	−36.763
400	61.348	287.602	272.948	5.862	193.882	253.816	−33.145
450	64.388	295.009	274.993	9.007	193.864	261.310	−30.332
500	66.926	301.928	277.344	12.292	193.938	268.801	−28.081
600	70.806	314 495	282.511	19.190	194.281	283.745	−24.702
700	73.531	325.626	287.890	26.415	194.788	298.617	−22.283
800	75.485	335.579	293.241	33.871	195.389	313.410	−20.464
900	76.920	344.557	298.452	41.495	196.044	328.124	−19.044
1000	77.999	352.720	303.477	49.243	196.731	342.762	−17.904
1100	78.826	360.194	308.298	57.086	197.436	357.332	−16.968
1200	79.472	367.082	312.913	65.002	198.148	371.836	−16.186
1300	79.986	373.464	317.329	72.976	198.861	386.281	−15.521
1400	80.401	379.407	321.553	80.996	199.570	400.672	−14.949
1500	80.740	384.966	325.597	89.054	200.270	415.011	−14.452
1600	81.021	390.187	329.473	97.142	200.958	429.305	−14.015
1700	81.255	395.106	333.190	105.256	201.630	443.556	−13.629
1800	81.454	399.756	336.760	113.392	202.283	457.768	−13.284
1900	81.622	404.164	340.193	121.546	202.914	471.944	−12.975
2000	81.767	408.355	343.497	129.716	203.521	486.088	−12.695
2100	81.893	412.347	346.681	137.899	204.102	500.202	−12.442
2200	82.002	416.160	349.753	146 094	204.654	514.290	−12.211
2300	82.097	419.807	352.721	154.299	205.176	528.352	−11.999
2400	82.181	423.303	355.589	162.513	205.666	542.392	−11.805
2500	82.255	426.659	358.365	170.735	206.124	556.412	−11.626
2600	82.322	429.886	361.054	178.964	206.547	570.416	−11.460
2700	82.381	432.994	363.662	187.199	206.936	584.404	−11.306
2800	82.434	435.991	366.192	195.439	207.291	598.377	−11.163
2900	82.481	438.885	368.649	203.685	207.611	612.338	−11.029
3000	82.524	441.682	371.037	211.935	207.897	626.290	−10.905
3100	82.563	444.389	373.360	220.190	208.150	640.233	−10.788
3200	82.599	447.010	375.620	228.448	208.369	654.166	−10.678
3300	82.631	449.553	377.822	236.709	208.557	668.094	−10.575
3400	82.660	452.020	379.969	244.974	208.715	682.017	−10.478
3500	82.687	454.416	382.062	253.241	208.844	695.936	−10.386
3600	82.712	456.746	384.104	261.511	208.945	709.851	−10.300
3700	82.735	459.013	386.098	269.784	209.022	723.764	−10.218
3800	82.756	461.219	388.046	278.058	209.074	737.676	−10.140
3900	82.776	463.369	389.950	286.335	209.105	751.587	−10.066
4000	82.794	465.465	391.812	294.614	209.115	765.496	−9.996
4100	82.811	467.510	393.633	302.894	209.107	779.405	−9.930
4200	82.826	469.505	395.416	311.176	209.082	793.315	−9.866
4300	82.841	471.455	397.162	319.459	209.042	807.227	−9.806
4400	82.854	473.359	398.872	327.744	208.989	821.137	−9.748
4500	82.867	475.221	400.548	336.030	208.923	835.050	−9.693
4600	82.879	477.043	402.191	344.317	208.845	848.964	−9.640
4700	82.890	478.825	403.803	352.605	208.757	862.881	−9.590
4800	82.900	480.570	405.384	360.895	208.659	876.800	−9.542
4900	82.910	482.280	406.936	369.186	208.551	890.722	−9.495
5000	82.919	483.955	408.460	377.477	208.435	904.645	−9.451
5100	82.928	485.597	409.956	385.769	208.310	918.571	−9.408
5200	82.936	487.208	411.426	394.063	208.176	932.497	−9.367
5300	82.944	488.787	412.871	402.357	208.033	946.429	−9.328
5400	82.951	490.338	414.291	410.651	207.880	960.362	−9.290
5500	82.958	491.860	415.688	418.947	207.718	974.297	−9.253
5600	82.965	493.355	417.061	427.243	207.543	988.238	−9.218
5700	82.971	494.823	418.413	435.540	207.357	1002.180	−9.184
5800	82.977	496.266	419.743	443.837	207.158	1016.127	−9.151
5900	82.983	497.685	421.052	452.135	206.945	1030.074	−9.120
6000	82.988	499.080	422.341	460.434	206.715	1044.029	−9.089

PREVIOUS. CURRENT: December 1996 (1bar)

Chlorine Oxide (ClO_3) $Cl_1O_3(g)$

Phosphorus Chloride (PCl) IDEAL GAS $M_r = 66.42676$

$S^\circ(298.15\ \mathrm{K}) = [237.879]\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$

$\Delta_f H^\circ(0\ \mathrm{K}) = [129.6]\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_f H^\circ(298.15\ \mathrm{K}) = [129.0]\ \mathrm{kJ\cdot mol^{-1}}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^3\Sigma]$	0	3

$\omega_e = [472]\ \mathrm{cm^{-1}}$ $\omega_e x_e = [1.89]\ \mathrm{cm^{-1}}$ $\sigma = 1$
$B_e = [0.2443]\ \mathrm{cm^{-1}}$ $\alpha_e = [0.00098]\ \mathrm{cm^{-1}}$ $r_e = [2.04]\ \mathrm{\AA}$

Enthalpy of Formation

The selected $\Delta_f H^\circ(298.15\ \mathrm{K})$ was calculated by assuming that the second and third bonds in $PCl_3(g)$ are of equal strength, and that the first bond has a strength 20% greater than the other two. These assumptions wee used by Henderson and Scheffee.[1] The selected $\Delta_f H^\circ(298.15\ \mathrm{K})$ was calculated using these bond strengths and auxiliary data from JANAF Tables.

A $\Delta_f H^\circ(298.15\ \mathrm{K}) = 40\ \mathrm{kcal\cdot mol^{-1}}$ was estimated by O'Brien and Perrin.[2]

Sandoval *et al.*[3] have calculated a $\Delta_f H^\circ(298.15\ \mathrm{K})$ for PCl from an appearance potential. They selected the process $PCl_3 \rightarrow Cl^+ + e^- + PCl^+ Cl$ to explain this potential rather than the process $PCl_3 \rightarrow Cl^+ + e^- + P + Cl_2$. The reason for their selection was a calculated $\Delta_f H^\circ{+}(Cl)$, 10 kcal·mol^{-1} lower than the literature value (See Nat. Bur. Stand., Circ 500). Use of the JANAF $\Delta_f H^\circ(298.15\ \mathrm{K})$ for PCl_3 eliminates this difference. Therefore, the process of the reported appearance potential would apparently be the second process which does not involve the neutral PCl radial.

Heat Capacity and Entropy

The molecular constants were estimated by Gordon.[4]

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Phosphorus Chloride (PCl) $Cl_1P_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−9.338	129.612	129.612	INFINITE
100	29.561	203.014	267.234	−6.422	130.185	121.103	−63.258
200	32.631	224.417	240.997	−3.316	129.509	112.047	−29.264
250	33.861	231.837	238.446	−1.652	129.272	107.708	−22.504
298.15	34.718	237.879	237.879	0.	129.000	103.579	−18.147
300	34.745	238.094	237.879	0.064	128.989	103.421	−18.007
350	35.378	243.500	238.305	1.818	127.948	99.256	−14.813
400	35.840	248.256	239.258	3.599	127.537	95.186	−12.430
450	36.185	252.498	240.497	5.400	127.133	91.166	−10.582
500	36.449	256.324	241.892	7.216	126.736	87.191	−9.109
600	36.822	263.005	244.870	10.881	125.952	79.356	−6.909
700	37.073	268.702	247.878	14.577	125.179	71.651	−5.347
800	37.253	273.664	250.797	18.294	124.413	64.057	−4.182
900	37.391	278.060	253.587	22.026	123.653	56.558	−3.283
1000	37.502	282.006	256.235	25.771	122.897	49.144	−2.567
1100	37.595	285.585	258.743	29.526	122.144	41.805	−1.985
1200	37.675	288.859	261.118	33.289	57.822	35.613	−1.550
1300	37.747	291.878	263.370	37.061	57.849	33.761	−1.357
1400	37.812	294.678	265.507	40.839	57.874	31.907	−1.190
1500	37.873	297.288	267.540	44.623	57.896	30.051	−1.046
1600	37.930	299.735	269.476	48.413	57.916	28.194	−0.920
1700	37.983	302.036	271.325	52.209	57.934	26.336	−0.809
1800	38.035	304.208	273.092	56.010	57.949	24.477	−0.710
1900	38.085	306.266	274.784	59.816	57.963	22.617	−0.622
2000	38.133	308.221	276.407	63.627	57.974	20.757	−0.542
2100	38.181	310.082	277.967	67.442	57.982	18.896	−0.470
2200	38.227	311.860	279.468	71.263	57.987	17.034	−0.404
2300	38.272	313.560	280.913	75.088	57.987	15.173	−0.345
2400	38.317	315.190	282.308	78.917	57.983	13.311	−0.290
2500	38.361	316.755	283.654	82.751	57.974	11.450	−0.239
2600	38.405	318.260	284.957	86.589	57.958	9.589	−0.193
2700	38.448	319.710	286.217	90.432	57.937	7.730	−0.150
2800	38.491	321.109	287.438	94.279	57.909	5.870	−0.110
2900	38.534	322.461	288.623	98.130	57.874	4.013	−0.072
3000	38.576	323.768	289.773	101.986	57.831	2.156	−0.038
3100	38.618	325.034	290.890	105.845	57.782	0.301	−0.005
3200	38.660	326.260	291.976	109.709	57.727	−1.552	0.025
3300	38.702	327.451	293.033	113.577	57.665	−3.404	0.054
3400	38.744	328.607	294.063	117.450	57.598	−5.254	0.081
3500	38.785	329.730	295.066	121.326	57.526	−7.101	0.106
3600	38.826	330.823	296.044	125.207	57.450	−8.946	0.130
3700	38.868	331.888	296.998	129.091	57.371	−10.790	0.152
3800	38.909	332.925	297.930	132.980	57.291	−12.631	0.174
3900	38.950	333.936	298.840	136.873	57.211	−14.470	0.194
4000	38.991	334.923	299.730	140.770	57.131	−16.307	0.213
4100	39.031	335.886	300.600	144.671	57.053	−18.142	0.231
4200	39.072	336.827	301.452	148.576	56.979	−19.975	0.248
4300	39.113	337.747	302.285	152.486	56.910	−21.806	0.265
4400	39.154	338.647	303.101	156.399	56.846	−23.636	0.281
4500	39.194	339.527	303.901	160.316	56.790	−25.465	0.296
4600	39.235	340.389	304.685	164.238	56.743	−27.292	0.310
4700	39.275	341.233	305.454	168.163	56.705	−29.119	0.324
4800	39.316	342.060	306.208	172.093	56.677	−30.944	0.337
4900	39.356	342.871	306.948	176.026	56.662	−32.769	0.349
5000	39.397	343.667	307.674	179.964	56.659	−34.595	0.361
5100	39.437	344.447	308.387	183.906	56.669	−36.420	0.373
5200	39.477	345.214	309.088	187.851	56.694	−38.245	0.384
5300	39.518	345.966	309.777	191.801	56.733	−40.071	0.395
5400	39.558	346.705	310.454	195.755	56.788	−41.898	0.405
5500	39.598	347.431	311.120	199.713	56.858	−43.726	0.415
5600	39.639	348.145	311.775	203.675	56.946	−45.556	0.425
5700	39.679	348.847	312.419	207.641	57.050	−47.387	0.434
5800	39.719	349.537	313.053	211.610	57.171	−49.220	0.443
5900	39.759	350.217	313.677	215.584	57.309	−51.056	0.452
6000	39.799	350.885	314.292	219.562	57.465	−52.894	0.460

PREVIOUS: December 1963 (1 atm) CURRENT· December 1963 (1 bar)

Phosphorus Chloride (PCl) $Cl_1P_1(g)$

Lead Chloride (PbCl) IDEAL GAS $M_r = 242.653$ Lead Chloride (PbCl) $Cl_1Pb_1(g)$

$S°(298.15\ K) = 259.61 \pm 0.21\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 16.74 \pm 50.2\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = 15.06 \pm 50.2\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
X $^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	8274	2
A[$^2\Sigma$]	21866.9	[2]
B $2\Sigma^+$	34937.5	2

$\omega_e = 302.5\ cm^{-1}$ $\omega_ex_e = 0.88\ cm^{-1}$ $\sigma = 1$
$B_e = 0.1172\ cm^{-1}$ $\alpha_e = [0.00047]\ cm^{-1}$ $r_e = 2.180$ Å

Enthalpy of Formation

$\Delta_fH°(0\ K)$ is obtained from $D_0°$ (Pb–Cl) = 3.1 ± 0.5 eV (71.5 kcal·mol^{-1}) which is the recommended value given by Gaydon.[1] $D_0°$ is combined with $\Delta_fH°$(Pb, g, 0 K) = 46.91 ± 0.13 kcal·mol^{-1} and $\Delta_fH°$(Cl, g, 0 K) = 28.587 ± 0.002 kcal·mol^{-1} [2] to give $\Delta_fH°$(PbCl, g, 0 K) = 4.0 ± 12.0 kcal·mol^{-1}. $\Delta_fH°$ at 298.15 K is 3.6 ± 12.0 kcal·mol^{-1}. The recommended value for $D_0°$ is based mainly on results ($D_0°$(LBX) = 3.2 eV) of a linear Birge–Sponer extrapolation of the observed vibrational levels (v, 0–18)[3] for the ground state of PbCl. This same value for $D_0°$(LBX) is obtained from the results of two other spectrometric studies, Morgan[4] and Pannetier and Deschamps,[5] while the results of another similar study Cordes and Gehrke[6] lead to $D_0°$(LBX) = 2.7 eV. The values of $D_0°$(LBX) are increased by only 0.1 eV when corrected for the ionic character of PbCl by application of the Hildenbrand formula.[7] Other spectroscopic values for $D_0°$(LBS) based on linear Birge–Sponer extrapolations include 2.2 eV ($A^2\Sigma$, or $^2\Delta$)[5] and 2.4 eV ($B^2\Sigma$) by Cordes and Gehrke.[6] The dissociation products are assumed to be Pb(^{1}D) + Cl(^{2}P)($A^2\Sigma$, or $^2\Delta$) and Pb(^{3}P) + Cl(^{2}P) ($B^2\Sigma$). Also, Wieland and Newburgh[8] first reported $D_0°$ = 3.12 eV from observations of predissociation, but later work[9] gave 3.05, or possibly 3.40 eV. It is to be noted that our $\Delta_fH°$ values for PbCl and $PbCl_2$, JANAF[2], indicate no significant differences in the binding of these two molecules. The difference $D_0°$(PbCl–Cl)–$D_0°$(Pb–Cl) is equal to only 2.2 kcal·mol^{-1}.

Heat Capacity and Entropy

The vibrational constants, electronic states (except for $A^2\Sigma$), and levels are taken from the compilation of Rosen[10] for $Pb^{35}Cl$. The vibrational constants are adjusted for the natural isotopic abundances of chlorine. It is not clear whether the first excited state for PbCl is $^2\Sigma$ or $^2\Delta$. By analogy with that for PbF,[11] we assume the first excited state to be $^2\Sigma$. However, if this state is $^2\Delta$, the entropy is increased by only 0.006 cal·K^{-1}·mol^{-1} at 4000 K and 0.05 cal·K^{-1}·mol^{-1} at 6000 K. The rotational constant is taken from the results of a rotational analysis of two bands of the A–X system for $^{208}Pb^{35}Cl$ by Singh and Singh.[12] The rotational constant is adjusted for the natural isotopic abundances of lead and chlorine. The value for r_e is obtained from the adopted B_e value. The results of an earlier rotational analysis of the same bands by Rao and Rao[13] are in reasonable agreement with our adopted values. The value for α_e is estimated from the other constants assuming a Morse potential function.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.793	16.738	16.738	INFINITE
100	31.235	222.428	290.774	−6.835	16.474	7.365	−3.847
200	34.890	245.391	262.893	−3.500	15.765	−1.462	0.382
250	35.727	253.274	260.207	−1.733	15.418	−5.729	1.197
298.15	36.234	259.613	259.613	0.	15.062	−9.770	1.712
300	36.250	259.837	259.614	0.067	15.048	−9.924	1.728
350	36.597	265.453	260.056	1.889	14.657	−14.055	2.098
400	36.841	270.356	261.044	3.725	14.242	−18.129	2.367
450	37.021	274.707	262.325	5.572	13.805	−22.150	2.571
500	37.158	278.614	263.762	7.426	13.344	−26.120	2.729
600	37.358	285.408	266.820	11.153	12.366	−33.922	2.953
700	37.500	291.178	269.898	14.896	6.451	−40.757	3.041
800	37.611	296.193	272.878	18.652	5.340	−47.424	3.096
900	37.705	300.629	275.720	22.418	4.260	−53.955	3.131
1000	37.790	304.606	278.413	26.193	3.212	−60.367	3.153
1100	37.873	308.211	280.961	29.976	2.196	−66.675	3.166
1200	37.961	311.510	283.371	33.767	1.212	−72.892	3.173
1300	38.057	314.553	285.654	37.568	0.257	−79.029	3.175
1400	38.166	317.377	287.820	41.379	−0.686	−85.092	3.175
1500	38.289	320.014	289.880	45.202	−1.623	−91.089	3.172
1600	38.429	322.490	291.841	49.038	−2.560	−97.022	3.167
1700	38.585	324.824	293.713	52.888	−3.499	−102.898	3.162
1800	38.756	327.034	295.504	56.755	−4.443	−108.717	3.155
1900	38.941	329.135	297.219	60.640	−5.391	−114.485	3.147
2000	39.138	331.137	298.865	64.544	−6.346	−120.202	3.139
2100	39.345	333.051	300.448	68.468	−184.528	−118.756	2.954
2200	39.560	334.887	301.972	72.413	−185.106	−115.610	2.745
2300	39.780	336.650	303.441	76.380	−185.757	−112.437	2.554
2400	40.002	338.348	304.861	80.369	−186.484	−109.234	2.377
2500	40.225	339.985	306.233	84.380	−187.288	−105.999	2.215
2600	40.448	341.567	307.562	88.414	−188.169	−102.730	2.064
2700	40.668	343.098	308.850	92.470	−189.124	−99.426	1.924
2800	40.884	344.581	310.100	96.548	−190.152	−96.086	1.792
2900	41.095	346.019	311.313	100.647	−191.249	−92.707	1.670
3000	41.300	347.416	312.494	104.766	−192.408	−89.289	1.555
3100	41.499	348.773	313.642	108.906	−193.626	−85.832	1.446
3200	41.692	350.094	314.761	113.066	−194.896	−82.335	1.344
3300	41.877	351.380	315.851	117.244	−196.210	−78.797	1.247
3400	42.055	352.633	316.915	121.441	−197.563	−75.219	1.156
3500	42.226	353.854	317.953	125.655	−198.947	−71.600	1.069
3600	42.389	355.046	318.966	129.886	−200.356	−67.942	0.986
3700	42.546	356.209	319.957	134.133	−201.781	−64.244	0.907
3800	42.696	357.346	320.926	138.395	−203.218	−60.508	0.832
3900	42.840	358.457	321.875	142.672	−204.660	−56.734	0.760
4000	42.978	359.543	322.803	146.963	−206.100	−52.922	0.691
4100	43.110	360.606	323.712	151.267	−207.533	−49.075	0.625
4200	43.236	361.647	324.603	155.585	−208.954	−45.193	0.562
4300	43.358	362.665	325.476	159.914	−210.359	−41.277	0.501
4400	43.474	363.664	326.333	164.256	−211.742	−37.329	0.443
4500	43.586	364.642	327.173	168.609	−213.101	−33.350	0.387
4600	43.695	365.601	327.998	172.973	−214.433	−29.340	0.333
4700	43.799	366.542	328.808	177.348	−215.733	−25.303	0.281
4800	43.900	367.465	329.604	181.733	−217.001	−21.238	0.231
4900	43.997	368.371	330.386	186.128	−218.233	−17.146	0.183
5000	44.092	369.261	331.155	190.532	−219.428	−13.030	0.136
5100	44.184	370.135	331.910	194.946	−220.585	−8.891	0.091
5200	44.274	370.994	332.654	199.369	−221.703	−4.729	0.048
5300	44.361	371.838	333.385	203.801	−222.781	−0.546	0.005
5400	44.446	372.668	334.105	208.241	−223.819	3.657	−0.035
5500	44.529	373.484	334.814	212.690	−224.816	7.879	−0.075
5600	44.611	374.287	335.511	217.147	−225.773	12.118	−0.113
5700	44.691	375.078	336.198	221.612	−226.689	16.374	−0.150
5800	44.769	375.856	336.876	226.085	−227.566	20.646	−0.186
5900	44.846	376.622	337.543	230.566	−228.403	24.933	−0.221
6000	44.922	377.376	338.200	235.054	−229.202	29.233	−0.254

PREVIOUS: June 1973 (1 atm) CURRENT: June 1973 (1 bar)

Lead Chloride, Ion ($PbCl^+$) IDEAL GAS $M_r = 242.65245$ Lead Chloride, Ion ($PbCl^+$) $Cl_1Pb_1^+(g)$

$S°(298.15\ K) = [255.15 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 741.0 \pm 50.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [745.589]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1
$^3\Pi$	[30000]	6

$\omega_e = [283]\ cm^{-1}$ $\omega_e x_e = [0.82]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.1062]\ cm^{-1}$ $\alpha_e = [0.00043]\ cm^{-1}$ $r_e = [2.29]\ Å$

Enthalpy of Formation

The $PbCl^+$ ion has been observed in several mass spectrometric studies[1–4] of the vapors in equilibrium with both solid and liquid $PbCl_2$. Electric deflection experiments of mass spectrometrically detected $PbCl_2$ beams by Buchler *et al.*[5] have shown neutral $PbCl_2$ to be the precursor of the ion. Reported values for the AP of $PbCl^+$ are 11.7[1] and 10.7 cal·K^{-1}·mol^{-1}.[2,3,4] The higher value of AP was obtained by the method of linear extrapolation; thus, it is judged to be somewhat less reliable. Also, the lower value was obtained with more sensitive equipment. Therefore, we adopt AP = 10.7 ± 0.5 cal·K^{-1}·mol^{-1} for the process $PbCl_2(g) + e^- \rightarrow PbCl^+(g) + Cl(g) + 2e^-$, and we calculate $\Delta_f H°(PbCl^+, g, 0\ K) = 177.1 \pm 12.0\ kcal \cdot mol^{-1}$ by combining the value for AP with $\Delta_f H°(PbCl_2, g, 0\ K) = -41.1 \pm 0.3\ kcal \cdot mol^{-1}$ and $\Delta_f H°(Cl, g, 0\ K) = 28.587 \pm 0.002\ kcal \cdot mol^{-1}$.[6] $\Delta_f H°$ at 298.15 K is 178.2 kcal·mol^{-1}, and the corresponding IP for PbCl is 7.5 ± 1.0 cal·K^{-1}·mol^{-1}. Our adopted $\Delta_f H°$ is considered a maximum value, since unknown kinetic energy factors could have been involved in the dissociative ionization of $PbCl_2$.

Heat Capacity and Entropy

The dissociation energy of $PbCl^+$ ($D_0° = 69.5\ kcal \cdot mol^{-1}$) is slightly less than that for PbCl ($D_0° = 71.5\ kcal \cdot mol^{-1}$). This implies that somewhat weaker binding occurs in the ion relative to the neutral molecule. Thus, one might expect $r_e(PbCl^+, g) > r_e(PbCl, g)$. We assume an increase in r_e of 5% and obtain $r_e(PbCl^+) = 2.29$ Å with $r_e(PbCl) = 2.180$ Å.[6] The value of B_e is obtained from the estimated value for r_e. Values for ω_e and $\omega_e x_e$ are estimated by a procedure similar to that given for SrF^+.[6] The constant term (d_{ij}) used in Badger's rule[7] is based on molecular data for PbCl, PbS, CsCl, and BaCl.[6] The value of α_e is obtained from the other constants assuming a Morse potential function.

$PbCl^+$ has 10 valence electrons and is isoelectronic with the Group III A monochlorides. By analogy with the electronic states and levels for these isoelectronic molecules,[6,8] we estimate the ground state configuration to be $^1\Sigma$ with a triplet level lying at 30,000 cm^{-1}. The uncertainty in the latter value is believed to be no greater than 5000 cm^{-1}. If the triplet level is decreased to 25,000 cm^{-1}, the entropy increases only 0.01 cal·K^{-1}·mol^{-1} at 4000 K and 1.14 cal·K^{-1}·mol^{-1} at 6000 K. The enthalpy at 0 K is −2.357 kcal·mol^{-1}.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.860	741.001		
100	31.590	217.637	286.530	−6.889			
200	35.163	240.840	258.445	−3.521			
250	35.932	248.776	255.744	−1.742			
298.15	36.394	255.148	255.148	0.	745.589	715.833	−125.411
300	36.408	255.373	255.148	0.067	745.614	715.648	−124.605
350	36.723	261.010	255.593	1.896	746.269	710.602	−106.052
400	36.945	265.929	256.584	3.738	746.899	705.463	−92.124
450	37.108	270.290	257.869	5.590	747.505	700.247	−81.283
500	37.235	274.207	259.310	7.448	748.088	694.965	−72.602
600	37.420	281.013	262.377	11.182	749.195	684.235	−59.568
700	37.554	286.792	265.463	14.931	745.365	674.124	−50.304
800	37.660	291.814	268.449	18.691	746.337	663.881	−43.347
900	37.749	296.255	271.297	22.462	747.341	653.514	−37.929
1000	37.829	300.236	273.995	26.241	748.376	643.033	−33.589
1100	37.901	303.845	276.547	30.028	749.441	632.448	−30.032
1200	37.969	307.146	278.962	33.821	750.538	621.764	−27.065
1300	38.033	310.188	281.248	37.621	751.660	610.987	−24.550
1400	38.095	313.008	283.417	41.428	752.792	600.124	−22.391
1500	38.156	315.639	285.479	45.240	753.923	589.179	−20.517
1600	38.214	318.103	287.441	49.059	755.048	578.160	−18.875
1700	38.272	320.422	289.314	52.883	756.161	567.070	−17.424
1800	38.329	322.611	291.104	56.713	757.259	555.915	−16.132
1900	38.386	324.685	292.817	60.549	758.340	544.700	−14.975
2000	38.442	326.655	294.460	64.390	759.401	533.428	−13.932
2100	38.497	328.532	296.038	68.237	583.221	529.219	−13.164
2200	38.552	330.324	297.556	72.090	584.629	526.614	−12.503
2300	38.607	332.039	299.018	75.948	585.947	523.947	−11.899
2400	38.662	333.683	300.429	79.811	587.173	521.225	−11.344
2500	38.716	335.263	301.791	83.680	588.305	518.453	−10.832
2600	38.771	336.782	303.107	87.554	589.344	515.638	−10.359
2700	38.825	338.246	304.382	91.434	590.291	512.785	−9.920
2800	38.880	339.659	305.617	95.319	591.149	509.899	−9.512
2900	38.935	341.025	306.814	99.210	591.923	506.983	−9.132
3000	38.991	342.346	307.977	103.106	592.619	504.042	−8.776
3100	39.047	343.625	309.106	107.008	593.242	501.079	−8.443
3200	39.105	344.866	310.204	110.916	593.799	498.097	−8.131
3300	39.163	346.070	311.273	114.829	594.298	495.099	−7.837
3400	39.224	347.240	312.314	118.749	594.746	492.086	−7.560
3500	39.286	348.378	313.328	122.674	595.152	489.060	−7.299
3600	39.350	349.485	314.317	126.606	595.523	486.024	−7.052
3700	39.417	350.564	315.282	130.544	595.867	482.977	−6.818
3800	39.487	351.617	316.225	134.489	596.192	479.922	−6.597
3900	39.561	352.643	317.145	138.442	596.505	476.858	−6.387
4000	39.638	353.646	318.045	142.402	596.812	473.786	−6.187
4100	39.720	354.626	318.926	146.370	597.121	470.707	−5.997
4200	39.806	355.584	319.787	150.346	597.437	467.620	−5.816
4300	39.897	356.521	320.631	154.331	597.767	464.525	−5.643
4400	39.994	357.440	321.457	158.325	598.114	461.422	−5.478
4500	40.097	358.340	322.266	162.330	598.485	458.311	−5.320
4600	40.206	359.222	323.060	166.345	598.884	455.192	−5.169
4700	40.321	360.088	323.839	170.371	599.313	452.064	−5.024
4800	40.444	360.938	324.603	174.409	599.778	448.926	−4.885
4900	40.573	361.773	325.353	178.460	600.280	445.778	−4.752
5000	40.710	362.594	326.090	182.524	600.823	442.619	−4.624
5100	40.854	363.402	326.813	186.602	601.409	439.450	−4.501
5200	41.006	364.197	327.525	190.695	602.040	436.268	−4.382
5300	41.165	364.979	328.224	194.804	602.717	433.074	−4.268
5400	41.333	365.750	328.912	198.929	603.443	429.866	−4.158
5500	41.508	366.510	329.588	203.071	604.217	426.645	−4.052
5600	41.691	367.260	330.255	207.230	605.042	423.409	−3.949
5700	41.882	368.000	330.910	211.409	605.917	420.158	−3.850
5800	42.080	368.730	331.556	215.607	606.844	416.891	−3.755
5900	42.286	369.451	332.192	219.825	607.823	413.607	−3.662
6000	42.500	370.163	332.819	224.064	608.854	410.307	−3.572

PREVIOUS: June 1973 (1 atm) CURRENT June 1973 (1 bar)

Lead Chloride, Ion ($PbCl^+$) $Cl_1Pb_1^+(g)$

Sulfur Chloride (SCl) IDEAL GAS $M_r = 67.513$ Sulfur Chloride (SCl) $Cl_1S_1(g)$

$S°(298.15\ K) = [237.32 \pm 2.5]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [155.65 \pm 16.7]\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [156.46 \pm 16.7]\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[400]	[2]
[25000]	[4]

$\omega_e = [536]\ cm^{-1}$ $\omega_ex_e = [2.08]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.24060]\ cm^{-1}$ $\alpha_e = [0.00126]\ cm^{-1}$ $r_e = [2.04]$ Å

Enthalpy of Formation

The adopted results are $\Delta_fH°(SCl, g, 298.15\ K) = 37.2 \pm 4.0\ kcal{\cdot}mol^{-1}$ and $D_0°(S–Cl) = 57.1 \pm 4.0\ kcal{\cdot}mol^{-1}$. We calculate $\Delta_fH°$ from an estimated value for the primary bond dissociation energy of SCl_2 of $69.7 \pm 3.0\ kcal{\cdot}mol^{-1}$, using auxiliary heat of formation data from JANAF.[1] The value of $D_0°(SCl–Cl)$ is obtained from the relationship $D_0°(SCl–Cl)/\Delta_{at}H°(SCl_2) = 0.55 \pm 0.03$ with $\Delta_aH°(SCl_2) = 126.8 \pm 0.9\ kcal{\cdot}mol^{-1}$.[1] The value of the ratio is taken to be the mean of three values calculated[1] for $SF_2(0.53 \pm 0.05)$, $SiCl_2(0.57 \pm 0.01)$, and $SiF_2(0.54 \pm 0.03)$. Converting $\Delta_fH°$ to 298.15 K, we obtain $\Delta_fH°(SCl, g, 298.15\ K) = 37.4\ kcal{\cdot}mol^{-1}$ which is in reasonable agreement with the previous estimate made by Mills (35 ± 5),[2] McBride *et al.* (32.0),[3] and Benson (36.5 ± 2).[4]

Perona *et al.*[5] have measured the hydrogen chloride infrared emission from reactions involving H and D atoms with SCl_2. From the observed highest vibrational level of HCl, they estimated an upper limit to $D_0°(SCl–Cl)$ of $\leq 58\ kcal{\cdot}mol^{-1}$. From this result, we calculate $\Delta_fH°(SCl, g, 0\ K) \leq 25.5\ kcal{\cdot}mol^{-1}$ and $D_0°(SCl) \geq 68.8\ kcal{\cdot}mol^{-1}$. We note that the results from this study predict that $D_0°(S–Cl) > D_0°(SCl–Cl)$ which is inconsistent with established trends in the bond dissociation energies[1] for other mono– and dihalides, such as the silicon chlorides, silicon fluorides, and sulfur fluorides. Factors which can influence the $D_0°$ values estimated from infrared chemiluminescence studies have been discussed by Perona *et al.*[5] It seems likely that their estimate of $D°$ may be too low due to the formation of some HCl in higher vibrational levels by an energy exchange mechanism rather than what is actually produced by the H/SCl_2 chemical reaction. For these reasons, we believe that the $\Delta_fH°(0\ K)$ value ($19 \pm 3\ kcal{\cdot}mol^{-1}$ recently reported by Takacs[6] based primarily on his analysis of the chemiluminscence work of Perona *et al.*[5] is suspect. The results adopted here predict $D_0°(SCl–Cl) > D_0°(S–Cl)$ by roughly $13\ kcal{\cdot}mol^{-1}$ which seems reasonable by comparison with bond energy data[1] for other halide systems.

Heat Capacity and Entropy

We estimate the S–Cl bond length to lie between those for SCl_2 and S_2Cl_2.[1] The value of B_e is calculated from the adopted r_e. We use Badger's rule[7] to estimate a value for ω_e. The equation is written as $\omega_e^2 = 3.159 \times 10^6/\mu(r_e–d_{ij})$,[3] and we use molecular data[1] for SiCl to determine the constant $d_{ij} = 1.172$. The value of x_e is estimated from the expression $x_e\mu^{1/2} = 0.01595$ calculated from data for SiCl.[1] By analogy with SiCl, SiF, and SF, we expect the ground state electronic configuration for SCl to be.[2] The ground state splitting (400 cm^{-1}) and double pi state at 25000 cm^{-1} are estimated from those observed for SF.[1]

McBride *et al.*[3] have previously estimated thermal functions over an extended temperature range (0–6000 K), using molecular data similar to ours. Their entropies are consistently higher than our values by $0.6\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ at 298.15 K and $0.3\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ at 4000 K. The difference at 298.15 K arises primarily from the electronic contribution caused by treating the ground state as a single level[3] with a quantum weight of 4. We believe that the uncertainty in $S°(298.15\ K)$ should not exceed $\pm 0.6\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. Their estimate of $\omega_ex_e = 5.85\ cm^{-1}$,[3] obtained assuming a linear Birge–Sponer relation, seems rather high in comparison with similar data[1] for SiCl, SiF, and SF.

References

[1] JANAF Thermochemical Tables $SCl_2(g)$, 6–30–78; SF(g) and $SF_2(g)$, 6–30–76; SiF2(g) and $SiCl_2(g)$, 12–31–77; $S_2Cl_2(g)$, 6–30–78; SiF(g) and SiCl(g), 12–31–76; Cl(g), 6–30–72; F(g), 9–30–65.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.819	155.648	155.648	INFINITE
100	30.207	200.110	269.024	−6.891	156.430	147.122	−76.848
200	35.382	222.704	240.708	−3.601	156.560	137.743	−35.975
250	36.817	230.770	237.939	−1.792	156.540	133.040	−27.797
298.15	37.541	237.324	237.324	0.	156.465	128.520	−22.516
300	37.560	237.556	237.325	0.069	156.461	128.346	−22.347
350	37.916	243.376	237.783	1.958	156.323	123.671	−18.457
400	38.073	248.451	238.807	3.858	153.917	119.106	−15.554
450	38.130	252.939	240.132	5.763	153.009	114.800	−13.326
500	38.140	256.958	241.618	7.670	152.016	110.610	−11.555
600	38.110	263.909	244.771	11.483	150.428	102.484	−8.922
700	38.068	269.781	247.935	15.292	149.054	94.604	−7.059
800	38.037	274.862	250.991	19.097	147.798	86.912	−5.675
900	38.018	279.341	253.897	22.899	93.484	80.454	−4.669
1000	38.010	283.346	256.645	26.701	93.561	79.002	−4.127
1100	38.011	286.969	259.240	30.502	93.615	77.543	−3.682
1200	38.019	290.276	261.690	34.303	93.649	76.080	−3.312
1300	38.032	293.320	264.008	38.106	93.662	74.616	−2.998
1400	38.050	296.139	266.203	41.910	93.658	73.151	−2.729
1500	38.070	298.765	268.288	45.716	93.635	71.687	−2.496
1600	38.093	301.223	270.270	49.524	93.595	70.225	−2.293
1700	38.118	303.533	272.159	53.335	93.538	68.766	−2.113
1800	38.145	305.712	273.963	57.148	93.466	67.310	−1.953
1900	38.173	307.775	275.689	60.964	93.379	65.860	−1.811
2000	38.202	309.734	277.343	64.782	93.278	64.414	−1.682
2100	38.232	311.599	278.930	68.604	93.163	62.973	−1.566
2200	38.263	313.378	280.456	72.429	93.035	61.539	−1.461
2300	38.295	315.080	281.924	76.257	92.893	60.110	−1.365
2400	38.327	316.710	283.340	80.088	92.739	58.688	−1.277
2500	38.360	318.275	284.706	83.922	92.573	57.273	−1.197
2600	38.394	319.780	286.027	87.760	92.394	55.864	−1.122
2700	38.428	321.230	287.304	91.601	92.203	54.463	−1.054
2800	38.463	322.628	288.541	95.446	92.000	53.069	−0.990
2900	38.498	323.979	289.739	99.294	91.785	51.682	−0.931
3000	38.535	325.284	290.903	103.145	91.559	50.303	−0.876
3100	38.572	326.549	292.032	107.001	91.323	48.932	−0.824
3200	38.610	327.774	293.130	110.860	91.076	47.568	−0.776
3300	38.649	328.962	294.198	114.723	90.820	46.213	−0.731
3400	38.689	330.117	295.238	118.589	90.556	44.865	−0.689
3500	38.731	331.239	296.250	122.460	90.284	43.525	−0.650
3600	38.774	332.331	297.237	126.336	90.005	42.193	−0.612
3700	38.819	333.394	298.200	130.215	89.721	40.869	−0.577
3800	38.865	334.429	299.140	134.100	89.433	39.552	−0.544
3900	38.913	335.440	300.058	137.988	89.142	38.243	−0.512
4000	38.962	336.425	300.955	141.882	88.849	36.942	−0.482
4100	39.014	337.388	301.832	145.781	88.556	35.648	−0.454
4200	39.067	338.329	302.690	149.685	88.264	34.361	−0.427
4300	39.122	339.249	303.529	153.594	87.975	33.081	−0.402
4400	39.179	340.149	304.351	157.509	87.689	31.808	−0.378
4500	39.239	341.030	305.157	161.430	87.407	30.541	−0.355
4600	39.300	341.893	305.946	165.357	87.132	29.280	−0.332
4700	39.363	342.739	306.720	169.290	86.863	28.025	−0.311
4800	39.428	343.568	307.479	173.230	86.603	26.776	−0.291
4900	39.495	344.382	308.224	177.176	86.352	25.533	−0.272
5000	39.564	345.181	308.955	181.129	86.110	24.294	−0.254
5100	39.635	345.965	309.673	185.089	85.880	23.060	−0.236
5200	39.708	346.735	310.378	189.056	85.661	21.830	−0.219
5300	39.783	347.492	311.071	193.031	85.455	20.604	−0.203
5400	39.859	348.236	311.753	197.013	85.262	19.383	−0.187
5500	39.937	348.969	312.423	201.003	85.082	18.165	−0.173
5600	40.017	349.689	313.082	205.000	84.916	16.949	−0.158
5700	40.098	350.398	313.730	209.006	84.765	15.737	−0.144
5800	40.181	351.096	314.368	213.020	84.629	14.527	−0.131
5900	40.265	351 784	314.997	217.042	84.509	13.320	−0.118
6000	40.350	352.461	315.616	221.073	84.404	12.114	−0.105

PREVIOUS. June 1978 (1 atm) CURRENT: June 1978 (1 bar)

Sulfur Chloride, Ion (SCl$^+$) IDEAL GAS $M_r = 67.51245$

$S°(298.15\ K) = [236.63 \pm 2.5]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1055.66 \pm 2.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [1062.037]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$[X^3\Sigma]$	0	[3]
$[a^1\Delta]$	[7000]	[2]
$[b^1\Sigma]$	[12000]	[1]
$[A^3\Pi_r]$	[25000]	[6]

$\omega_e = [553]\ cm^{-1}$ $\omega_e x_e = [2.19]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.26333]\ cm^{-1}$ $\alpha_e = [0.00142]\ cm^{-1}$ $r_e = [1.95]$ Å

Enthalpy of Formation

Blais and Cottin[1] have measured the appearance potential (AP) of SCl$^+$(g) from SCl$_2$(g) as 12.5 ± 0.2 eV using the electron impact technique. Subsequent work by Hartmann *et al.*[2] using the same method led to AP(SCl$^+$/SCl$_2$) = 12.2 ± 0.1 eV which confirms the earlier results. We assume that the fragment ions produced in the dissociative ionization process $e^- + SCl_2(g) = SCl^+(g) + Cl(g) + 2\ e^-$ are formed with no excitation energy or excess kinetic energy, and we calculate the adopted value of $\Delta_f H°(0\ K) = 252.3 \pm 5.0\ kcal \cdot mol^{-1}$ by combining the mean value (284.795 kcal·mol^{-1}) of these two AP's with $\Delta_f H°$ data[3] for Cl(g) and SCl$_2$(g).

Blais and Cottin[1] have also reported the electron impact AP for SCl$^+$(g) from S$_2$Cl$_2$(g) as 13.6 ± 0.2 eV. Assuming that the ionization process is $e^- + S_2Cl_2(g) = SCl^+(g) + SCl(g) + 2e^-$, their AP value gives $\Delta_f H°(SCl^+, g, 0\ K) = 272.8\ kcal \cdot mol^{-1}$ which is about 20 kcal·mol^{-1} higher than the adopted value. Comparison of JANAF IPs[3] for SF (10.09 ± 0.1 eV), SF$_2$ (10.29 ± 0.3 eV), and SCl$_2$(9.46 ± 0.02 eV) suggests that the ionization value for SCl should lie near 9.3 eV. Our adopted data for SCl(g) and SCl$^+$(g) give IP(SCl) = 9.33 ± 0.4 eV. The higher $\Delta_f H°$ value of 272.8 kcal·mol^{-1} corresponds to IP(SCl) = 10.2 ev which appears to be too high by comparison with the difference in the IPs for SF and SF$_2$ and the highly reliable IP value for SCl$_2$.[3]

$\Delta_f H°(298.15\ K)$ is obtained from the adopted $\Delta_f H°(0\ K)$ value by using JANAF enthalpies $H°(0\ K)–H°(298.15\ K)$[3] for S(α, cr), Cl$_2$(g), and e$^-$(g). $\Delta_f H°(298.15\ K)$ determined for the direct ionization $SCl = SCl^+ + e^-$ from our tables differs from a room–temperature threshold energy due to inclusion of the enthalpies of all the species in this ionization process and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −1.481 kcal·mol^{-1} if it is to be used in the ion convention which excludes the enthalpy of the electron. The S–Cl bond strength to form S$^+$(g) and Cl(g) by dissociation is calculated to be 80.8 ± 5.0 kcal·mol^{-1}.

Heat Capacity and Entropy

The value of r_e has been selected such that when it is substituted into the equation for Badger's rule[5] written as $\omega_{e2} = 3.159 \times 10^6/\mu(r_e - d_{ij})^3$, a value of ω_e(553 cm^{-1}) is obtained which agrees with that (552.3 cm^{-1}) determined for P^{35}Cl by Coxon and Wickramaaratchi.[6] The value of d_{ij} is taken equal to 1.10 based on the molecular data for SiCl[3] and P^{35}Cl.[6] This procedure gives $r_e = 1.95$ Å which is only slightly lower than the S–Cl bond lengths[3] measured for SCl$_2$(2.015 Å) and S$_2$Cl$_2$(2.057 Å). We calculate B_e from the estimated value of r_e. Using the expression $x_e \mu^{1/2} = 0.01623$, x_3 is determined to be 0.00396 which gives $\omega_e x_e = 2.19\ cm^{-1}$ when multiplied by the estimated value of ω_e. The value of the constant in the above expression is based on the values determined for SiCl and PCl. The value of α_e is determined from the other estimated molecular constants assuming a Morse potential function.

Examination of the electronic configurations and levels for diatomic halides having 12 valence electrons, such as PF[3] PCl[6], NCl, and NF[7] suggests that the ground state for SCl$^+$ is most likely $^3\Sigma$, and several low–lying excited states are expected. We estimate the relative term value for the $a^1\Delta$ state from that observed for PF (7090.41 cm^{-1}). Relative term values for the $b^1\Sigma$ and $A^3\Pi_r$ states are estimated by analogy with those observed for PCl.[6] As discussed by Coxon and Wickramaaratchi[6] for PCl, other singlet ($^1\Pi$) and triplet ($^3\Pi_i$ and $^3\Sigma$) states may be expected to lie in the range 20000–35000 cm^{-1}, similar to those observed for the isoelectronic molecules O$_2$, S$_2$, and SO.[3] Inclusion of estimated term values for these additional levels changes our entropy by only about 0.05 cal·K^{-1}·mol^{-1} at 4500 K, and we prefer to omit these levels at this time. The adopted electronic entropy contribution from the excited states amounts to 0.01 cal·K^{-1}·mol^{-1} at 1500 K, and this contribution increases to 0.51 cal·K^{-1}·mol^{-1}at 4500 K.

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[3] JANAF Thermochemical Tables: Cl(g), 6–30–72; SCl$_2$, SCl$_2$+(g) and S$_2$Cl$_2$(g), 6–30–78; SF$^+$(g), 6–30–76; SF$_2$+(g) and SiCl(g), 12–31–76; PF(g) and SO(g), 6–30–77; O$_2$(g) and e$^-$(g), 3–31–77; S$_2$(g) and S(α, cr), 9–30–77; Cl$_2$(g), 9–30–65.
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Sulfur Chloride, Ion (SCl$^+$) Cl$_1$S$_1^+$(g)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0	0.	0.	INFINITE	−9.183	1055.659		
100	29.303	202.547	265.263	−6.272			
200	31.737	223.512	239.676	−3.233			
250	33.002	230.735	237.187	−1.613			
298.15	33.958	236.633	236.633	0.	1062.037	1028.043	−180.109
300	33.989	236.844	236.634	0.063	1062.065	1027.832	−178.961
350	34.732	242.142	237.051	1.782	1062.798	1022.068	−152.535
400	35.291	246.818	237.985	3.533	1061.282	1016.290	−132.714
450	35.716	251.000	239.203	5.309	1061.283	1010.656	−117.314
500	36.046	254.781	240.575	7.103	1061.217	1005.037	−104.996
600	36.515	261.397	243.509	10.733	1061.524	993.779	−86.516
700	36.829	267.051	246.478	14.401	1062.088	982.446	−73.311
800	37.055	271.985	249.365	18.096	1062.801	971.021	−63.401
900	37.229	276.360	252.126	21.810	1010.477	960.582	−55.751
1000	37.375	280.290	254.749	25.541	1012.561	954.926	−49.880
1100	37.508	283.858	257.236	29.285	1014.638	949.062	−45.067
1200	37.639	287.127	259.592	33.042	1016.706	943.009	−41.048
1300	37.774	290.145	261.828	36.813	1018.766	936.784	−37.640
1400	37.917	292.950	263.952	40.597	1020.820	930.400	−34.714
1500	38.070	295.571	265.973	44.397	1022.870	923.870	−32.172
1600	38.234	298.033	267.901	48.212	1024.915	917.204	−29.944
1700	38.407	300.356	269.743	52.044	1026.959	910.409	−27.973
1800	38.589	302.557	271.505	55.893	1029.002	903.494	−26.219
1900	38.777	304.648	273.195	59.762	1031.046	896.466	−24.646
2000	38.970	306.642	274.818	63.649	1033.091	889.330	−23.227
2100	39.165	308.548	276.379	67.556	1035.140	882.091	−21.941
2200	39.362	310.375	277.883	71.482	1037.192	874.755	−20.769
2300	39.557	312.129	279.334	75.428	1039.248	867.326	−19.698
2400	39.751	313.816	280.736	79.394	1041.307	859.807	−18.713
2500	39.941	315.443	282.092	83.378	1043.369	852.202	−17.806
2600	40.127	317.013	283.405	87.382	1045.434	844.515	−16.967
2700	40.308	318.531	284.678	91.403	1047.502	836.748	−16.188
2800	40.483	320.000	285.913	95.443	1049.573	828.904	−15.463
2900	40.652	321.424	287.113	99.500	1051.646	820.986	−14.788
3000	40.815	322.805	288.280	103.573	1053.720	812.997	−14.156
3100	40.972	324.145	289.416	107.663	1055.796	804.939	−13.563
3200	41.122	325.449	290.521	111.767	1057.874	796.814	−13.007
3300	41.267	326.716	291.599	115.887	1059.953	788.623	−12.483
3400	41.406	327.950	292.650	120.021	1062.034	780.370	−11.989
3500	41.539	329.152	293.676	124.168	1064.117	772.055	−11.522
3600	41.667	330.324	294.678	128.328	1066.202	763.681	−11.081
3700	41.790	331.468	295.657	132.501	1068.290	755.249	−10.662
3800	41.909	332.584	296.614	136.686	1070.381	746.761	−10.265
3900	42.023	333.674	297.550	140.883	1072.477	738.217	−9.887
4000	42.134	334.739	298.467	145.090	1074.577	729.620	−9.528
4100	42.242	335.781	299.364	149.309	1076.682	720.970	−9.185
4200	42.346	336.800	300.243	153.539	1078.794	712.268	−8.858
4300	42.448	337.798	301.105	157.778	1080.914	703.516	−8.546
4400	42.548	338.775	301.950	162.028	1083.041	694.715	−8.247
4500	42.645	339.732	302.779	166.288	1085.177	685.865	−7.961
4600	42.741	340.670	303.593	170.557	1087.322	676.968	−7.687
4700	42.836	341.591	304.391	174.836	1089.478	668.024	−7.424
4800	42.929	342.493	305.176	179.124	1091.645	659.034	−7.172
4900	43.021	343.380	305.947	183.422	1093.824	649.999	−6.929
5000	43.112	344.250	306.704	187.728	1096.015	640.919	−6.696
5100	43.202	345.104	307.448	192.044	1098.219	631.795	−6.471
5200	43.291	345.944	308.181	196.369	1100.436	622.628	−6.254
5300	43.380	346.769	308.901	200.702	1102.668	613.418	−6.046
5400	43.468	347.581	309.610	205.045	1104.913	604.166	−5.844
5500	43.556	348.379	310.308	209.396	1107.173	594.872	−5.650
5600	43.643	349.165	310.994	213.756	1109.449	585.537	−5.462
5700	43.730	349.938	311.671	218.124	1111.739	576.161	−5.280
5800	43.816	350.700	312.337	222.502	1114.045	566.745	−5.104
5900	43.902	351.449	312.994	226.888	1116.367	557.289	−4.934
6000	43.987	352.188	313.641	231.282	1118.704	547.793	−4.769

PREVIOUS: September 1978 (1 atm) CURRENT September 1978 (1 bar)

Sulfur Chloride (S_2Cl) IDEAL GAS $M_r = 99.573$ Sulfur Chloride (S_2Cl) $Cl_1S_2(g)$

$S°(298.15 K) = [291.7 \pm 2.1] J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0 K) = 79.5 \pm 8.4 kJ\cdot mol^{-1}$
$\Delta_f H°(298.15 K) = 78.6 \pm 8.4 kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^2B_1]$	0	[2]
$[^2A_1]$	23000	[2]
$[^2A_1]$	26000	[2]
$[^2A_2]$	30000	[2]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[500](1)
[200](1)
[550](1)

Point Group: $[C_s]$ $\sigma = [1]$
Bond Distances: S–Cl = [2.00] Å S–S = [1.90] Å
Bond Angle: S–S–Cl = 105°
Product of Moments of Inertia: $I_AI_BI_C = [4.34028 \times 10^{-114}] g^3\cdot cm^6$

Enthalpy of Formation

Perona *et al.*[1] have studied the infrared emission from vibrationally excited HCl and DCl formed in the reaction of H and D atoms on S_2Cl_2. From their observation that the highest HCl vibrational level occupied was $\nu = 7$, they obtained an upper limit estimate of the first bond dissociation energy for S_2Cl_2 of $D_0^\circ(S_2Cl–Cl) \leq 53 kcal\cdot mol^{-1}$. Combining this value with $\Delta_f H°$ data for gaseous Cl and S_2Cl_2,[2] we calculate that $\Delta_f H°(S_2Cl, g) = \leq 20.8 kcal\cdot mol^{-1}$. A recent independent analysis of these thermochemical data for S_2Cl_2/S_2Cl was made by Takacs[3] who reported $\Delta_f H°(S_2Cl, g, 0 K) = 17 \pm 2 kcal\cdot mol^{-1}$ based on slightly different auxiliary $\Delta_f H$ datum for S_2Cl_2 ($-7 7 kcal\cdot mol^{-1}$) than what ($-3.6 kcal\cdot mol^{-1}$) was used here. In the same paper, Perona *et al.*[1] also used the infrared chemiluminescence technique to measure bond dissociation energies for Cl_2 and the first S–Cl bond in SCl_2. While this technique leads to results in accord with the known thermochemistry of Cl_2/Cl,[2] it appears to give biased results in the case of SCl_2 (see SCl(g) table for discussion). Factors which can adversely influence the D_0° values determined from infrared chemiluminescence studies have been discussed by Perona *et al.*[1]

In a recent review of the thermochemistry of sulfur–containing species, Benson[4] has shown that in R_2S_2 compounds with R equal to H, alkyl, or aryl the first R–S bond dissociation energy exceeds the second one by $9.5 \pm 1.0 kcal\cdot mol^{-1}$. Assuming this same trend holds for R=Cl, we obtain $\Delta_r H° = 9.5 kcal\cdot mol^{-1}$ for $S_2Cl_2(g) + S_2(g) = 2 S_2Cl(g)$ which leads to $\Delta_f H°(S_2Cl, g, 0 K) = 18.3 \pm 1.0 kcal\cdot mol^{-1}$ by combining the value of $\Delta_r H°$ with JANAF $\Delta_f H°$ values for S_2Cl_2 and S_2.[2]

We choose to adopt a $\Delta_f H°$ value of $19.0 \pm 2.0 kcal\cdot mol^{-1}$ which is a weighted average of the two results derived above. The values of $\Delta_f H°$ at 298.15 K and of $\Delta_a H°(0 K)$ are $18.8 \pm 2.0 kcal\cdot mol^{-1}$ and $140.9 \pm 2.0 kcal\cdot mol^{-1}$, respectively. Using JANAF data,[2] we find bond dissociation energies in the S_2Cl radical are $D_0^\circ(S_2–Cl) = 40.2 kcal\cdot mol^{-1}$ and $D_0^\circ(S–SCl) = 83.9 kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

S_2Cl has 19 valence electrons, and according to the Walsh correlation diagram,[5] the radical should have a bent structure with a bond angle somewhate greater than that (102°)[2] found for the 20 valence electron molecule SCl_2. We adopt a Cl–S–S angle of 105° which is intermediate between the measured angles for SCl_2 and S_2Cl_2.[2] CNDO and INDO calculations[6] on S_2Cl as a function of bond angle show an energy minimum at 100°, supporting our adopted value. The S–Cl and S–S bond distances are estimated from experimentally measured structural data[2] for S_2Cl_2, SCl_2, and S_2. The principal moments of inertia are: $I_A = 5.0613 \times 10^{-39}$, $I_B = 26.8624 \times 10^{-39}$, and $I_C = 31.9237 \times 10^{-39} g\cdot cm^2$.

Wight and Andrews[7] have observed an absorption band system at 21930–26178 cm^{-1} during mercury are photolysis of Ar/S_2Cl_2matrices and alkali metal S_2Cl_2 matrix reactions. They assigned this band system to S_2Cl and suggested that the S–Cl stretching frequency was ≥490 cm^{-1} based on the observed vibrational spacing in the absorption spectrum. We estimate $\nu_1 = 500 cm^{-1}$based on the S–Cl stretching frequencies for S_2Cl_2 (466 and 461 cm^{-1}),[2] SCl_2(528 cm^{-1}),[2] and SCl_2+ (530 ± 30 cm^{-1}).[8] The ν_2 bending and ν_3 S–S stretching frequencies are estimated by similar comparisons to that for ν_1. The value of is ν_3 chosen to lie between those[2,9] observed for S_2Cl_2 (546 cm^{-1}) and S_3(590 cm^{-1}).

An absorption band system has been observed at 22000–26000 cm^{-1} when gaseous S_2Cl_2 is flash photolyzed,[10,11] when Ar/S_2Cl_2 matrices are mercury arc photolyzed during deposition,[7] and when S_2Cl_2 is reacted with alkali metal atoms in argon matrices.[7] Wight and Andrews,[7] along with McGrath,[10] have assigned this spectrum to the S_2Cl radical while Donovan *et al.*[11] believe that portions of the spectrum are due

Continued on page 937

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	C_p°	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.474	79.499	79.499	INFINITE
100	38.122	243.386	333.376	−8.999	80.139	67.755	−35.391
200	45.979	272.300	296.209	−4.782	79.553	55.544	−14.507
250	48.894	282.889	292.515	−2.406	79.080	49.595	−10.362
298.15	50.954	291.686	291.686	0.	78.559	43.963	−7.702
300	51.021	292.002	291.687	0.094	78.538	43.748	−7.617
350	52.557	299.988	292.315	2.686	77.937	37.997	−5.671
400	53.677	307.083	293.726	5.343	72.857	32.511	−4.245
450	54.510	313.456	295.570	8.049	70.824	27.571	−3.200
500	55.140	319.233	297.652	10.791	68.663	22.886	−2.391
600	56.008	329.370	302.117	16.352	65.238	14.065	−1.225
700	56.558	338.048	306.645	21.982	62.339	5.771	−0.431
800	56.927	345.626	311.054	27.657	59.742	−2.131	0.139
900	57.186	352.346	315.276	33.364	−48.925	−7.557	0.439
1000	57.374	358.382	319.290	39.092	−48.777	−2.968	0.155
1100	57.514	363.857	323.096	44.837	−48.650	1.606	−0.076
1200	57.622	368.866	326.705	50.594	−48.548	6.170	−0.269
1300	57.706	373.482	330.128	56.360	−48.473	10.727	−0.431
1400	57.773	377.761	333.379	62.135	−48.426	15.279	−0.570
1500	57.828	381.749	336.472	67.915	−48.408	19.829	−0.690
1600	57.872	385.482	339.420	73.700	−48.419	24.378	−0.796
1700	57.910	388.992	342.234	79.489	−48.460	28.929	−0.889
1800	57.941	392.303	344.924	85.281	−48.529	33.483	−0.972
1900	57.967	395.436	347.501	91.077	−48.626	38.042	−1.046
2000	57.990	398.410	349.973	96.875	−48.749	42.606	−1.113
2100	58.010	401.240	352.347	102.675	−48.898	47.177	−1.173
2200	58.027	403.939	354.631	108.477	−49.072	51.756	−1.229
2300	58.042	406.519	356.832	114.280	−49.270	56.344	−1.280
2400	58.056	408.989	358.954	120.085	−49.490	60.940	−1.326
2500	58.069	411.360	361.003	125.891	−49.734	65.547	−1.370
2600	58.081	413.637	362.984	131.699	−49.999	70.163	−1.410
2700	58.092	415.830	364.901	137.507	−50.284	74.790	−1.447
2800	58.104	417.942	366.758	143.317	−50.590	79.428	−1.482
2900	58.116	419.982	368.558	149.128	−50.915	84.077	−1.514
3000	58.129	421.952	370.305	154.941	−51.259	88.738	−1.545
3100	58.143	423.858	372.002	160.754	−51.621	93.410	−1.574
3200	58.158	425.704	373.652	166.569	−51.999	98.095	−1.601
3300	58.176	427.494	375.256	172.386	−52.393	102.791	−1.627
3400	58.195	429.231	376.818	178.204	−52.802	107.500	−1.652
3500	58.217	430.919	378.340	184.025	−53.225	112.221	−1.675
3600	58.242	432.559	379.823	189.848	−53.661	116.954	−1.697
3700	58.270	434.155	381.270	195.673	−54.107	121.699	−1.718
3800	58.301	435.709	382.683	201.502	−54.564	126.457	−1.738
3900	58.337	437.224	384.062	207.334	−55.029	131.227	−1.758
4000	58.376	438.702	385.409	213.169	−55.501	136.008	−1.776
4100	58.419	440.144	386.727	219.009	−55.980	140.802	−1.794
4200	58.467	441.552	388.016	224.854	−56.463	145.607	−1.811
4300	58.520	442.928	389.277	230.703	−56.949	150.424	−1.827
4400	58.577	444.274	390.511	236.558	−57.437	155.253	−1.843
4500	58.639	445.592	391.721	242.418	−57.925	160.092	−1.858
4600	58.706	446.881	392.906	248.286	−58.413	164.942	−1.873
4700	58.778	448.144	394.068	254.160	−58.899	169.803	−1.887
4800	58.854	449.383	395.207	260.041	−59.383	174.674	−1.901
4900	58.936	450.597	396.325	265.931	−59.862	179.555	−1.914
5000	59.022	451.789	397.423	271.829	−60.336	184.446	−1.927
5100	59.114	452.958	398.500	277.735	−60.804	189.346	−1.939
5200	59.209	454.107	399.559	283.652	−61.265	194.256	−1.951
5300	59.310	455.236	400.599	289.577	−61.718	199.174	−1.963
5400	59.415	456.345	401.621	295.514	−62.163	204.101	−1.974
5500	59.524	457.437	402.626	301.460	−62.598	209.036	−1.985
5600	59.637	458.510	403.614	307.418	−63.023	213.978	−1.996
5700	59.754	459.567	404.586	313.388	−63.438	218.928	−2.006
5800	59.874	460.607	405.543	319.369	−63.841	223.886	−2.016
5900	59.998	461.632	406.485	325.363	−64.233	228.850	−2.026
6000	60.126	462.641	407.413	331.369	−64.612	233.820	−2.036

PREVIOUS: June 1978 (1 atm) CURRENT: June 1978 (1 bar)

Chlorosilylidyne (SiCl) IDEAL GAS $M_r = 63.5385$ Clorosilylidyne (SiCl) $Cl_1Si_1(g)$

$\Delta_fH°(0\ K) = 196.25 \pm 6.7\ kJ{\cdot}mol^{-1}$
$S°(298.15\ K) = 237.833 \pm 0.21\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = 198.32 \pm 6.7\ kJ{\cdot}mol^{-1}$

Electronic States and Molecular Constants ($\sigma = 1$)

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	w_ex_e, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å	Source
X $^2\Pi_{1/2}$	0	2	533.5	2.15	0.2539	0.00154	2.063	3
$^2\Pi_{3/2}$	207.0	2	533.5	2.15	0.2539	0.00154	2.063	3
A $^2\Sigma^+$	23010	2	295.2	0.72	0.1970	0.0007	2.352	3
B $^2\Sigma^+$	34107	2	703.8	3.9	0.2769	0.0020	1.984	6,7
B'$^2\Delta$	35618	4	509.1	5.6	0.2598	0.00240	2.035	10
C $^2\Pi$	41165	4	671.5	2.2	0.2865	0.0009	1.942	12,13
D $^2\Pi$	44943	4	656.8	3.8	[0.2539]	[0.00154]	[2.063]	15

Enthalpy of Formation

The adopted value is based upon a 3rd law analysis of effusion mass spectrometric data by Farber[1] who obtained $\Delta_rH°(298.15\ K) = 27.1\ kcal{\cdot}mol^{-1}$ for $Si(g) + SiCl_2(g) = 2\ SiCl(g)$. With auxiliary JANAF data[2] this yields $\Delta_fH°(298.15\ K) = 47.4 \pm 1.6\ kcal{\cdot}mol^{-1}$. The error estimate is somewhat higher than that given by Farber and should more accurately reflect the uncertainties in relative cross–section values. A value of $88.3 \pm 3.0\ kcal{\cdot}mol^{-1}$ is obtained for $D_0°$ using auxiliary JANAF data.[2] A linear Birge– Sponer extrapolation of the ground state vibrational data[3] yields $D_0° = 93.8\ kcal{\cdot}mol^{-1}$ in good agreement with the adopted value. Similar extrapolations for other electronic states yield higher values; Gaydon[4] obtained $104 \pm 12\ kcal{\cdot}mol^{-1}$ from the B' $^2\Delta$ state. The value of $D_0°$ may be compared to the average (per bond) enthalpies of atomization of 94.7, 96, and 101.9 $kcal{\cdot}mol^{-1}$ for $SiCl_4$, $SiCl_3$, and $SiCl_2$, respectively.[2]

Heat Capacity and Entropy

Vibrational and rotational constants and splitting for the ground state are taken from the analysis of the A–X system by Singhal and Verma.[3] These are in excellent agreement with those of several other investigators.[5–10,12,13,15] Spectroscopic information for the A $^2\Sigma$ state is also taken from Singhal and Verma[3] and yields different molecular constants than an earlier study by Sanii and Verma.[5] Molecular constants for the B$^2\Sigma$ state are taken from Ovcharenko and Kuzyakov[6] and Rai *et al.*[7] and show good agreement with those of Ovcharenko *et al.*[8] and Mishra and Khanna.[9] The molecular constants for the B' $^2\Delta$ state are taken from Verma[10] and are in good agreement with the less precise measurements by Ovcharenko *et al.*[11] The vibrational properties of the C $^2\pi$ state were taken from Jevons[12] while the rotational constants are from Pandey *et al.*[13] The latter differ slightly from those of Ovcharenko and Kuzyakov.[14] The spin splittings of 2.727 cm^{-1} [10] and 10–12 cm^{-1} [13,14] for the B' and C states, respectively, have been ignored in our calculations. The vibrational constants for the D $^2\Pi$ state were taken from Oldershaw and Robinson;[15] since no rotational study is available, we have used the ground state B_e and α_e as first approximations in our calculations. This introduces a nearly negligible error in the thermal functions. Oldershaw and Robinson[15] has observed two additional sets of high energy levels but these are not included due to uncertainties in their states. It should be recognized that the $^4\Sigma^-$ state observed for SiF and SiI[2] has not been discovered for SiCl, by analogy with SiF and SiI it is expected to lie at 26,000 ± 3,000 cm^{-1}. The stated uncertainty in the entropy should account for this level as well as the splittings mentioned above. The ground state is treated as two distinct levels due to the splitting of this state as expressed by the spin coupling constant ($A = 207.2\ cm^{-1}$). This leads to slightly biased results at low temperatures (below 500 K); the stated uncertainty in $S°(298.15\ K)$ should account for this also. All molecular constant data has been corrected to reflect the natural isotopic abundances of Si and Cl.

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[2] JANAF Thermochemical Tables: Si(g), 3–31–67; $SiCl_2$(g), 12–31–70; Cl(g), 6–30–72; $SiCl_3$(g), 12–31–69; $SiCl_4$(g), 12–31–70; SiF(g),SiI(g), 12–31–76.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.885	196.245	196.245	INFINITE
100	32.744	200.342	268.867	−6.853	197.555	187.355	−97.864
200	34.712	223.757	241.075	−3.463	198.247	176.825	−46.182
298.15	35.780	237.833	237.833	0.	198.322	166.278	−29.131
300	35.795	238.054	237.833	0.066	198.319	166.080	−28.917
400	36.442	248.448	239.246	3.681	198.078	155.364	−20.288
500	36.834	256.626	241.933	7.346	197.679	144.729	−15.120
600	37.088	263.365	244.960	11.043	197.184	134.184	−11.682
700	37.266	269.097	248.009	14.761	196.618	123.728	−9.233
800	37.399	274.082	250.963	18.495	195.993	113.357	−7.401
900	37.504	278.493	253.782	22.240	195.316	103.067	−5.982
1000	37.591	282.449	256.454	25.995	194.592	92.856	−4.850
1100	37.667	286.035	258.983	29.758	193.824	82.719	−3.928
1200	37 734	289.316	261.376	33.528	193.014	72.654	−3.163
1300	37.795	292.339	263.643	37.304	192.164	62.658	−2.518
1400	37.851	295.142	265.794	41.087	191.273	52.729	−1.967
1500	37.905	297.755	267.838	44.875	190.341	42.865	−1.493
1600	37.956	300.203	269.786	48.668	189.369	33.065	−1.079
1700	38.004	302.505	271.643	52.466	138.177	23.774	−0.730
1800	38.052	304.679	273.419	56.269	137.352	17.068	−0.495
1900	38.098	306.738	275.119	60.076	136.526	10.408	−0.286
2000	38.143	308.693	276.749	63.888	135.700	3.792	−0 099
2100	38.187	310.555	278.315	67.705	134.872	−2.783	0.069
2200	38.231	312.332	279.821	71.526	134.043	−9.319	0.221
2300	38.275	314.033	281.272	75.351	133.212	−15.817	0.359
2400	38.318	315.663	282.671	79.180	132.378	−22.278	0.485
2500	38.362	317.228	284.022	83.014	131.540	−28.705	0.600
2600	38.405	318.733	285.328	86.853	130.697	−35.098	0.705
2700	38.449	320.183	286.593	90.695	129.851	−41.459	0.802
2800	38.493	321.583	287.817	94.543	128.999	−47.788	0.892
2900	38.539	322.934	289.005	98.394	128.141	−54.087	0.974
3000	38.585	324.241	290.158	102.250	127.279	−60.356	1.051
3100	38.632	325.507	291.278	106.111	126.412	−66.596	1.122
3200	38.681	326.735	292.367	109.977	125.540	−72.808	1.188
3300	38.732	327.926	293.427	113.847	124 664	−78.993	1.250
3400	38.784	329 083	294.458	117.723	123.785	−85.151	1.308
3500	38.839	330.208	295.464	121.604	122.904	−91.284	1.362
3600	38.896	331.303	296.444	125.491	−262.130	−86.930	1.261
3700	38.955	332.369	297.401	129.384	−262.599	−82.057	1.158
3800	39.017	333.409	298.335	133.282	−263.067	−77.171	1.061
3900	39.082	334.423	299.247	137.187	−263.533	−72.273	0.968
4000	39.151	335.414	300.139	141.099	−263.996	−67.363	0.880
4100	39.222	336.381	301.011	145.017	−264.453	−62.442	0.796
4200	39.296	337.327	301.865	148.943	−264.903	−57.509	0.715
4300	39.374	338.253	302.700	152.877	−265.344	−52.566	0.639
4400	39.456	339.159	303.518	156.818	−265.773	−47.613	0.565
4500	39.541	340.047	304.320	160.768	−266.190	−42.650	0.495
4600	39.630	340.917	305.106	164.727	−266.592	−37.678	0.428
4700	39.722	341.770	305.877	168.694	−266.978	−32.697	0.363
4800	39.819	342.607	306.634	172.671	−267.346	−27.709	0.302
4900	39.919	343.429	307.377	176.658	−267.695	−22.712	0.242
5000	40.023	344.237	308.106	180.655	−268.024	−17.710	0.185
5100	40.131	345.030	308.822	184.663	−268.331	−12.700	0.130
5200	40.242	345.811	309.526	188.681	−268.616	−7.685	0.077
5300	40.358	346.578	310.218	192.711	−268.877	−2.665	0.026
5400	40.477	347.334	310.898	196.753	−269.114	2.361	−0.023
5500	40.600	348.078	311.567	200.807	−269.325	7.390	−0.070
5600	40.726	348.810	312.226	204.873	−269.511	12.423	−0.116
5700	40.856	349.532	312.874	208.952	−269.670	17.459	−0.160
5800	40.990	350.244	313.512	213.045	−269.804	22.497	−0.203
5900	41.128	350.946	314.141	217.150	−269.910	27.538	−0.244
6000	41.268	351.638	314.760	221.270	−269.988	32.580	−0.284

PREVIOUS· December 1976 (1 atm) CURRENT· December 1976 (1 bar)

Strontium Chloride (SrCl) IDEAL GAS $M_r = 123.073$ Strontium Chloride (SrCl) $Cl_1Sr_1(g)$

$\Delta_fH°(0\ K) = -122.49 \pm 8.4\ kJ{\cdot}mol^{-1}$

(298.15 K) = 252.284 ± 0.42 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = -123.85 \pm 8.4\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$X\ ^2\Sigma^+$	0.0	2	$D\ ^2\Sigma$	28822.9	2
$A\ ^2$	14818.3	2	$E\ ^2\Sigma$	32201.8	2
	15112.8	2	$F\ ^2\Pi$	32909.4	2
$B\ ^2\Sigma$	15779.5	2		32978.6	2
$C\ ^2\Pi$	25244.7	2	$G^2\Delta$	34086.7	2
	25399.9	2		34112.8	2
			$H\ ^2\Sigma$	34256.7	2

$\omega_e = 300.94\ cm^{-1}$ $\omega_ex_e = 0.97\ cm^{-1}$ $\sigma = 1$

$B_e = [0.10271 \pm 0.003]\ cm^{-1}$ $\alpha_e = [0.00043]\ cm^{-1}$ $r_e = [2.55 \pm 0.04]$ Å

Enthalpy of Formation

$\Delta_fH°$ is a weighted average of results from three gas–phase equilibrium reactions studied mass spectrometrically by Hildenbrand[1] and Potter *et al.*[2] Analyses of these data are summarized below. The overall range of values is less than 4 kcal·mol^{-1}, suggesting the approximate uncertainty in $\Delta_fH°$. From the adopted $\Delta_fH°$ we calculate $D_0° = 98.2 \pm 2$ kcal·mol^{-1}. Independent methods give 98 ± 4,[3] ≥99,[4] 95.6 ± 1.6,[5] 97 ± 6[6] and 88.1 kcal·mol^{-1}.[7]

Electron–impact data[3] gave $D_0°$(ClSr–Cl) = 112.8 ± 3.3 and we use $\Delta_{at}H°(SrCl_2) = 210.8 \pm 3$ kcal·mol^{-1} to derive $D_0° = 98 \pm 4$ kcal·mol^{-1}. Chemiluminescence from crossed beams of Sr atoms with Cl_2 gave an approximate lower limit of 99 kcal·mol^{-1}.[4] Flame studies gave $D_0° = 95.6 \pm 1.6$ kcal·mol^{-1} [5] and $D_0°$(ClSr–Cl) = 114 ± 5 kcal·mol^{-1};[6] we derive $D_0° = 97 \pm 6$ kcal·mol^{-1} from the latter value using $\Delta_{at}H°(SrCl_2) = 210.8 \pm 3$ kcal·mol^{-1}. Ryabova *et al.*[6,5] considered the flames to involve $SrCl_2$, SrOHCl and SrOH as well as SrCl. Schofield and Sugden[8] inferred that the flames involved mainly $SrCl_2$ rather than SrCl as assumed in earlier flame studies. Gaydon[9] discounted a value of $D_0°$ derived from limited spectroscopic data on the ground state. Novikov and Gurvich[7] published additional emission spectra and derived $D_0° = 88.1$ kcal·mol^{-1} by parabolic extrapolation. This value should be considered as approximate in light of Gaydon's precautionary notes, especially since the observed levels extend only to about 0.3 of the dissociation limit. Hildenbrand[1] found that ionicity corrections bring the Birge–Sponer extrapolation into reasonable agreement with $D_0°$.

Source	Reaction	T/K	$\Delta_rH°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	δS cal·K^{-1}·mol^{-1}	$\Delta_fH°$(298.15 K) kcal·mol^{-1}	$D_0°$
[1] Hildenbrand (1970)	A	1305–1416	16.9 ± 4.2	14.93 ± 0.6	1.5 ± 3.1	−29.49±1.0	98.3
[2] Potter (1970)	A	1235–1540	13.6 ± 1.1	13.97 ± 0.5	−0.3 ± 0.8	−29.97 ± 1.0	98.8
[1] Hildenbrand (1970)	B	1305–1416	19.7 ± 4.5	22.65 ± 0.7	−2.2 ± 3.3	−28.45 ± 2.0	97.3
[2] Potter (1970)	B	1235–1540	7.0 ± 4.7	18.79 ± 2.6	−8.6 ± 3.4	−32.31 ± 3.2	101.1
[1] Hildenbrand (1970)	C	1661		2.07 ± 2	−30.72 ± 3.6	99.6	

Reactions: (A) $Sr(g) + SrCl_2(g) = 2SrCl(g)$; (B) $Sr(g) + AlCl(g) = SrCl(g) + Al(g)$; (C) $Ca(g) + SrCl(g) = CaCl(g) + Sr(g)$.

Heat Capacity and Entropy

Electronic levels and vibrational constants are based on the review of Rosen[10] as modified by the additional data of Novikov and Gurvich.[7] Vibrational constants are adjusted for natural isotopic abundances. B_e is calculated from r_e which is estimated by comparison of the bond lengths of MX_2(M=Mg, Ca, Sr, Ba and X=F, Cl) with those of MgCl, CaCl and MF(M=Mg, Ca, Sr, Ba). The value of α_e is estimated from the Morse potential function.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.799	−122.487	−122.487	INFINITE
100	31.264	215.070	283.467	−6.840	−122.483	−131.734	68.811
200	34.916	238.054	255.566	−3.503	−123.153	−140.725	36.754
250	35.747	245.942	252.879	−1.734	−123.496	−145.084	30.314
298.15	36.252	252.284	252.284	0.	−123.846	−149.204	26.140
300	36.268	252.509	252.285	0.067	−123.860	−149.362	26.006
350	36.613	258.127	252.728	1.890	−124.250	−153.582	22.921
400	36.856	263.033	253.716	3.727	−124.665	−157.744	20.599
450	37.035	267.385	254.998	5.574	−125.107	−161.852	18.787
500	37.173	271.294	256.435	7.430	−125.575	−165.910	17.333
600	37.374	278.091	259.495	11.158	−126.593	−173.884	15.138
700	37.517	283.863	262.574	14.902	−127.718	−181.678	13.557
800	37.628	288.880	265.555	18.660	−128.950	−189.303	12.360
900	37.721	293.318	268.398	22.427	−130.917	−196.696	11.416
1000	37.803	297.296	271.093	26.204	−132.043	−203.945	10.653
1100	37.877	300.903	273.641	29.988	−141.070	−210.715	10.006
1200	37.945	304.201	276.052	33.779	−143.106	−216.957	9.444
1300	38.010	307.241	278.336	37.577	−145.141	−223.028	8.961
1400	38.073	310.060	280.503	41.381	−147.174	−228.944	8.542
1500	38.135	312.689	282.562	45.191	−149.205	−234.713	8.173
1600	38.196	315.152	284.523	49.008	−151.234	−240.348	7.847
1700	38.259	317.470	286.393	52.831	−290.177	−244.676	7.518
1800	38.324	319.659	288.181	56.660	−290.342	−241.994	7.022
1900	38.394	321.733	289.893	60.496	−290.511	−239.304	6.579
2000	38.469	323.704	291.534	64.339	−290.687	−236.604	6.179
2100	38.552	325.583	293.111	68.190	−290.871	−233.895	5.818
2200	38.644	327.378	294.629	72.049	−291.070	−231.178	5.489
2300	38.746	329.098	296.090	75.919	−291.288	−228.450	5.188
2400	38.861	330.750	297.500	79.799	−291.532	−225.713	4.913
2500	38.990	332.339	298.862	83.691	−291.807	−222.965	4.659
2600	39.133	333.871	300.179	87.597	−292.122	−220.206	4.424
2700	39.291	335.350	301.455	91.518	−292.484	−217.433	4.206
2800	39.466	336.782	302.691	95.456	−292.902	−214.646	4.004
2900	39.656	338.171	303.890	99.412	−293.384	−211.843	3.816
3000	39.863	339.518	305.056	103.388	−293.939	−209.022	3.639
3100	40.087	340.829	306.189	107.385	−294.576	−206.181	3.474
3200	40.327	342.106	307.291	111.406	−295.302	−203.318	3.319
3300	40.582	343.350	308.365	115.451	−296.124	−200.431	3.173
3400	40.852	344.566	309.412	119.523	−297.051	−197.518	3.034
3500	41.137	345.754	310.433	123.622	−298.088	−194.575	2.904
3600	41.435	346.917	311.431	127.751	−299.240	−191.602	2.780
3700	41.746	348.057	312.405	131.910	−300.511	−188.594	2.662
3800	42.069	349.174	313.358	136.100	−301.905	−185.551	2.551
3900	42.403	350.271	314.291	140.324	−303.423	−182.470	2.444
4000	42.746	351.349	315.204	144.581	−305.065	−179.348	2.342
4100	43.099	352.409	316.098	148.873	−306.832	−176.183	2.245
4200	43.460	353.452	316.975	153.201	−308.717	−172.974	2.151
4300	43.827	354.479	317.836	157.565	−310.725	−169.719	2.062
4400	44.201	355.491	318.680	161.967	−312.848	−166.415	1.976
4500	44.580	356.488	319.509	166.406	−315.082	−163.063	1.893
4600	44.963	357.472	320.324	170.883	−317.355	−159.664	1.813
4700	45.349	358.443	321.124	175.398	−319.773	−156.210	1.736
4800	45.737	359.402	321.912	179.953	−322.277	−152.704	1.662
4900	46.128	360.349	322.687	184.546	−324.860	−149.144	1.590
5000	46.518	361.285	323.449	189.178	−327.508	−145.532	1.520
5100	46.909	362.210	324.200	193.850	−330.199	−141.868	1.453
5200	47.299	363.125	324.940	198.560	−332.960	−138.148	1.388
5300	47.688	364.029	325.669	203.310	−335.763	−134.375	1.324
5400	48.074	364.924	326.388	208.098	−338.600	−130.549	1.263
5500	48.458	365.810	327.096	212.924	−341.461	−126.669	1.203
5600	48.838	366.686	327.796	217.789	−344.339	−122.738	1.145
5700	49.214	367.554	328.485	222.692	−347.223	−118.755	1.088
5800	49.585	368.413	329.167	227.632	−350.107	−114.722	1.033
5900	49.952	369.264	329.839	232.609	−352.773	−110.663	0.980
6000	50.312	370.107	330.503	237.622	−355.602	−106.536	0.927

PREVIOUS December 1972 (1 atm) CURRENT· December 1972 (1 bar)

Titanium Chloride (TiCl) **IDEAL GAS** $M_r = 83.333$ **Titanium Chloride (TiCl)** **$Cl_1Ti_1(g)$**

$S°(298.15\ K) = 249.214 \pm 8.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [154.13 \pm 41.8]\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [154.39 \pm 41.8]\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
[$^4\Sigma$]	0	[4]
	[1000]	[4]
	[2000]	[4]
	[4000]	[4]
	[6000]	[4]
	[8000]	[4]
	[10000]	[4]

$\omega_e = 379.7\ cm^{-1}$ $\omega_e x_e = 3.41\ cm^{-1}$ $\sigma = 1$
$B_e = [0.146]\ cm^{-1}$ $\alpha_e = [0.0013]\ cm^{-1}$ $r_e = [2.3]$ Å

Enthalpy of Formation

The enthalpy of formation, $\Delta_fH°(298.15\ K)$, of TiCl(g) is calculated from the dissociation energy which is estimated as 105 kcal·mol^{-1}. This estimate is obtained from the relation $D(TiCl_4) < D_0°(TiCl) < D(TiCl_3)$, where D represents the average energy per bond, which is valid for the titanium fluorides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of $TiF_2(g)$ by Zmbov and Margrave.[1]

Extrapolations of the vibrational levels reported by Shenyaskaya *et al.*,[2] Rao[3] and Mace and Packer[4] yield values of the dissociation energy which are very low with respect to bond energy relations.

Heat Capacity and Entropy

The vibrational frequency, ω_e, and anharmonic vibrational term, $\omega_e x_e$, were reported by Shenyavskaya *et al.*[2] The interatomic distance is estimated from Guggenheimer's relation.[5] B_e is calculated from r_e. The ground state term and electronic levels are estimated from the ground state multiplet of Ti^+.[6] α_e is estimated from the Morse potential function.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.680	154.130	154.130	INFINITE
100	30.251	212.708	280.196	−6.749	155.045	144.050	−75.244
200	34.252	234.946	252.532	−3.517	154.840	133.093	−34.760
250	35.893	242.769	249.820	−1.763	154.622	127.681	−26.677
298.15	37.297	249.214	249.214	0.	154.390	122.513	−21.464
300	37.348	249.445	249.215	0.069	154.380	122.315	−21.297
350	38.622	255.300	249.674	1.969	154.134	116.990	−17.460
400	39.709	260.530	250.710	3.928	153.891	111.701	−14.587
450	40.614	265.261	252.068	5.937	153.654	106.441	−12.355
500	41.351	269.580	253.607	7.987	153.424	101.208	−10.573
600	42.402	277.220	256.922	12.179	152.974	90.807	−7.905
700	43.031	283.808	260.303	16.453	152.525	80.481	−6.006
800	43.387	289.579	263.610	20.776	152.073	70.220	−4.585
900	43.581	294.702	266.785	25.125	151.571	60.018	−3.483
1000	43.688	299.300	269.811	29.489	150.945	49.877	−2.605
1100	43.754	303.467	272.684	33.861	150.128	39.808	−1.890
1200	43.804	307.276	275.410	38.239	145.130	29.942	−1.303
1300	43.853	310.784	277.998	42.622	144.646	20.362	−0.818
1400	43.907	314.036	280.457	47.010	144.084	10.823	−0.404
1500	43.969	317.067	282.798	51.404	143.432	1.326	−0.046
1600	44.040	319.907	285.030	55.804	142.678	−8.124	0.265
1700	44.118	322.580	287.161	60.212	141.809	−17.523	0.538
1800	44.201	325.104	289.199	64.628	140.813	−26.867	0.780
1900	44.288	327.496	291.152	69.052	139.675	−36.152	0.994
2000	44.376	329.770	293.027	73.486	123.698	−44.920	1.173
2100	44.465	331.937	294.829	77.928	121.492	−53.297	1.326
2200	44.553	334.007	296.563	82.379	119.289	−61.568	1.462
2300	44.638	335.990	298.234	86.838	117.087	−69.740	1.584
2400	44.721	337.891	299.847	91.306	114.887	−77.816	1.694
2500	44.799	339.719	301.406	95.782	112.687	−85.800	1.793
2600	44.874	341.477	302.913	100.266	110.486	−93.696	1.882
2700	44.943	343.172	304.373	104.757	108.283	−101.507	1.964
2800	45.009	344.808	305.788	109.254	106.078	−109.237	2.038
2900	45.070	346.388	307.161	113.758	103.869	−116.887	2.105
3000	45.126	347.917	308.494	118.268	101.656	−124.462	2.167
3100	45.179	349.398	309.790	122.783	99.439	−131.963	2.224
3200	45.227	350.833	311.050	127.304	97.218	−139.392	2.275
3300	45.272	352.225	312.277	131.829	94.992	−146.751	2.323
3400	45.313	353.577	313.472	136.358	92.762	−154.044	2.367
3500	45.352	354.891	314.637	140.891	90.529	−161.270	2.407
3600	45.388	356.169	315.773	145.428	88.293	−168.433	2.444
3700	45.421	357.413	316.881	149.969	−323.044	−167.745	2.368
3800	45.453	358.625	317.964	154.512	−324.049	−163.534	2.248
3900	45.482	359.806	319.022	159.059	−325.110	−159.297	2.134
4000	45.511	360.958	320.056	163.609	−326.224	−155.031	2.024
4100	45.538	362.082	321.067	168.161	−327.388	−150.737	1.920
4200	45.564	363.180	322.057	172.716	−328.600	−146.413	1.821
4300	45.590	364.252	323.026	177.274	−329.857	−142.061	1.726
4400	45.615	365.301	323.975	181.834	−331.156	−137.679	1.634
4500	45.640	366.326	324.904	186.397	−332.493	−133.267	1.547
4600	45.664	367.329	325.816	190.962	−333.866	−128.824	1.463
4700	45.689	368.312	326.710	195.530	−335.271	−124.352	1.382
4800	45.714	369.274	327.586	200.100	−336.706	−119.849	1.304
4900	45.740	370.217	328.447	204.673	−338.167	−115.316	1.229
5000	45.766	371.141	329.292	209.248	−339.652	−110.753	1.157
5100	45.792	372.048	330.121	213.826	−341.157	−106.160	1.087
5200	45.819	372.937	330.936	218.406	−342.680	−101.538	1.020
5300	45.847	373.810	331.737	222.990	−344.218	−96.886	0.955
5400	45.876	374.667	332.524	227.576	−345.768	−92.204	0.892
5500	45.905	375.509	333.298	232.165	−347.328	−87.494	0.831
5600	45.936	376.337	334.059	236.757	−348.896	−82.756	0.772
5700	45.967	377.150	334.808	241.352	−350.468	−77.989	0.715
5800	46.000	377.950	335.545	245.951	−352.044	−73.195	0.659
5900	46.033	378.737	336.270	250.552	−353.621	−68.374	0.605
6000	46.068	379.511	336.984	255.157	−355.197	−63.526	0.553

PREVIOUS: December 1968 (1 atm) CURRENT December 1968 (1 bar)

Titanium Chloride (TiCl) **$Cl_1Ti_1(g)$**

Tungsten Chloride (WCl) IDEAL GAS $M_r = 219.303$ Tungsten Chloride (WCl) $Cl_1W_1(g)$

$S°(298.15\ K) = [261.895]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [553.74 \pm 41.8]\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [553.54 \pm 41.8]\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$[^2\Delta]$	0	[4]
	[5000]	[2]
	[15000]	[20]

$\omega_e = [455.4]\ cm^{-1}$ $\omega_ex_e = [1.46]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.11105]\ cm^{-1}$ $\alpha_e = [0.00042]\ cm^{-1}$ $r_e = [2.26]$ Å

Enthalpy of Formation

The enthalpy of formation, $\Delta_fH°(WCl, g, 298.15\ K) = 132.3\ kcal{\cdot}mol^{-1}$, is calculated from the bond dissociation energy, $D_0^\circ(W\text{–}Cl, 298.15\ K) = 100 \pm 10\ kcal{\cdot}mol^{-1}$. This estimated $\Delta_aH°(298.15\ K)$ is obtained from the average bond dissociation energy for $WCl_x(g) \rightarrow W(g) + xCl(g)$ where x = 2,4,5,6, using all JANAF values.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in $WCl_6(g)$. This distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental vibrational frequency ω_e.[1] The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D° + 0.5\ \omega_e) = 0.0032$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the Morse potential function.

The ground state configuration, low lying electronic levels and their quantum weights are assumed to be the same as those estimated for WF(g).[2]

References

[1] K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946).
[2] JANAF Thermochemical Table; WF(g), 3–31–67.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.370	553.736	553.736	INFINITE
100	29.633	226.867	291.391	−6.452	554.546	542.271	−283.253
200	32.811	248.370	265.027	−3.331	554.141	530.118	−138.453
250	34.017	255.829	262.465	−1.659	553.847	524.145	−109.514
298.15	34.843	261.895	261.895	0.	553.543	518.452	−90.831
300	34.869	262.111	261.896	0.064	553.531	518.234	−90.233
350	35.472	267.534	262.323	1.824	553.207	512.377	−76.468
400	35.908	272.300	263.278	3.609	552.877	506.567	−66.151
450	36.231	276.549	264.521	5.413	552.541	500.798	−58.131
500	36.478	280.380	265.918	7.231	552.199	495.067	−51.719
600	36.826	287.064	268.902	10.897	551.492	483.707	−42.110
700	37.066	292.760	271.913	14.593	550.750	472.467	−35.256
800	37.256	297.722	274.836	18.309	549.972	461.336	−30.122
900	37.426	302.120	277.628	22.043	549.157	450.306	−26.135
1000	37.595	306.072	280.278	25.794	548.306	439.367	−22.950
1100	37.771	309.663	282.788	29.562	547.420	428.516	−20.349
1200	37.955	312.958	285.167	33.349	546.501	417.747	−18.184
1300	38.146	316.003	287.423	37.154	545.550	407.056	−16.356
1400	38.341	318.837	289.567	40.978	544.567	396.439	−14.791
1500	38.537	321.489	291.608	44.822	543.553	385.894	−13.438
1600	38.733	323.982	293.554	48.685	542.507	375.417	−12.256
1700	38.926	326.336	295.414	52.568	541.428	365.007	−11.215
1800	39.116	328.567	297.194	56.470	540.317	354.661	−10.292
1900	39.305	330.687	298.902	60.391	539.172	344.378	−9.468
2000	39.492	332.707	300.542	64.331	537.992	334.156	−8.727
2100	39.682	334.639	302.120	68.290	536.777	323.994	−8.059
2200	39.875	336.489	303.640	72.268	535.525	313.891	−7.453
2300	40.074	338.266	305.107	76.265	534.237	303.845	−6.901
2400	40.281	339.976	306.525	80.283	532.912	293.856	−6.396
2500	40.499	341.625	307.896	84.322	531.550	283.923	−5.932
2600	40.729	343.218	309.224	88.383	530.155	274.046	−5.506
2700	40.972	344.759	310.512	92.468	528.700	264.223	−5.112
2800	41.228	346.254	311.762	96.578	527.152	254.455	−4.747
2900	41.499	347.705	312.976	100.714	525.473	244.745	−4.408
3000	41.783	349.117	314.138	104.878	523.636	235.096	−4.093
3100	42.081	350.492	315.308	109.071	521.601	225.511	−3.800
3200	42.390	351.833	316.428	113.295	519.336	215.995	−3.526
3300	42.711	353.142	317.521	117.550	516.819	206.554	−3.269
3400	43.041	354.422	318.588	121.837	514.015	197.193	−3.030
3500	43.378	355.674	319.629	126.158	510.863	187.920	−2.805
3600	43.722	356.901	320.648	130.513	507.267	178.743	−2.593
3700	44.069	358.104	321.644	134.902	468.364	169.863	−2.398
3800	44.419	359.284	322.619	139.327	467.172	161.811	−2.224
3900	44.768	360.442	323.574	143.786	466.013	153.791	−2.060
4000	45.116	361.580	324.510	148.280	464.886	145.800	−1.904
4100	45.460	362.698	325.428	152.809	463.793	137.836	−1.756
4200	45.798	363.798	326.328	157.372	462.735	129.899	−1.616
4300	46.130	364.879	327.212	161.969	461.712	121.986	−1.482
4400	46.453	365.944	328.080	166.598	460.725	114.097	−1.355
4500	46.767	366.991	328.933	171.259	459.775	106.230	−1.233
4600	47.069	368.022	329.772	175.951	458.861	98.384	−1.117
4700	47.360	369.038	330.597	180.672	457.983	90.557	−1.006
4800	47.637	370.038	331.408	185.422	457.141	82.748	−0.900
4900	47.901	371.023	332.206	190.199	456.336	74.957	−0.799
5000	48.151	371.993	332.993	195.002	455.566	67.181	−0.702
5100	48.387	372.949	333.767	199.829	454.831	59.421	−0.609
5200	48.607	373.891	334.529	204.679	454.129	51.675	−0.519
5300	48.813	374.818	335.281	209.550	453.462	43.942	−0.433
5400	49.003	375.733	336.021	214.441	452.826	36.221	−0.350
5500	49.179	376.633	336.752	219.350	452.222	28.512	−0.271
5600	49.339	377.521	337.472	224.276	451.648	20.813	−0.194
5700	49.485	378.396	338.182	229.218	451.104	13.124	−0.120
5800	49.616	379.257	338.883	234.173	450.587	5.445	−0.049
5900	49.733	380 107	339.574	239.140	450.098	−2.226	0.020
6000	49.837	380.943	340.257	244.119	449.634	−9.888	0.086

PREVIOUS June 1967 (1 atm) CURRENT: June 1967 (1 bar)

Tungsten Chloride (WCl) $Cl_1W_1(g)$

Zirconium Chloride (ZrCl) **IDEAL GAS** $M_r = 126.673$

$S°(298.15\ K) = [254.195 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 206.141 \pm 20.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 205.434 \pm 20.9\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]
[3000]	[4]
[6000]	[4]
[12000]	[4]
[18000]	[4]
[24000]	[4]
[30000]	[4]

Ground State Configuration: [$^4\Sigma$]

$\omega_e = [437]\ cm^{-1}$ $\omega_e x_e = [1.1]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.1248]\ cm^{-1}$ $\alpha_e = [0.00042]\ cm^{-1}$ $r_e = [2.3]$ Å

Heat of Formation

Potter[1] investigated mass spectrometrically the gaseous equilibria among ZrCl, $ZrCl_2$, $ZrCl_3$ and $ZrCl_4$. Ion intensities were measured 2.5 eV above the ionization threshold. Using the reported equiilibrium constants for the reaction $ZrCl_3(g) + ZrCl(g) = 2\ ZrCl_2(g)$ in the temperature range 1978–2274 K, second and third law analyses give the heats of reaction at 298 K as -10.36 and -12.83 kcal·mol^{-1}, respectively. The third law drift is 1.4 ± 2.5 cal·K^{-1}·mol^{-1}. Based on the third law $\Delta_r H°(298.15\ K)$ and $\Delta_f H°(ZrCl_2, g, 298.15\ K) = -44.5$ kcal·mol^{-1}[2] and $\Delta_f H°(ZrCl_3, g, 298.15\ K) = -125.3$ kcal·mol^{-1},[3] we obtain $\Delta_f H°(ZrCl, g, 298.15\ K) = 49.1$ kcal·mol^{-1} which is adopted in the tabulation.

Farber *et al.*[4] also studied mass spectrometrically the reaction Zr(cr) + Cl(g). The reported a second law heat of reaction $\Delta_r H°(298.15\ K) = 8.7 \pm 1.4$ kcal·mol^{-1}. Using the equilibrium constants K = I(ZrCl)/I(Cl) which we calculated from their reported ion intensities of run 3 in the temperature range 1667–1896 K, we obtain $\Delta_r H°(298.15\ K) = 20.3$ kcal·mol^{-1} by the third law method. The third law drift is 6.1 ± 2.4 cal·K^{-1}·mol^{-1}. The heat of formation is derived as $\Delta_f H°(ZrCl, g, 298.15\ K) = 49.2$ kcal·mol^{-1}.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in $ZrCl_4(g)$. The bond distance is then used with Guggenheimer's relation[5] for polar molecules to calculate the fundamental vibrational frequency ω_e. The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D° + 0.5\ \omega_e) = 0.0025$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the More potential function. The moment of inertia is $22.425 \times 10^{-39}\ g·cm^2$.

The ground state configuration is taken from the ground state multiplet of Zr^+ reported by Moore.[6] The electronic levels and the quantum weights are estimated to be the same as those of ZrF(g).

References

[1] N. D. Potter, Aeronutronic Div., Philco–Ford Corp., Newport Beach, Calif., private communication, dated (December 4, 1969).
[2] JANAF Thermochemical Tables, $ZrCl_2(g)$ and $ZrCl_3(g)$, 12–31–69.
[3] M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Monrovia, Calif., Rep. No. AFRPL–TR–67–244, Contract F04611–67–C–0010, (November,1967).
[4] K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946).
[5] C. E. Moore, "Atomic Energy Levels," Vol. II, U. S. Nat. Bur. Stand. Circ. 467, (1952).

Zirconium Chloride (ZrCl) $Cl_1Zr_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.411	206.112	206.112	INFINITE
100	29.736	219.074	283.981	−6.491	206.689	195.638	−102.191
200	33.033	240.706	257.458	−3.350	206.118	184.783	−48.260
250	34.211	248.212	254.882	−1.667	205.775	179.488	−37.502
298.15	35.004	254.309	254.309	0.	205.434	174.456	−30.564
300	35.030	254.526	254.310	0.065	205.421	174.264	−30.342
350	35.607	259.972	254.739	1.831	205.058	169.100	−25.237
400	36.032	264.755	255.698	3.623	204.685	163.989	−21.415
450	36.367	269.019	256.946	5.433	204.302	158.924	−18.447
500	36.655	272.866	258.348	7.259	203.910	153.903	−16.078
600	37.190	279.596	261.345	10.951	203.095	143.978	−12.534
700	37.744	285.370	264.374	14.698	202.239	134.192	−10.014
800	38.336	290.449	267.322	18.501	201.343	124.532	−8.131
900	38.947	294.999	270.149	22.365	200.400	114.986	−6.674
1000	39.553	299.134	272.844	26.291	199.401	105.549	−5.513
1100	40.131	302.932	275.409	30.275	198.339	96.215	−4.569
1200	40.667	306.447	277.851	34.315	193.496	87.202	−3.796
1300	41.155	309.721	280.178	38.407	192.833	78.371	−3.149
1400	41.590	312.788	282.399	42.545	192.169	69.591	−2.596
1500	41.972	315.670	284.522	46.723	191.489	60.859	−2.119
1600	42.302	318.390	286.554	50.937	190.776	52.173	−1.703
1700	42.586	320.963	288.503	55.182	190.016	43.533	−1.338
1800	42.825	323.404	290.375	59.453	189.192	34.940	−1.014
1900	43.025	325.725	292.175	63.746	188.291	26.395	−0.726
2000	43.191	327.937	293.908	68.057	187.296	17.899	−0.467
2100	43.327	330.047	295.579	72.383	186.195	9.456	−0.235
2200	43.438	332.065	297.192	76.721	163.650	1.814	−0.043
2300	43.526	333.998	298.751	81.070	161.877	−5.503	0.125
2400	43.597	335.852	300.258	85.426	160.105	−12.742	0.277
2500	43.653	337.633	301.718	89.789	158.331	−19.908	0.416
2600	43.696	339.346	303.132	94.156	156.554	−27.002	0.542
2700	43.729	340.996	304.504	98.528	154.771	−34.028	0.658
2800	43.755	342.587	305.836	102.902	152.982	−40.988	0.765
2900	43.775	344.123	307.130	107.278	151.185	−47.884	0.862
3000	43.790	345.607	308.388	111.657	149.381	−54.718	0 953
3100	43.801	347.043	309.612	116.036	147.568	−61.491	1.036
3200	43.811	348.434	310.804	120.417	145.746	−68.206	1.113
3300	43.819	349.782	311.964	124.798	143.917	−74.863	1.185
3400	43.825	351.090	313.096	129.180	142.080	−81.466	1.252
3500	43.832	352.361	314.200	133.563	140.236	−88.014	1.314
3600	43.839	353.596	315.277	137.947	138.386	−94.509	1.371
3700	43.846	354.797	316.329	142.331	136.531	−100.953	1.425
3800	43.854	355.966	317.357	146.716	134.673	−107.346	1.476
3900	43.863	357.105	318.361	151.102	132.812	−113.691	1.523
4000	43.873	358.216	319.344	155.489	130.950	−119.988	1.567
4100	43.884	359.300	320.305	159.877	129.088	−126.238	1.608
4200	43.896	360.357	321.246	164.266	127.229	−132.443	1.647
4300	43.909	361.390	322.168	168.656	125.372	−138.604	1.684
4400	43.924	362.400	323.071	173.047	123.520	−144.722	1.718
4500	43.940	363.387	323.956	177.441	121.674	−150.797	1.750
4600	43.957	364.353	324.824	181.835	119.835	−156.832	1.781
4700	43.975	365.299	325.675	186.232	118.005	−162.827	1.810
4800	43.994	366.225	326.510	190.630	−444.752	−157.165	1.710
4900	44.014	367.132	327.330	195.031	−446.213	−151.159	1.611
5000	44.035	368.021	328.135	199.433	−447.680	−145.122	1.516
5100	44.057	368.894	328.925	203.838	−449.150	−139.057	1.424
5200	44.079	369.749	329.702	208.245	−450.621	−132.962	1.336
5300	44.102	370.589	330.466	212.654	−452.090	−126.839	1.250
5400	44.126	371.414	331.217	217.065	−453.556	−120.689	1.167
5500	44.150	372.224	331.955	221.479	−455.016	−114.511	1.088
5600	44.175	373.019	332.681	225.895	−456.470	−108.307	1.010
5700	44.200	373.801	333.396	230.314	−457.915	−102.077	0.935
5800	44.226	374.570	334.099	234.735	−459.349	−95.821	0.863
5900	44.251	375.327	334.791	239.159	−460.772	−89.541	0.793
6000	44.277	376.071	335.473	243.586	−462.182	−83.238	0.725

PREVIOUS December 1969 (1 atm) CURRENT: December 1969 (1 bar)

0 to 6000 K Ideal Diatomic Gas

$D_0^\circ = 239.242 \pm 0.012$ kJ·mol^{-1} (natural abundance)
$S^\circ(298.15\ K) = 223.071 \pm 0.040$ J·K^{-1}·mol^{-1}

$\Delta_f H^\circ(0\ K) = 0$ kJ·mol^{-1}
$\Delta_f H^\circ(298.15\ K) = 0$ kJ·mol^{-1}

Spectroscopic Data for ^{35}Cl in cm$^{-1(a)}$

State	T_e	D_0°	ω_e	$\omega_e x_e^{(c)}$	B_e	$10^3 \cdot \alpha_e^{(d)}$	$10^7 \cdot D_e$	r_e, Å	Reference
$^1\Sigma_g^+$	0	19997.28	559.751	2.6943	0.24415	1.5163	1.9195	1.9879	[1](r_e),[2]
$^3\Pi_o^+$	17832.8	20879.64$^{(b)}$	246.7	2.6747	0.16254	2.022	2.365$^{(e)}$	2.4354	[1](r_e),[3]

(a) Constants for ground state applicable to v ≤ 40 only.
(b) The $^3\Pi_o^+$ state dissociates to $Cl(^2P_{3/2}) + Cl(^2P_{1/2})$.
(c) $-3.32527 \times 10^{-3}(v+1/2)^3 - 2.27337 \times 10^{-4}(v+1/2)^4$ for $^1\Sigma_g^+$; $-0.23826(v+1/2)^3 + 9.4555 \times 10^{-3}(v+1/2)^4$ for $^3\Pi_o^+$
(d) $-3.9078 \times 10^{-6}(v+1/2)^2 + 7.0811 \times 10^{-8}(v+1/2)^3$ for $^1\Sigma_g^+$; $-1.102 \times 10^{-4}(v+1/2)^2 + 9.2 \times 10^{-7}(v+1/2)^3$ for $^3\Pi_o^+$
(e) $+2.25 \times 10^{-8}(v+1/2) - 1.5 \times 10^{-9}(v+1/2)^2$

Heat of Formation

Zero by definition. Refer to the monoatomic cholorine gas table for a discussion of the dissociation energy.

Heat Capacity and Entropy

The thermal functions are calculated using a direct summation technique. Included in the calculation are the ground state plus the $^3\Pi_o^+$ excited state at $T_e = 17833$ cm^{-1}. To account, in an approximate way, for the presence of the $^3\Pi_o^-$, $^3\Pi_{1u}$, and $^3\Pi_{2u}$ excited states (all near $T_e = 17000$ cm^{-1}) the rotational states of the $^3\Pi_o^+$ state are artificially weighted byt a factor of six.

For the ground state only, the calculation is performed including the so-called quasi-bound rotational levels above the dissociation limit.[4,5] For a given vibrational quantum number, V, the summation over rotational states is carried out up to a rotational quantum number, J, given by $J = J_{lim}(1 - V/V_{max})$, where J_{lim} and V_{max} were determined by Gurvich *et al.*[3] to be 418 and 61, respectively. We adopt the $^{35}Cl_2$ ground state spectroscopic constants and dissociation energy of Douglas and Hoy[1] who gave Dunham type coefficients which fitted the spectroscopic data for $V \leq 40$. For $41 \leq V \leq 60$, we use the exact G_v, B_v, and D_v data as given by Douglas and Hoy.[1]

For the $^3\Pi_o^+$ state, we use the spectroscopic constants given in Gurvich *et al.*[3] as deduced from Clyne and Coxon.[6] The excited states contribute significantly to the heat capacity above 3000 K but the affect on the Gibbs free energy function is considerably smaller (amounting to only 0.4 J·K^{-1}·mol^{-1} at 6000 K). The rotational levels are extrapolated to high J values according to the method of Khachkuruzov[7] who proposed a simpler form of Wooley's method.[8]

The spectroscopic constants of the hypothetical natural abundance species are determined from the $^{35}Cl_2$ data using a standard reduced mass scaling routine. Our adopted value for S°(298.15 K) differs by 0.003 J·K^{-1} mol^{-1} from values recommended by CODATA[11] and Gurvich *et al.*[3] and by 0.007 J·K^{-1}·mol^{-1} from the value recommended by Wagman *et al.*[9] For this comparison, the values reported by CODATA[11] and Gurvich *et al.*[3] are increased by 0.1094 J·K^{-1}·mol^{-1} to account for a change in standard–state pressure from 1 atm to 1 bar.

Phase Data

Hultgren *et al.*[10] had recommended a triple point, 172.16 K (0.01374 atm) and a boiling point, 239.10 K (1 atm). These values should prove reasonably accurate, although they have not been evaluated by the present authors, and are furnished for the convenience of the reader. As a result of the low values, the reference state for chlorine is chosen to be the ideal diatomic gas at all temperatures. This may differ from the choice of other authors.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−9.181	0.	0.	0.
100	29.299	189.007	251.696	−6.269	0.	0.	0.
200	31.720	209.964	226.120	−3.231	0.	0.	0.
250	32.988	217.183	223.633	−1.613	0.	0.	0.
298.15	33.949	223.079	223.079	0.	0.	0.	0.
300	33.981	223.289	223.080	0.063	0.	0.	0.
350	34.731	228.586	223.496	1.782	0.	0.	0.
400	35.296	233.263	224.431	3.533	0.	0.	0.
450	35.728	237.446	225.648	5.309	0.	0.	0.
500	36.064	241.228	227.020	7.104	0.	0.	0.
600	36.546	247.849	229.956	10.736	0.	0.	0.
700	36.872	253.509	232.926	14.408	0.	0.	0.
800	37.109	258.449	235.814	18.108	0.	0.	0.
900	37.291	262.831	238.577	21.828	0.	0.	0.
1000	37.438	266.767	241.203	25.565	0.	0.	0.
1100	37.562	270.342	243.692	29.315	0.	0.	0.
1200	37.672	273.615	246.051	33.077	0.	0.	0.
1300	37.771	276.634	248.289	36.849	0.	0.	0.
1400	37.864	279.437	250.415	40.631	0.	0.	0.
1500	37.954	282.052	252.438	44.422	0.	0.	0.
1600	38.042	284.504	254.366	48.221	0.	0.	0.
1700	38.131	286.813	256.207	52.030	0.	0.	0.
1800	38.223	288.995	257.969	55.848	0.	0.	0.
1900	38.322	291.065	259.657	59.675	0.	0.	0.
2000	38.428	293.033	261.277	63.512	0.	0.	0.
2100	38.544	294.911	262.834	67.361	0.	0.	0.
2200	38.672	296.707	264.333	71.222	0.	0.	0.
2300	38.813	298.429	265.778	75.096	0.	0.	0.
2400	38.966	300.084	267.173	78.985	0.	0.	0.
2500	39.132	301.678	268.522	82.889	0.	0.	0.
2600	39.308	303.216	269.827	86.811	0.	0.	0.
2700	39.493	304.703	271.091	90.751	0.	0.	0.
2800	39.685	306.143	272.317	94.710	0.	0.	0.
2900	39.880	307.539	273.508	98.688	0.	0.	0.
3000	40.075	308.894	274.665	102.686	0.	0.	0.
3100	40.267	310.211	275.791	106.703	0.	0.	0.
3200	40.451	311.492	276.886	110.739	0.	0.	0.
3300	40.624	312.740	277.954	114.793	0.	0.	0.
3400	40.783	313.955	278.995	118.864	0.	0.	0.
3500	40.925	315.139	280.011	122.949	0.	0.	0.
3600	41.048	316.294	281.003	127.048	0.	0.	0.
3700	41.149	317.420	281.972	131.158	0.	0.	0.
3800	41.226	318.518	282.919	135.277	0.	0.	0.
3900	41.278	319.590	283.846	139.402	0.	0.	0.
4000	41.305	320.636	284.753	143.532	0.	0.	0.
4100	41.306	321.656	285.640	147.663	0.	0.	0.
4200	41.280	322.651	286.510	151.792	0.	0.	0.
4300	41.229	323.621	287.361	155.918	0.	0.	0.
4400	41.152	324.568	288.196	160.037	0.	0.	0.
4500	41.051	325.492	289.015	164.147	0.	0.	0.
4600	40.927	326.393	289.818	168.246	0.	0.	0.
4700	40.781	327.272	290.605	172.332	0.	0.	0.
4800	40.615	328.129	291.378	176.402	0.	0.	0.
4900	40.429	328.964	292.137	180.454	0.	0.	0.
5000	40.226	329.779	292.882	184.487	0.	0.	0.
5100	40.007	330.573	293.613	188.499	0.	0.	0.
5200	39.774	331.348	294.331	192.488	0.	0.	0.
5300	39.528	332.103	295.037	196.454	0.	0.	0.
5400	39.271	332.840	295.730	200.394	0.	0.	0.
5500	39.004	333.558	296.411	204.307	0.	0.	0.
5600	38.729	334.258	297.081	208.194	0.	0.	0.
5700	38.447	334.941	297.739	212.053	0.	0.	0.
5800	38.159	335.608	298.386	215.883	0.	0.	0.
5900	37.867	336.257	299.023	219.685	0.	0.	0.
6000	37.571	336.891	299.649	223.456	0.	0.	0.

PREVIOUS: September 1965 (1 atm) CURRENT: June 1982 (1 bar)

Cobalt Chloride ($CoCl_2$) **CRYSTAL** **M_r = 129.8392** **Cobalt Chloride ($CoCl_2$)** **$Cl_2Co_1(cr)$**

$S°(298.15\ K) = 109.265 \pm 0.21\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 1013 \pm 2\ K$

$\Delta_fH°(0\ K) = -314.39 \pm 1.7\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -312.54 \pm 1.7\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = [44.77 \pm 6.3]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The adopted value for $\Delta_fH°(298.15\ K)$ of $-74.7\ kcal{\cdot}mol^{-1}$ is that given in NBS Technical Note 270–4.[1] This value is based mainly on results derived from heat of solution measurements on Co(cr)[2] and $CoCl_2(cr)$[3] in aqueous HCl, $\Delta_fH°(CoCl_2,\ cr,\ 298.15\ K) = -74.9 \pm 1.0\ kcal{\cdot}mol^{-1}$, and from a 3rd law analysis of several sets of equilibrium data.[4–11] Results of earlier heat of solution measurements on Co(cr)[12,13] in aqueous HCl are in reasonable agreement ($\pm 0.4\ kcal{\cdot}mol^{-1}$) with those used in our calculations,[2] while the results of Thomsen[14] are some $2\ kcal{\cdot}mol^{-1}$ more negative. Results of a 2nd and 3rd law analysis of the equilibrium data with JANAF functions are tabulated below. Auxiliary $\Delta_fH°$ data used in the analysis are (in $kcal{\cdot}mol^{-1}$): $\Delta_fH°(HCl,\ g,\ 298.15\ K) = -22.063 \pm 0.05$ and $\Delta_fH°(FeCl_2,\ cr,\ 298.15\ K) = -81.7 \pm 0.1$.[15]

Source	Reaction*	Method	Data Points	T/K	$\Delta_rH°(298.15\ K)$, $kcal{\cdot}mol^{-1}$ 2nd law	3rd law	Drift $cal{\cdot}K^{-1}{\cdot}mol^{-1}$	$\Delta_fH°(298.15\ K)$ $kcal{\cdot}mol^{-1}$
Crut[4]	A	Static	1	718		23.4		67.5
Jellinek and Uloth[5]	A	Dynamic	3	673–873	36.5	30.46 ± 1.59	−7.8 ± 1.7	74.6 ± 1.7
Sano[6]	A	Static	7	759–831	32.8	30.66 ± 0.16	−2.8 ± 0.4	74.8 ± 0.3
Partington and Towndrow[7]	A	Static	5	673–773	32.9	30.91 ± 0.30	−2.7 ± 1.5	75.0 ± 0.4
Shchukarev *et al.*[8]	A		10	573–973	28.8	29.91 ± 0.39	1.4 ± 0.2	74.0 ± 0.5
Egan[9]	B	emf	2	673;723	−74.1	−75.09 ± 0.10	−1.5	75.1 ± 0.1
Hamby and Scott[10]	B	emf	1	973		−73.09		73.1
Sheldon and Gee[11]	C	emf	Equation	490–760	−6.4	−7.10 ± 0.22	−1.1 ± 0.02	74.6 ± 0.3

*Reactions: (A) $CoCl_2(cr) + H_2(g) = Co(cr) + 2\ HCl(g)$(B) $Co(cr) + Cl_2(g) = CoCl_2(cr)$(C) $Fe(cr) + CoCl_2(cr) = FeCl_2(cr) + Co(cr)$

Three[5–7] of the five sets of equilibrium data on the H_2 reduction of $CoCl_2(cr)$ yield $\Delta_fH°$ values which are in good agreement ($\pm 0.3\ kcal{\cdot}mol^{-1}$) with the value ($-74.9\ kcal{\cdot}mol^{-1}$) obtained by solution calorimetry.[2,3] Also, the results obtained from our analysis of the recent emf study of reaction (C) provide further confirmation for the adopted value of $\Delta_fH°$.

Heat Capacity and Entropy

$C_p°$ data below 300 K are based on the low temperature measurements of Chisholm and Stout[16] (11–300 K) and Kostryukova[17] (1.8–4 K). The $C_p°$ data of Kostryakova[17] below 3 K involve bias due to the presence of trace amounts of water in the $CoCl_2$ sample. His results[17] contain a small anomaly near 2.8 K which presumably arises from the $CoCl_2{\cdot}6\ H_2O$ anti-ferromagnetic transition at 2.3 K.[18] The effect of the hexahydrate on the $C_p°$ data above 3 K is judged to be negligible. The $C_p°$ data above 3 K are joined graphically with those of Chisholm and Stout at 11 K.[16] The latter data set contains a lambda peak at 24.71 K. $C_p°$ near the maximum is $4.1\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, and the enthalpy associated with the transition is on the order of a few calories. The existence of this anomaly has been confirmed from heat capacity measurements by Shalyt[19] (30–75 K, $T_{trs} = 24.9$ K) and Trapeznikowa *et al.*[20] (13–130 K, $T_{trs} = 24.90$ K).This anomaly is apparently associated with the cooperative ordering of the magnetic moments of the cobaltous ions.The latter two sets of $C_p°$ data are judged to be less reliable than that of Chisholm and Stout[16] and are not used in the calculation of $S°(298.15\ K)$. $S°(298.15\ K)$ is obtained from integration of the adopted $C_p°$'s and is based on $S°(3\ K) = 0.003\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ $C_p°$ data above 300 K are estimated from C_p curves for $FeCl_2$[15] and $MnCl_2$.[21] The results of the only high temperature enthalpy study[22] reported for $CoCl_2(cr)$ have been analyzed by Kelley.[21] However, a comparison of these $C_p°$'s with those for the isostructural chlorides $FeCl_2$[15] and $MnCl_2$[21] indicate that these values are probably too high by 3.5% at 400 K and 27.3% at 1000 K. Other comparisons[21,15] exist which indicate that it is not unusual for the $C_p°$ data of these Russian workers to be in error by several percent.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_fH°$ (kJ·mol⁻¹)	$\Delta_fG°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−15.801	−314.394	−314.394	INFINITE
100	48.158	36.945	173.312	−13.637	−315.663	−299.689	156.541
200	71.337	79.256	116.256	−7.400	−314.374	−284.115	74.203
298.15	78.492	109.266	109.266	0.	−312.545	−269.647	47.241
300	78.576	109.751	109.267	0.145	−312.508	−269.381	46.903
400	81.714	132.821	112.391	8.172	−310.520	−255.304	33.339
500	83.387	151.243	118.382	16.431	−308.570	−241.727	25.253
600	84.600	166.552	125.170	24.829	−306.698	−228.536	19.896
700	85.939	179.699	132.042	33.360	−304.875	−215.653	16.092
800	86.818	191.234	138.735	41.999	−303.536	−202.967	13.252
900	87.529	201.501	145.149	50.717	−301.883	−190.496	11.056
1000	88.241	210.762	151.255	59.507	−300.401	−178.201	9.308
1013.000	88.316	211.902	152.026	60.655	--- CRYSTAL <--> LIQUID ---		
1100	88.826	219.200	157.054	68.361	−299.134	−166.045	7.885
1200	89.370	226.952	162.560	77.271	−298.121	−153.993	6.703
1300	89.872	234.126	167.793	86.233	−297.514	−142.010	5.706
1400	90.374	240.804	172.772	95.245	−297.441	−130.053	4.852
1500	90.876	247.057	177.518	104.308	−296.317	−118.134	4.114

PREVIOUS.   CURRENT: June 1973

Cobalt Chloride ($CoCl_2$) LIQUID M_r = 129.8392 Cobalt Chloride ($CoCl_2$) $Cl_2Co_1(l)$

$S°(298.15\ K) = [-149.021]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$T_{fus} = 1013 \pm 2\ K$

$\Delta_fH°(298.15\ K) = [-271.514]\ kJ{\cdot}mol^{-1}$

$\Delta_{fus}H° = [44.8 \pm 6.3\ ]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°$ is calculated from that of the crystal by addition of the estimated value for $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1013\ K)-H°(298.15\ K)$, between the crystal and liquid. Independent values of $\Delta_fH°(l)$ (or $\Delta_fH°(cr)$) can be obtained from a 2nd and 3rd law analysis of two sets[1] [2] of emf data for the formation cell of molten $CoCl_2$. Results of our analysis of these data are tabulated below.

Source	Points	T/K	$\Delta_rH°(298.15\ K)$, $kcal{\cdot}mol^{-1}$ 2nd law	3rd law	Drift $cal{\cdot}K^{-1}{\cdot}mol^{-1}$	$\Delta_fH°(l)$ $kcal{\cdot}mol^{-1}$	$\Delta_fH°(cr)$ $kcal{\cdot}mol^{-1}$
Devoto and Guzzi[1]	4	1023–1173	−75.8	−65.77 ± 1.2	9.2 ± 1.8	−65.8	−75.6
Hamby and Scott[2]	2	1073–1173	−65.9	−63.67 ± 0.3	2.0	−63.7	−73.5

Even though both data sets contain few points and show significant positive drift, we note that the average $\Delta_fH°(cr)$ value ($-74.6\ kcal{\cdot}mol^{-1}$) obtained from these results is in excellent agreement with our adopted value ($-74.7\ kcal{\cdot}mol^{-1}$).

Heat Capacity and Entropy

$C_p°$ is assumed constant at $23.70\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ in the temperature range 700–2000 K and is estimated from liquid heat capacities[3] for $FeCl_2$, $MgCl_2$, $CaCl_2$ and $NiCl_2$.[4] A glass transition is assumed at 700 K below which $C_p°$ is that of the crystal. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} is that obtained by Schafer and Krehl[5] from cooling curve measurements. Other reported values for T_{fus} are 997 K[6] and 1008 K.[7] Our adopted value for T_{fus} is that selected by Brewer *et al.*,[8] while Kelley[9] chose T_{fus} = 1000 K. $\Delta_{fus}H°$ is calculated from $\Delta_{fus}H° = \Delta_{fus}S° \times T_{fus}$ with $\Delta_{fus}S° = 3.51 \pm 0.5\ cal{\cdot}K^{-1}\,g{\cdot}atom^{-1}$ $\Delta_{fus}S°$ is estimated from similar data[3] [4] for the isostructural chlorides $FeCl_2$, $MgCl_2$, $MnCl_2$, $NiCl_2$, and $CdCl_2$. Kelley[9] has analyzed freezing point depression data for several binary systems which involve $CoCl_2$. Unfortunately, the values of $\Delta_{fus}H°$ derived by Kelley[9] are very discrepant and probably of no use in defining $\Delta_{fus}H°$. Reported values fall in the range 6.71–8.75 $kcal{\cdot}mol^{-1}$, and Kelley[9] recommended $\Delta_{fus}H° = 7.39\ kcal{\cdot}mol^{-1}$. This value is 3.31 $kcal{\cdot}mol^{-1}$ less than our estimated value and is also inconsistent with $\Delta_fH°$ values derived for the crystal and liquid from equilibrium data. See the enthalpy of formation section for $CoCl_2$(cr, l). The discrepancies which arise in Kelley's analysis of the freezing point data may be associated with the ability of the divalent cobalt ion to form complex ions.

Vaporization Data

Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ ($J{\cdot}K^{-1}mol^{-1}$)	$S°$ ($J{\cdot}K^{-1}mol^{-1}$)	$-[G°-H°(T_r)]/T$ ($J{\cdot}K^{-1}mol^{-1}$)	$H°-H°(T_r)$ ($kJ{\cdot}mol^{-1}$)	$\Delta_fH°$ ($kJ{\cdot}mol^{-1}$)	$\Delta_fG°$ ($kJ{\cdot}mol^{-1}$)	log K_f
0							
100							
200							
298.15	78.492	149.021	149.021	0.	−271.514	−240.469	42.129
300	78.576	149.507	149.023	0.145	−271.477	−240.276	41.836
400	81.714	172.577	152.147	8.172	−269.489	−230.175	30.058
500	83.387	190.999	158.137	16.431	−267.539	−220.574	23.043
600	84.600	206.307	164.925	24.829	−265.667	−211.358	18.400
700	85.941	219.448	171.797	33.355	−263.849	−202.451	15.107
700.000	85.941	219.448	171.797	33.355	GLASS <--> LIQUID		
700.000	99.161	219.448	171.797	33.355	TRANSITION		
800	99.161	232.689	178.600	43.271	−261.233	−193.827	12.656
900	99.161	244.368	185.271	53.187	−258.381	−185.575	10.770
1000	99.161	254.816	191.712	63.103	−255.774	−177.628	9.278
1013.000	99.161	256.097	192.530	64.392	--- CRYSTAL <--> LIQUID ---		
1100	99.161	264.267	197.885	73.019	−253.444	−169.928	8.069
1200	99.161	272.895	203.782	82.936	−251.426	−162.428	7.070
1300	99.161	280.832	209.408	92.852	−249.865	−155.078	6.231
1400	99.161	288.181	214.775	102.768	−248.888	−147.827	5.515
1500	99.161	295.022	219.899	112.684	−246.910	−140.675	4.899
1600	99.161	301.422	224.797	122.600	−244.688	−133.664	4.364
1700	99.161	307.433	229.483	132.516	−242.375	−126.796	3.896
1800	99.161	313.101	233.972	142.432	−256.339	−119.770	3.476
1900	99.161	318.462	238.279	152.348	−254.300	−112.238	3.086
2000	99.161	323.549	242.417	162.264	−252.271	−104.814	2.737

PREVIOUS: CURRENT: June 1973

Cobalt Chloride (CoCl$_2$)

CRYSTAL-LIQUID

0 to 1013 K crystal
above 1013 K liquid

Refer to the individual tables for details.

M_r = 129.8392 **Cobalt Chloride (CoCl$_2$)** **Cl$_2$Co$_1$(cr,l)**

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = p° = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K$_f$
0	0.	0.	INFINITE	−15.801	−314.394	−314.394	INFINITE
100	48.158	36.945	173.312	−13.637	−315.663	−299.689	156.541
200	71.337	79.256	116.256	−7.400	−314.374	−284.115	74.203
298.15	78.492	109.266	109.266	0.	−312.545	−269.647	47.241
300	78.576	109.751	109.267	0.145	−312.508	−269.381	46.903
400	81.714	132.821	112.391	8.172	−310.520	−255.304	33.339
500	83.387	151.243	118.382	16.431	−308.570	−241.727	25.253
600	84.600	166.552	125.170	24.829	−306.698	−228.536	19.896
700	85.939	179.699	132.042	33.360	−304.875	−215.653	16.092
800	86.818	191.234	138.735	41.999	−303.536	−202.967	13.252
900	87.529	201.501	145.149	50.717	−301.883	−190.496	11.056
1000	88.241	210.762	151.255	59.507	−300.401	−178.201	9.308
1013.000	88.316	211.902	152.026	60.655	CRYSTAL <−−> LIQUID TRANSITION		
1013.000	99.161	256.097	152.026	105.423			
1100	99.161	264.267	160.585	114.050	−253.444	−169.928	8.069
1200	99.161	272.895	169.589	123.967	−251.426	−162.428	7.070
1300	99.161	280.832	177.845	133.883	−249.865	−155.078	6.231
1400	99.161	288.181	185.467	143.799	−248.888	−147.827	5.515
1500	99.161	295.022	192.545	153.715	−246.910	−140.675	4.899
1600	99.161	301.422	199.152	163.631	−244.688	−133.664	4.364
1700	99.161	307.433	205.347	173.547	−242.375	−126.796	3.896
1800	99.161	313.101	211.177	183.463	−256.339	−119.770	3 476
1900	99.161	318.462	216.684	193.379	−254.300	−112.239	3.086
2000	99.161	323.549	221.901	203.295	−252.271	−104.814	2.737

PREVIOUS: CURRENT: June 1973

Cobalt Chloride (CoCl$_2$) **Cl$_2$Co$_1$(cr,l)**

Cobalt Chloride (CoCl$_2$) IDEAL GAS M_r = 129.8392 Cobalt Chloride (CoCl$_2$) Cl$_2$Co$_1$(g)

$S°(298.15\ K) = [298.51 \pm 8.4]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -95.0 \pm 8\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -93.7 \pm 8\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$^4\Sigma_g^-$	0	[4]	$^4\Sigma_g^-$	[10425]	[4]
$^4\phi_g$	[210]	[8]	$^4\Delta_g$	[14197]	[8]
$^4\Pi_g$	[2804]	[8]	$^4\Pi_g$	[21270]	[8]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[325] (1)
94.5 (2)
493 (1)

Point Group: $D_{\infty h}$
Bond Distance: Co–Cl = 2.117 Å; Bond Angle: Cl–Co–Cl = 180° Rotational constant: $B_0 = 0.053048$ cm^{-1}; $\sigma = 2$

Enthalpy of Formation

$\Delta_f H°$ is calculated from $\Delta_{sub}H° = 52.3 \pm 1.7$ kcal·mol^{-1} by addition of $\Delta_f H°$(CoCl$_2$, cr, 298.15 K) = -74.7 ± 0.3 kcal·mol^{-1}.[1] The adopted value for $\Delta_{sub}H°$ is based on results of a 2nd and 3rd law analysis of extensive sublimation data reported by Hill *et al.*[2] These studies included both Knudsen–effusion and torsion–effusion measurements which were performed in platinum–10% rhodium effusion cells. Orifice diameters of the cells varied from 0.0518 cm to 0.1645 cm. The extent of dimerization (~1–2%) was also determined from mass spectrometric measurements, and the measured vapor pressures were corrected to represent equilibrium pressure of the monomer. Results of our analysis of sixty–four vapor pressure points measured in five different cells are given below. Derived $\Delta_f H$ values show no significant trends with orifice size; thus, a mean value of the five results is adopted. Also included in this table is a value for $\Delta_f H$ which was obtained from an analysis of equilibrium data[3] for CoO(cr) + Cl2(g) = CoCl$_2$(g) + 1/2 O$_2$(g). Orlov[3] has not reported sufficient information to allow a small correction to be made for dimerization; even so, his results still give a value for $\Delta_f H°$(−22.1 kcal·mol^{-1}) which agrees fairly well with that adopted.

Source	Method	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
2	Knudsen–Cell A	680–800	13		52.35 ± 0.13	0.4 ± 0.5	22.4 ± 0.4
2	Knudsen–Cell B	697–814	14[a]	51.9	52.29 ± 0.10	0.5 ± 0.4	22.4 ± 0.4
2	Knudsen–Cell C	715–810	10	52.9	52.14 ± 0.16	−0.9 ± 0.9	22.6 ± 0.5
2	Torsion–Cell A	759–834	10	56.7	52.38 ± 0.52	−5.4 ± 3.2	22.3 ± 0.8
2	Torsion–Cell B	745–824	15	55.0	52.30 ± 0.17	−3.4 ± 0.4	22.4 ± 0.5
3	Transpiration	1323–1523	Equation	16.6	34.77 ± 2.1	12.7	22.1 ± 2.2[b]

[a] Two points rejected due to failure of a statistical test. [b] $\Delta_f H°$(CoO, cr, 298.15 K) = −56.82 ± 0 10 kcal·mol^{-1}.[1]

Other vapor pressures for CoCl$_2$(cr, l) have been measured by static[4] and transpiration[5,6] methods. In all three studies the presence of a small amount of dimer in the saturated vapor was not considered. JANAF pressures based on (a) selected values of the heats of sublimation and vaporization for the monomer and dimer, (b) the mass spectrometric value of $2\Delta_{sub}H$(monomer)– $\Delta_{sub}H$(dimer) = −38.99 kcal·mol^{-1} (see Co$_2$Cl$_4$(g) table) at 298.15 K, and (c) adopted entropies for the condensed and gaseous species are compared with the observed total pressures in the table given below.

Source	Method	Process	T/K	Mole Fraction Dimer Calc. Range	P_{calc}/P_{obs} Range
4	Static	Sublimation	906–997	0.051.0.086	0.073–0.156
4	Static	Vaporization	1022–1256	0.082–0.092	0.198–0.816
5	Transpiration	Vaporization	1015–1144	0.090–0.092	0.531–0.743
6	Transpiration	Sublimation	925–1010	0.057–0.091	0.875–1.096
6	Transpiration	Vaporization	1019–1073	0.092	0.825–0.883

Our predictions agree reasonably well with the transpiration data of Schafer and Krehl,[6] while the static measurements of Maier[4] show significant deviations from our pressures, particularly at lower temperatures. We note that JANAF analysis[1] of Maier's vapor pressures for BaCl$_2$, AlCl$_3$, and FeCl$_2$ indicate the existence of temperature dependent errors in his measurements; thus, the CoCl$_2$ results are probably not reliable. The transpiration data of Kulkarni and Dadape[5] show similar discrepancies.

Heat Capacity and Entropy

Measurements of the infrared[7-9] and electronic[10-12] spectra of both matrix–isolated and gaseous CoCl$_2$ have been interpreted on the basis of a linear structure of $D_{\infty h}$ symmetry. This structure is adopted, and the Co–Cl bond length is taken to be equal to the value determined by

Continued on page 937

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.271	−95.041	−95.041	INFINITE
100	51.604	236.844	350.003	−11.316	−94.519	−98.535	51.469
200	57.705	275.056	303.902	−5.769	−93.920	−102.821	26.854
250	58.855	288 064	299.478	−2.853	−93.778	−105.064	21.952
298.15	59.623	298.500	298.500	0.	−93.722	−107.244	18.789
300	59.648	298.869	298.501	0.110	−93.720	−107.328	18.687
350	60.221	308.109	299.230	3.108	−93.704	−109.598	16.357
400	60.657	316.180	300.855	6.130	−93.738	−111.866	14.608
450	61.011	323.346	302.963	9.172	−93.821	−114.128	13.248
500	61.318	329.790	305.329	12.230	−93.947	−116.378	12.158
600	61.872	341.019	310.369	18.390	−94.314	−120.832	10.519
700	62.395	350.596	315.448	24.604	−94.808	−125.214	9.344
800	62.891	358.961	320.375	30.868	−95.843	−129.456	8.453
900	63.344	366.395	325.083	37.181	−96.596	−133.614	7.755
1000	63.737	373.090	329.555	43.535	−97.550	−137.678	7.192
1100	64.064	379.181	333.793	49.926	−98.746	−141.635	6.726
1200	64.324	384.767	337.812	56.346	−100.223	−145.471	6.332
1300	64.522	389.924	341.625	62.789	−102.135	−149.168	5.994
1400	64.666	394.711	345.247	69.249	−104.615	−152.696	5.697
1500	64.765	399.176	348.696	75.720	−106.081	−156.077	5.435
1600	64.828	403.358	351.983	82.200	−107.295	−159.369	5.203
1700	64.862	407.289	355.121	88.685	−108.414	−162.589	4.996
1800	64.875	410.997	358.124	95.172	−125.807	−165.450	4.801
1900	64.873	414.505	361.000	101.660	−127.196	−167.615	4.608
2000	64.860	417.832	363.759	108.146	−128.597	−169.706	4.432
2100	64.842	420.996	366.410	114.631	−130.011	−171 727	4.271
2200	64.821	424.012	368.960	121.115	−131.438	−173.680	4 124
2300	64.799	426.893	371.417	127.595	−132.882	−175.568	3.987
2400	64.779	429.650	373.786	134.074	−134.342	−177.392	3.861
2500	64.762	432.294	376.074	140.551	−135.820	−179.156	3.743
2600	64.748	434.834	378.285	147.027	−137.316	−180.860	3.634
2700	64.738	437.277	380.425	153.501	−138.832	−182.506	3.531
2800	64.733	439.632	382.498	159.975	−140.367	−184.095	3.434
2900	64.733	441.903	384.507	166.448	−141.923	−185.630	3.344
3000	64.738	444.098	386.457	172.921	−143.497	−187.110	3.258
3100	64.747	446.221	388.351	179.396	−145.090	−188.538	3.177
3200	64.761	448.277	390.192	185.871	−521.514	−188.141	3.071
3300	64.778	450.270	391.982	192.348	−521.715	−177.720	2.813
3400	64.800	452.204	393.725	198.827	−521.932	−167.292	2.570
3500	64.825	454.083	395.423	205.308	−522.165	−156.858	2.341
3600	64.853	455.909	397.078	211.792	−522.413	−146.418	2.124
3700	64.884	457.686	398.692	218.279	−522.674	−135.970	1.920
3800	64.917	459.417	400.268	224.769	−522.949	−125.515	1.725
3900	64.952	461.104	401.806	231.262	−523.234	−115.052	1.541
4000	64.989	462.749	403.309	237.759	−523.529	−104.582	1.366
4100	65.028	464.354	404.778	244.260	−523.832	−94.105	1.199
4200	65.068	465.922	406.216	250.765	−524.143	−83.620	1.040
4300	65.108	467.453	407.622	257.274	−524.458	−73.127	0.888
4400	65.149	468.950	408.999	263.786	−524.778	−62.628	0.743
4500	65.191	470.415	410.347	270.303	−525.100	−52.121	0.605
4600	65.232	471.848	411.669	276.825	−525.424	−41.606	0.472
4700	65.274	473.251	412.964	283.350	−525.748	−31.085	0.345
4800	65.315	474.626	414.235	289.879	−526.072	−20.557	0.224
4900	65.356	475.973	415.481	296.413	−526.394	−10.022	0.107
5000	65.396	477.294	416.704	302.950	−526.714	0.519	−0.005
5100	65.435	478.589	417.905	309.492	−527.032	11.067	−0.113
5200	65.474	479.860	419.084	316.037	−527.346	21.621	−0.217
5300	65.511	481.108	420.243	322.587	−527.658	32.181	−0.317
5400	65.548	482.333	421.381	329.140	−527.966	42.747	−0.413
5500	65.583	483.536	422.500	335.696	−528.271	53.319	−0.506
5600	65.617	484.718	423.601	342.256	−528.573	63.896	−0.596
5700	65.650	485.880	424.683	348.820	−528.873	74.478	−0.683
5800	65.681	487.022	425.748	355.386	−529.170	85.066	−0.766
5900	65.711	488.145	426.796	361.956	−529.422	95.656	−0.847
6000	65.740	489.249	427.828	368.528	−529.706	106.252	−0.925

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

Cesium Chloride ($(CsCl)_2$) IDEAL GAS $M_r = 336.71688$

$S°(298.15\ K) = [383.445 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -656.08 \pm 10.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -659.82 \pm 10.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}	υ, cm^{-1}
[140](1)	[76](1)
[67](1)	[151](1)
[141](1)	[156](1)

Ground State Quantum Weight: [1] $\sigma = [4]$
Point Group: [D_{2h}]
Bond Distance: Cs–Cl = [3.18] Å
Bond Angle: Cl–Cs–Cl = [93.2]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.62360 \times 10^{-111}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Datz[1] studied the molecular association equilibrium in cesium chloride vapors by measuring the temperature dependence of the molecular weight of gaseous CsCl. The molecular weights were determined by measurement of the absolute pressure exerted by a known weight of completely vaporized salt contained in an isothermal fused silica bulb of known volume The pressure sensing element was a fused silica manometer containing Au(l). Based on the reported results, we derive the equilibrium constants for the reaction $Cs_2Cl_2(g) = 2CsCl(g)$ in the temperature range 1224–1418 K. The enthalpy change of this reaction is evaluated by the 2nd and 3rd law method as 39.3 ± 1.1 and 42.9 ± 0.6 kcal·mol^{-1}, respectively. The drift in the 3rd law value is equivalent to an entropy error of 2.7 ± 0.8 cal·K^{-1}·mol^{-1}. Using the 3rd law $\Delta_r H°$ and $\Delta_f H°$(CsCl, g, 298.15 K) = −57.4 kcal·mol^{-1}, we obtain $\Delta_f H°$(298.15 K) = −157.7 ± 2.5 kcal·mol^{-1} (−659.817 ± 10.5 kJ·mol^{-1}) for $Cs_2Cl_2(g)$, which is adopted.

Schrier[2] determined the vapor pressures of molten cesium chloride at temperatures between 1165 and 1387 K by the boiling point or manometric method. The vapor analysis was performed using the transpiration method. An inert gas, N_2, was passed over the CsCl sample at a given temperature. The salt vapor entrained by the carrier gas was collected, weighed and analyzed. The data obtained were combined with the boiling point measurements to yield the average molecular weight of the vapor. Association into dimer was postulated. The mole fraction in the vapor and the partial pressure of CsCl(g) and $Cs_2Cl_2(g)$ were calculated. The equilibrium constants, 1209–1350 K, for dissociation of the Cs_2Cl_2 dimer were derived. Using the reported equilibrium constants, we evaluate the enthalpy change $\Delta_r H°$(298.15 K) of the reaction $Cs_2Cl_2(g) = 2CsCl(g)$ to be 34.1 ± 2.9 and 43.2 ± 0.9 kcal·mol^{-1} by the 2nd and 3rd law methods. Based on the 3rd law $\Delta_r H°$(298.15 K) value and $\Delta_f H°$(CsCl, g, 298.15 K) = −57.4 kcal·mol^{-1}, we obtain $\Delta_f H°$(298.15 K) = −158.0 kcal·mol^{-1} for $Cs_2Cl_2(g)$, which is in agreement with the adopted value.

Miller and Kusch[3] made an analysis of the velocity distribution of the CsCl molecules which escape through an ideal aperture from an isothermal enclosure. They found that there was no definite evidence that any species other than diatomic molecules were present in the beams in measurable amounts, in other words, the dimerization must be small, e.g. <1.5%. However, according to our calculation the concentration of dimer is 15–34% in the temperature range 600–900 K, and 33–20% at the temperatures 1000–1600 K.

Heat Capacity and Entropy

The molecular structure is assumed to be planar, having D_{2h} symmetry. Based on the bond distances of Cs–Cs and Cl–Cl estimated by Berkowitz,[4] the Cs–Cl bond distance and Cl–Cs–Cl bond angle are calculated. The vibrational frequencies were calculated by Berkowitz,[5] on the basis of the potential function for an ionic model. The principal moments of inertia are: $I_A = 62.8570 \times 10^{-39}$, $I_B = 210.7205 \times 10^{-39}$, and $I_C = 273.5775 \times 10^{-39}\ g \cdot cm^2$.

References

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[3] R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956).
[4] J. Berkowitz, J. Chem. Phys. 29, 1386 (1958).
[5] J. Berkowitz, J. Chem. Phys. 32, 1519 (1960).

Cesium Chloride ($(CsCl)_2$) $Cl_2Cs_2(g)$

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−20.880	−656.082	−656.082	INFINITE
100	71.695	298.145	454.495	−15.635	−658.046	−657.970	343.688
200	79.843	351.168	390.868	−7.940	−658.750	−657.609	171.750
250	80.993	369.121	384.785	−3.916	−659.184	−657.277	137.330
298.15	81.617	383.445	383.445	0.	−659.817	−656.856	115.079
300	81.635	383.950	383.446	0.151	−659.848	−656.838	114.366
350	82.029	396.566	384.442	4.243	−664.864	−655.599	97.843
400	82.287	407.537	386.658	8.352	−665.676	−654.219	85.432
450	82.465	417.240	389.527	12.471	−666.474	−652.739	75.768
500	82.593	425.935	392.741	16.597	−667.266	−651.171	68.027
600	82.760	441.010	399.567	24.866	−668.843	−647.804	56.396
700	82.862	453.776	406.423	33.147	−670.427	−644.172	48.069
800	82.928	464.845	413.049	41.437	−672.023	−640.312	41.808
900	82.973	474.615	419.357	49.732	−673.637	−636.252	36.927
1000	83.005	483.359	425.328	58.031	−809.528	−624.612	32.626
1100	83.029	491.271	430.969	66.333	−809.133	−606.139	28.783
1200	83.048	498.497	436.299	74.637	−808.749	−587.702	25.582
1300	83.062	505.145	441.343	82.942	−808.375	−569.297	22.875
1400	83.073	511.301	446.123	91.249	−808.011	−550.920	20.555
1500	83.082	517.032	450.661	99.557	−807.659	−532.569	18.546
1600	83.090	522.395	454.979	107.865	−807.323	−514.240	16.788
1700	83.096	527.432	459.094	116.175	−807.006	−495.933	15.238
1800	83.101	532.182	463.024	124.485	−806.713	−477.643	13.861
1900	83.106	536.675	466.783	132.795	−806.452	−459.368	12.629
2000	83.109	540.938	470.385	141.106	−806.230	−441.107	11.521
2100	83.113	544.993	473.842	149.417	−806.058	−422.855	10.518
2200	83.115	548.860	477.165	157.728	−805.946	−404.610	9.607
2300	83.118	552.554	480.363	166.040	−805.906	−386.369	8.775
2400	83.120	556.092	483.445	174.352	−805.949	−368.128	8.012
2500	83.122	559.485	486.419	182.664	−806.089	−349.883	7.310
2600	83.124	562.745	489.293	190.976	−806.339	−331.630	6.663
2700	83.125	565.882	492.072	199.289	−806.713	−313.365	6.062
2800	83.126	568.905	494.762	207.601	−807.223	−295.084	5.505
2900	83.128	571.822	497.369	215.914	−807.883	−276.782	4.985
3000	83.129	574.640	499.898	224.227	−808.708	−258.455	4.500
3100	83.130	577.366	502.353	232.540	−809.709	−240.097	4.046
3200	83.131	580.006	504.739	240.853	−810.901	−221.704	3.619
3300	83.131	582.564	507.059	249.166	−812.213	−203.277	3.218
3400	83.132	585.045	509.316	257.479	−813.787	−184.801	2.839
3500	83.133	587.455	511.515	265.792	−815.575	−166.276	2.482
3600	83.133	589.797	513.657	274.105	−817.588	−147.697	2.143
3700	83.134	592.075	515.745	282.419	−819.807	−129.061	1.822
3800	83.134	594.292	517.783	290.732	−822.259	−110.362	1.517
3900	83.135	596.451	519.773	299.046	−824.924	−91.597	1.227
4000	83.135	598.556	521.716	307.359	−827.868	−72.757	0.950
4100	83.136	600.609	523.616	315.673	−831.059	−53.840	0.686
4200	83.136	602.612	525.473	323.986	−834.497	−34.843	0.433
4300	83.137	604.569	527.290	332.300	−838.185	−15.760	0.191
4400	83.137	606.480	529.068	340.614	−841.534	3.344	−0.040
4500	83.137	608.348	530.809	348.927	−844.494	22.462	−0.261
4600	83.138	610.175	532.514	357.241	−848.564	41.772	−0.474
4700	83.138	611.963	534.186	365.555	−852.825	61.172	−0.680
4800	83.138	613.714	535.824	373.869	−857.269	80.666	−0.878
4900	83.138	615.428	537.432	382.183	−861.887	100.254	−1.069
5000	83.139	617.108	539.008	390.496	−866.667	119.937	−1.253
5100	83.139	618.754	540.556	398.810	−871.600	139.718	−1.431
5200	83.139	620.368	542.075	407.124	−875.608	159.442	−1.602
5300	83.139	621.952	543.568	415.438	−880.674	179.395	−1.768
5400	83.139	623.506	545.034	423.752	−885.289	199.358	−1.928
5500	83.140	625.032	546.474	432.066	−890.178	219.442	−2.084
5600	83.140	626.530	547.890	440.380	−895.424	239.664	−2.235
5700	83.140	628.001	549.283	448.694	−900.731	259.981	−2.382
5800	83.140	629.447	550.653	457.008	−906.089	280.391	−2.525
5900	83.140	630.868	552.000	465.322	−911.485	300.893	−2.664
6000	83.140	632.266	553.326	473.636	−916.906	321.487	−2.799

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

Copper Chloride ($CuCl_2$) CRYSTAL $M_r = 134.4520$ Copper Chloride ($CuCl_2$) $Cl_2Cu_1(cr)$

$S°(298.15\ K) = 108.085\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -206.65 \pm 6.3\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -205.85 \pm 6.3\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Shchukarev and Oranskaya[1] have reported equilibrium constants for the dissociation $CuCl_2(cr) \rightarrow CuCl(cr/l) + 0.5\ Cl_2(g)$, which are in general agreement with earlier reports by Ephraim[2] and Tarasenkov *et al.*[3] These data were subjected to third law analysis which revealed a significant trend of 13 ± 0.5 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$, indicating that equilibrium conditions were not reached. However an average value of $\Delta_r H°(298.15\ K) = 16.5 \pm 1.9\ kcal{\cdot}mol^{-1}$ yields a heat of formation of $CuCl_2(cr) = -49.5 \pm 2.5\ kcal{\cdot}mol^{-1}$ which is in good agreement with the adopted value taken from NBS Circlular 500.[4]

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 11–300 K by Stout and Chisholm.[5] The integration of this data from $S°(10\ K) = 0.111\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ gave $S°(298.15\ K) = 25.833\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. The heat capacity above 298.15 K was obtained by smooth extrapolation of the above data, since the heat capacities of Krestovnikov and Karetnikov[6] were not compatible with the low temperature data.

Decomposition Data

The temperature of decomposition, $T_{dcm} = 766$ K, was estimated from the table for $CuCl_2(cr)$, $CuCl(l)$ and $Cl_2(g)$ so that the pressure of Cl_2 is 1 bar.

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.983	−206.648	−206.648	INFINITE
100	46.777	41.020	167.042	−12.602	−207.848	−192.046	100.314
200	65.647	80.525	114.499	−6.795	−207.091	−176.458	46.086
298.15	71.881	108.085	108.085	0.	−205.853	−161.680	28.326
300	71.923	108.530	108.087	0.133	−205.828	−161.405	28.103
400	75.061	129.678	110.949	7.492	−204.433	−146.806	19.171
500	77.278	146.679	116.450	15.115	−202.947	−132.569	13.849
600	78.785	160.906	122.706	22.920	−201.393	−118.638	10.328
700	79.956	173.142	129.057	30.860	−199.800	−104.971	7.833
800	80.885	183.881	135.253	38.903	−198.181	−91.535	5.977
900	81.655	193.453	141.197	47.030	−196.550	−78.302	4.545
1000	82.370	202.093	146.862	55.232	−194.919	−65.251	3.408
1100	83.001	209.974	152.246	63.501	−193.306	−52.362	2.486
1200	83.607	217.222	157.363	71.831	−191.732	−39.619	1.725
1300	84.190	223.937	162.229	80.221	−190.242	−27.004	1.085
1400	84.750	230.197	166.863	88.668	−201.992	−14.093	0.526
1500	85.287	236.063	171.282	97.170	−200.566	−0.721	0.025

PREVIOUS: CURRENT: March 1966

Phosphoryl Chloride Fluoride ($POFCl_2$) IDEAL GAS $M_r = 136.877563$ Phosphoryl Chloride Fluoride ($POCl_2F$) $Cl_2F_1O_1P_1(g)$

$S°(298.15 \text{ K}) = 320.381 \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = [-758.8] \text{ kJ·mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = [-765.7] \text{ kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
207 (1)	372 (1)	620 (1)
254 (1)	386 (1)	894 (1)
330 (1)	547 (1)	1331 (1)

Ground State Multiplicity = [1] $\sigma = 1$
Point Group = C_s
Bond Distances: P–Cl = 1.99 ± 0.04 Å; P–F = 1.50 ± 0.03 Å; P–O = 1.54 ± 0.03 Å
Bond Angles: Cl–P–Cl = F–P–Cl = 103°; O–P–Cl = O–P–F = 115.35°
Product of the Moments of Inertia: $I_A I_B I_C = 4.70925 \times 10^{-113} \text{ g}^3\text{·cm}^6$

Enthalpy of Formation

The $\Delta_f H°(298.15 \text{ K})$ of $POFCL_2$ was estimated to be -183 kcal·mol^{-1} from the $\Delta_f H°(298.15 \text{ K})$ of $POCl_3$ by assuming bond energies of 120 kcal·mol^{-1} for $D_0°$(P–F) and 80 kcal·mol^{-1} for $D_0°$(P–Cl). The $D_0°$(P–F) and $D_0°$(P–Cl) values were taken from Neale *et al.*[1,2]

Essentially the same $\Delta_f H°(298.15 \text{ K})$ may be obtained by assuming a $\Delta_r H° = 0$ for the following reaction:

$$POCl_3(g) + POF_3(g) \rightarrow POCl_2F(g) + POF_2Cl(g)$$

Heat Capacity and Entropy

The molecular constants were determined by Brockway and Beach[3] and by Williams *et al.*[4] Brockway and Beach used electron diffraction. Williams *et al.*[4] measured microwave spectra. Brockway and Beach[3] assumed that the F–P–F and F–P–Cl angles were equal in POF_2Cl and $POFCl_2$. An analysis of their data by Williams *et al.*[4] indicates that the angles in POF_2Cl, $POFCl_2$, and $POCl_3$, and POF_3 should be 103° rather than the reported 106° ± 3°. The principal moments of inertia are: $I_A = 26.9230 \times 10^{-39}$, $I_B = 37.9561 \times 10^{-39}$, and $I_C = 46.0837 \times 10^{-39}$ g·cm^6.

The Raman spectra and vibrational frequencies for $POFCl_2$ were reported by Delwaulle and Francois.[5] These frequency assignments are summarized by Delwaulle and Francois.[6]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.431	−758.808	−758.808	INFINITE
100	44.533	253.224	381.368	−12.814	−761.896	−749.365	391 428
200	66.285	291.266	327.264	−7.199	−764.503	−735.924	192.204
250	73.746	306.896	321.658	−3.690	−765.184	−728.696	152.253
298.15	79.319	320.381	320.381	0.	−765.672	−721.622	126.425
300	79.508	320.873	320.383	0.147	−765.688	−721.349	125.598
350	84.039	333.482	321.368	4.240	−766.782	−713.857	106.537
400	87.659	344.949	323.610	8.536	−767.117	−706.272	92.230
450	90.586	355.449	326.573	12.994	−767.342	−698.651	81.097
500	92.977	365.121	329.950	17.585	−767.483	−691.011	72.189
600	96.579	382.412	337.288	27.074	−767.575	−675.704	58.825
700	99.094	397.499	344.835	36.865	−767.492	−660.397	49.279
800	100.901	410.856	352.269	46.870	−767.293	−645.110	42.121
900	102.232	422.821	359.455	57.030	−767.016	−629.853	36.556
1000	103.235	433.646	366.341	67.305	−766.685	−614.630	32.105
1100	104.007	443.523	372.915	77.669	−766.319	−599.442	28.465
1200	104.613	452.600	379.183	88.101	−829.501	−583.210	25.386
1300	105.095	460.993	385.157	98.587	−828.321	−562.734	22.611
1400	105.485	468.797	390.856	109.117	−827.137	−542.349	20.235
1500	105.805	476.086	396.298	119.682	−825.956	−522.048	18.179
1600	106 070	482.923	401.500	130.276	−824.780	−501.826	16.383
1700	106.292	489.360	406.481	140.895	−823.612	−481.677	14.800
1800	106.479	495.441	411.256	151.533	−822.455	−461.597	13.395
1900	106.639	501.202	415.840	162.189	−821.311	−441.580	12.140
2000	106.776	506.676	420.246	172.860	−820.180	−421.624	11.012
2100	106.895	511.888	424.486	183.544	−819.065	−401.723	9 992
2200	106.999	516.864	428.573	194.239	−817.965	−381.875	9.067
2300	107.089	521.622	432.516	204.943	−816.881	−362.078	8.223
2400	107.169	526.181	436.325	215.656	−815.815	−342.327	7.451
2500	107.240	530.558	440.007	226.377	−814.764	−322.620	6.741
2600	107.303	534.765	443.571	237.104	−813.731	−302.954	6.086
2700	107.359	538.816	447.024	247.837	−812.714	−283.328	5.481
2800	107.409	542.721	450.373	258.576	−811.713	−263.740	4.920
2900	107.455	546.491	453.622	269.319	−810.727	−244.187	4.398
3000	107.496	550.135	456.779	280.067	−809.755	−224.668	3.912
3100	107.533	553.660	459.848	290.818	−808.796	−205.180	3.457
3200	107.567	557.075	462.833	301.573	−807.848	−185.725	3.032
3300	107.597	560.385	465.739	312.331	−806.910	−166.298	2.632
3400	107.626	563.598	468.570	323.093	−805.979	−146.899	2.257
3500	107.651	566.718	471.330	333.856	−805.055	−127.528	1.903
3600	107.675	569.751	474.022	344.623	−804.133	−108.183	1.570
3700	107.697	572.701	476.649	355.391	−803.212	−88.864	1.255
3800	107.717	575.574	479.215	366.162	−802.289	−69.569	0.956
3900	107.736	578.372	481.722	376.935	−801.362	−50.299	0.674
4000	107.753	581.100	484.172	387.709	−800.428	−31.053	0.406
4100	107.769	583.761	486.569	398.485	−799.485	−11.830	0.151
4200	107.784	586.358	488.914	409.263	−798.529	7.369	−0.092
4300	107.798	588.894	491.210	420.042	−797.559	26.546	−0.322
4400	107.811	591.372	493.458	430.822	−796.572	45.700	−0.543
4500	107.823	593.795	495.661	441.604	−795.566	64.831	−0.753
4600	107.834	596.165	497.820	452.387	−794.540	83.939	−0.953
4700	107.845	598.484	499.938	463.171	−793.491	103.026	−1.145
4800	107.855	600.755	502.014	473.956	−792.417	122.089	−1.329
4900	107.864	602.979	504.052	484.742	−791.318	141.130	−1.504
5000	107.873	605.158	506.053	495.528	−790.192	160.148	−1.673
5100	107.881	607.295	508.017	506.316	−789.038	179.144	−1.835
5200	107.889	609.389	509.946	517.105	−787.855	198.116	−1.990
5300	107.896	611.445	511.842	527.894	−786.642	217.066	−2.139
5400	107.903	613.462	513.705	538.684	−785.400	235.992	−2.283
5500	107.910	615.442	515.537	549.475	−784.128	254.895	−2.421
5600	107.916	617.386	517.338	560.266	−782.825	273.775	−2.554
5700	107.922	619.296	519.110	571.058	−781.493	292.630	−2.682
5800	107.928	621.173	520.854	581.850	−780.130	311.463	−2.805
5900	107.933	623.018	522.570	592.643	−778.738	330.271	−2.924
6000	107.938	624.832	524.259	603.437	−777.318	349.056	−3.039

PREVIOUS: March 1963 (1 atm) CURRENT: March 1963 (1 bar)

Iron Chloride ($FeCl_2$) CRYSTAL $M_r = 126.753$ Iron Chloride ($FeCl_2$) $Cl_2Fe_1(cr)$

$S°(298.15 K) = 117.947 \pm 3.3 J·K^{-1}·mol^{-1}$
$T_{fus} = 950 K$

$\Delta_fH°(0 K) = -344.419 \pm 0.42 kJ·mol^{-1}$
$\Delta_fH°(298.15 K) = -341.833 \pm 0.42 kJ·mol^{-1}$
$\Delta_{fus}H° = 43.012 \pm 0.21 kJ·mol^{-1}$

Enthalpy of Formation

Koehler and Coughlin[1] determined $\Delta_rH°(298.15 K) = -4.06 \pm 0.05 kcal·mol^{-1}$ for $Fe(\alpha) + 2 HCl(12.731 H_2O) = FeCl_2(cr) + H_2(g)$ by solution calorimetry. This leads to $\Delta_fH°(FeCl_2, cr, 298.15 K) = -81.7 \pm 0.1 kcal·mol^{-1}$ which is adopted in the tabulation. The value $\Delta_fH°(298.15 K) [HCl(12.731 H_2O)] = -38.812 kcal·mol^{-1}$[2] is used in the calculation.

Li and Gregory[3] also determined calorimetrically $\Delta_rH°(298.15 K) = -19.5 \pm 0.2 kcal·mol^{-1}$ for $FeCl_2(cr) \rightarrow Fe^{++}(aq) + 2 Cl^-(aq)$ in aqueous solution at concentrations near 10^{-3} molal. Using $\Delta_fH°(Fe^{++}$, aq, ∞ 298.15 K) $= -21.3 kcal·mol^{-1}$[4] and $\Delta_fH°(Cl^-$, aq, ∞ 298.15 K) $= -39.952 kcal·mol^{-1}$,[2] we have obtained $\Delta_fH°(FeCl_2, cr, 298.15 K) = -81.7 kcal·mol^{-1}$ which is in excellent agreement with the adopted value.

Kangro and Petersen[5] determined the equilibrium constants for the reaction $FeCl_2(cr) + H_2(g) = Fe(cr) + 2 HCl(g)$ in the temperature range from 484–662 °C. By use of 2nd and 3rd law analyses, the enthalpy of reaction is evaluated as 37.81 and 38.24 $kcal·mol^{-1}$, respectively. Using the 3rd law $\Delta_rH°(298.15 K)$, we obtain $\Delta_fH°(FeCl_2, cr, 298.15 K) = -82.36 \pm 0.5 kcal·mol^{-1}$ which is in reasonable agreement with the value adopted.

Heat Capacity and Entropy

Kelley and Moore[6] measured the low temperature heat capacities in the temperature range from 53.2–295.0 K and made an extrapolation to 0 K which yielded an entropy of $5.19 \pm 0.8 cal·K^{-1}·mol^{-1}$ at 50.12 K. This value also includes the uncoupling energy of $Fe^+ + (R \ln 5 = 3.2 cal·K^{-1}·mol^{-1})$. We have adopted the measured heat capacities, but made a minor adjustment of the entropy at 53.2 K to 4.93 $cal·K^{-1}·mol^{-1}$ which is still within the limit of uncertainty, but yields the entropy at 298.15 K as 28.19 $cal·K^{-1}·mol^{-1}$. The latter was found by E. F. Westrum.[7]

Moore[8] measured high temperature enthalpy data from 670.5 to 941 K by drop calorimetry. The low temperature heat capacities and high temperature enthalpy data were smoothly joined at 298.15 K. The $C_p°$ values above 941 K were obtained by graphical extrapolation. Oetting and Gregory[9] measured high temperature heat capacities in the temperature range from 60 to 500 C in a constant heating adiabatic calorimeter. Their $C_p°$ values are in good agreement with those found by Moore.[8]

Fusion Data

T(fus) and $\Delta_{fus}H°$ were taken from Moore.[8]

Sublimation Data

$\Delta_{sub}H°(298.15 K)$ for the monomer and dimer are calculated from the adopted enthalpies of formation of the crystal and the respective gaseous species.

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−16.273	−344.419	−344.419	INFINITE
100	50.895	44.782	181.905	−13.712	−345.192	−330.163	172.460
200	70.734	88.442	124.802	−7.272	−343.558	−315.664	82.443
298.15	76.664	117.947	117.947	0.	−341.833	−302.342	52.969
300	76.735	118.421	117.948	0 142	−341.800	−302.097	52.600
400	79.668	140.921	120.996	7.970	−340.070	−289.125	37.756
500	81.638	158.919	126.840	16.039	−338 424	−276.581	28.894
600	83.107	173.937	133.473	24.278	−336.904	−264.358	23.014
700	84.375	186.845	140.197	32.654	−335.526	−252.378	18.833
800	85.508	198.187	146.751	41 149	−334.345	−240.583	15.708
900	86.504	208.317	153.039	49.751	−333.492	−228.919	13.286
950.000	86.944	213.006	156.072	54.087	--- CRYSTAL <--> LIQUID ---		
1000	87.354	217.476	159.032	58.445	−333.282	−217.320	11.352
1100	88.013	225.834	164.730	67.214	−333.906	−205.678	9.767
1200	88.554	233.516	170.147	76.043	−333.928	−194.039	8.446
1300	88.962	240.621	175.298	84.920	−332.267	−182.449	7.331
1400	89.287	247.226	180.202	93.833	−330.663	−170.986	6.380
1500	89.507	253.394	184.879	102.773	−329.125	−159.634	5.559
1600	89.684	259.177	189.343	111.733	−327.659	−148.383	4.844
1700	89.817	264.618	193.613	120.708	−327.220	−137.202	4.216
1800	89 907	269.754	197.702	129.695	−326.248	−126.053	3.658
1900	89 953	274.617	201.623	138.688	−339.460	−114.254	3.141
2000	89 956	279.231	205.389	147.684	−338.904	−102.416	2.675

PREVIOUS June 1965   CURRENT: December 1970

Iron Chloride ($FeCl_2$) LIQUID $M_r = 126.753$ Iron Chloride ($FeCl_2$) $Cl_2Fe_1(l)$

$S°(298.15\ K) = [139.876]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$T_{fus} = 950\ K$

$\Delta_f H°(298.15\ K) = [-311\ 336]\ kJ{\cdot}mol^{-1}$

$\Delta_{fus} H° = 43.012 \pm 0.21\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(FeCl_2, l, 298\ 15\ K)$ is calculated from $\Delta_f H°(cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(950\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Moore[1] derived the constant heat capacity from enthalpy data measured in the temperature range from 950 to 1100 K in a drop calorimeter. The constant $C_p°$ is assumed for all the other temperatures. The entropy is calculated a manner similar to that used for the enthalpy of formation.

Fusion Data

T_{fus} and $\Delta_{fus} H°$ were taken from Moore.[1]

Vaporization Data

The boiling point, $T_{vap} = 1297\ K$, is the calculated temperature at which the sum of the partial pressures of $FeCl_2(g)$ and $Fe_2Cl_4(g)$ over $FeCl_2(l)$ reaches one atmosphere. At T_{vap}, the mole fraction of the dimer is 0 1635. The enthalpy of vaporization is calculated to be the difference between the enthalpies of formation at 1297 K for one mole of $FeCl_2(l)$ vaporizing to the equilibrium mixture of 0.719 moles of $FeCl_2(g)$ and 0.1403 moles of $Fe_2Cl_4(g)$.

Reference

[1] G. E. Moore, J. Amer. Chem. Soc. 65, 1700 (1943).

Enthalpy Reference Temperature = T_r = 298.15 K | Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	102.173	139.876	139.876	0.	−311.336	−278.383	48.772
300	102.173	140.508	139.878	0.189	−311.256	−278.179	48.435
400	102.173	169.902	143.886	10.406	−307.137	−267.784	34.969
500	102.173	192.701	151.454	20.624	−303.343	−258.391	26.994
600	102.173	211.330	159.928	30.841	−299.844	−249.734	21.741
700	102.173	227.080	168.425	41.058	−296.624	−241.641	18.031
800	102.173	240.723	176.628	51.276	−293.721	−233.988	15.278
900	102.173	252.757	184.432	61.493	−291.253	−226.675	13.156
950.000	102.173	258.281	188.174	66.602	--- CRYSTAL <--> LIQUID ---		
1000	102.173	263.522	191.812	71.710	−289.520	−219.603	11.471
1100	102.173	273.260	198.781	81.928	−288.695	−212.637	10.097
1200	102.173	282.151	205.363	92.145	−287.330	−205.802	8.958
1300	102.173	290.329	211.589	102.362	−284.328	−199.130	8.001
1400	102.173	297.901	217.487	112.580	−281.420	−192.686	7.189
1500	102.173	304.950	223.085	122.797	−278.604	−186.447	6.493
1600	102.173	311.544	228.410	133.014	−275.881	−180.393	5.889
1700	102.173	317.738	233.484	143.232	−274.200	−174.487	5.361
1800	102.173	323.578	238.329	153.449	−271.997	−168.686	4.895
1900	102.173	329.103	242.962	163.666	−283.985	−162.302	4.462
2000	102.173	334.343	247.402	173.884	−282.207	−155.944	4.073

PREVIOUS: June 1965 CURRENT: December 1970

Iron Chloride ($FeCl_2$) CRYSTAL-LIQUID

0 to 950 K crystal
above 950 K liquid

Refer to the individual tables for details.

M_r = 126.753 Iron Chloride ($FeCl_2$) $Cl_2Fe_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.273	−344.419	−344.419	INFINITE
100	50.895	44.782	181.905	−13.712	−345.192	−330.163	172.460
200	70.734	88.442	124.802	−7.272	−343.558	−315.664	82.443
298.15	76.664	117.947	117.947	0.	−341.833	−302.342	52.969
300	76.735	118.421	117.948	0.142	−341.800	−302.097	52.600
400	79.668	140.921	120.996	7.970	−340.070	−289.125	37.756
500	81.638	158.919	126.840	16.039	−338.424	−276.581	28.894
600	83.107	173.937	133.473	24.278	−336.904	−264.358	23.014
700	84.375	186.845	140.197	32.654	−335.526	−252.378	18.833
800	85.508	198.187	146.751	41.149	−334.345	−240.583	15.708
900	86.504	208.317	153.039	49.751	−333.492	−228.919	13.286
950.000	86.944	213.006	156.072	54.087	CRYSTAL <−−> LIQUID TRANSITION		
950.000	102.173	258.281	156.072	97.099			
1000	102.173	263.522	161.315	102.207	−289.520	−219.603	11.471
1100	102.173	273.260	171.056	112.425	−288.695	−212.637	10.097
1200	102.173	282.151	179.949	122.642	−287.330	−205.802	8.958
1300	102.173	290.329	188.129	132.859	−284.328	−199.130	8.001
1400	102.173	297.901	195.703	143.077	−281.420	−192.686	7.189
1500	102.173	304.950	202.754	153.294	−278.604	−186.447	6.493
1600	102.173	311.544	209.350	163.511	−275.881	−180.393	5.889
1700	102.173	317.738	215.545	173.729	−274.200	−174.487	5.361
1800	102.173	323.578	221.386	183.946	−271.997	−168.686	4.895
1900	102.173	329.103	226.911	194.163	−283.985	−162.302	4.462
2000	102.173	334.343	232.153	204.381	−282.207	−155.944	4.073

PREVIOUS: CURRENT: December 1970

Iron Chloride ($FeCl_2$) $Cl_2Fe_1(cr,l)$

Iron Chloride ($FeCl_2$) IDEAL GAS $M_r = 126.753$ Iron Chloride ($FeCl_2$) $Cl_2Fe_1(g)$

$S°(298.15\ K) = 299.28 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -141.59 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -141.00 \pm 2.1\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^5\Delta$	0	10
$^5\Pi$	4600	10
$^5\Sigma$	7140	5

Vibrational Frequencies and Degeneracies
ν, cm^{-1}

[327](1)
[327](1)
88 (2)
492 (1)

Point Group: $[D_{\infty h}]$ $\sigma = 2$
Bond Distance: Fe–Cl = [2.17] Å
Bond Angle: Cl–Fe–Cl = [180]°
Rotational Constant: B_0 = [0.050489] cm^{-1}

Enthalpy of Formation

Using the Gibbs energy functions of monomeric and dimeric $FeCl_2(g)$ with the adopted enthalpy of dimerization at 298.15 K, $\Delta_{dim}H° = -35.7\ kcal \cdot mol^{-1}$,[1] we have derived partial pressure of monomeric $FeCl_2$ from the reported pressure data.[2-7] Schafer and Krehl[4] determined K_p for the equilibrium reaction C assuming the dimer concentration was insignificant at the equilibrium conditions.

Source	Method	Reaction	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 3rd law	2nd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
2	Static	A	1012–1179	29	40.61 ± 0.11	41.3	−0.6 ± 0.2	−33.80
3	Static	A	972–1268	22	40.70 ± 0.40	39.1	1.1 ± 0.4	−33.71
4	Carrier gas	A	980–1106	6	40.71 ± 0.27	41.7	−0.9 ± 1.3	−33.70
5	Mass spectrometric	B	621–701	8^a	47.74 ± 0.11	45.7	3.1 ± 0.3	−33.96
6	Torsion effusion	B	685–760	Eqn	43.38 ± 0.11	47.0	1.9	−33.32
7	Torsion effusion	B	725–825	Eqn	48.28 ± 0.17	49.9	−2.2	−33.42
7	Mass effusion (Mo cell)	B	725–825	Eqn	48.53 ± 0.14	49.9	−1.7	−33.17
7	Mass effusion (Fe cell)	B	725–825	Eqn	48.37 ± 0.12	49.5	−1.5	−33.33
14	Torsion effusion	B	643–715	28	48.28 ± 0.08	49.1	−1.1 ± 0.3	−33.42
4	Equilibrium	C	1205–1375	9	≥10.47 ± 0.50	5.1	4.2 ± 0.1	≥−33.66

Reaction: A) $FeCl_2(l) \rightarrow FeCl_2(g)$; B) $FeCl_2(cr) \rightarrow FeCl_2(g)$; C) $Fe(cr) + 2\ HCl(g) + H_2(g)$.
^{a}1 point rejected due to failure of a statistical test.

The adopted value, $\Delta_f H°(FeCl_2, g, 298.15\ K) = -33.7\ kcal^{-1}\ mol$, is in very good agreement with those derived from the reactions A and C. The adopted value is also between the more discrepant results for reaction B derived from mass spectrometry and from effusion studies. This implies that the total pressures calculated from the monomer and dimer tables fit the observed vapor pressures over liquid much better than those over solid. For the liquid, the ratio of the calculated to the observed vapor pressure is about 1.0 ± 0.1 and for the solid, the ratio is about 1.3 ± 0.2

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicated that other transition metal dichlorides are linear.[8] The bond distance is estimated by comparison with that of $Fe_2Cl_6(g)$ reported by Zasorin *et al.*[9] The ground state ($^5\Delta$), low lying electronic levels and the quantum weights were obtained from the work of Dekock and Gruen.[10]

The asymmetric stretching frequency was observed in the infrared spectra of the vapor at 492 cm^{-1} by Leroi[11] and at 494 cm^{-1} in Ar matrices by Thompson and Carlson[12] and Frey *et al.*[13] Normal coordinate analysis yields the stretching force constant k_1 = 2.23 md/Å which leads to the stretching vibrational frequency, ν_1 = 327 cm^{-1}, by a valence force field model. The bending frequency, ν_2 = 88 cm^{-1} was observed in the matrix infrared spectra.[12]

Continued on page 938

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−14.277	−141.590	−141.590	INFINITE
100	45.723	242.588	347.586	−10.500	−141.148	−145.899	76.210
200	53.738	277.015	304.447	−5.486	−140.941	−150.761	39.375
250	56.054	289.272	300.223	−2.738	−140.949	−153.217	32.013
298.15	57.570	299.283	299.283	0.	−141.001	−155.575	27.256
300	57.618	299.639	299.284	0.107	−141.004	−155.666	27.104
350	58.695	308.607	299.990	3.016	−141.099	−158.102	23.595
400	59.456	316.497	301.570	5.971	−141.237	−160.522	20.962
450	60.010	323.534	303.626	8.958	−141.423	−162.922	18.912
500	60.425	329.879	305.940	11.970	−141.662	−165.299	17.269
600	60.999	340.950	310.879	18.043	−142.307	−169.969	14.797
700	61.392	350.384	315.865	24.163	−143.184	−174.514	13.022
800	61.713	358.603	320.705	30.319	−144.343	−178.914	11.682
900	62.022	365.890	325.328	36.506	−145.905	−183.147	10.630
1000	62.346	372.441	329.717	42.724	−148.171	−187.173	9.777
1100	62.695	378.399	333.876	48.976	−151.312	−190.907	9.065
1200	63.067	383.870	337.817	55.263	−153.876	−194.412	8.463
1300	63.456	388.934	341.557	61.590	−154.766	−197.754	7.946
1400	63.852	393.651	345.111	67.955	−155.709	−201.026	7.500
1500	64.244	398.069	348.496	74.360	−156.706	−204.229	7.112
1600	64.625	402.228	351.726	80.803	−157.757	−207.363	6.770
1700	64.986	406.157	354.813	87.284	−159.813	−210.411	6.465
1800	65.322	409.881	357.770	93.800	−161.311	−213.344	6.191
1900	65.630	413.421	360.606	100.348	−176.969	−215.491	5.924
2000	65.907	416.795	363.332	106.925	−178.831	−217.470	5.680
2100	66.152	420.016	365.955	113.528	−180.679	−219.356	5.456
2200	66.364	423.099	368.483	120.154	−182.516	−221.155	5.251
2300	66.545	426.053	370.922	126.800	−184.347	−222.870	5.062
2400	66.696	428.888	373.279	133.462	−186.176	−224.506	4.886
2500	66.819	431.613	375.558	140.138	−188.007	−226.066	4.723
2600	66.915	434.236	377.765	146.825	−189.845	−227.552	4.572
2700	66.987	436.763	379.904	153.520	−191.692	−228.967	4.430
2800	67.038	439.200	381.978	160.222	−193.552	−230.313	4.297
2900	67.068	441.553	383.992	166.927	−195.427	−231.593	4.171
3000	67.081	443.827	385.949	173.635	−197.319	−232.808	4.054
3100	67.079	446.027	387.851	180.343	−199.231	−233.960	3.942
3200	67.063	448.156	389.703	187.050	−549.462	−227.626	3.716
3300	67.035	450.219	391.506	193.755	−549.512	−217.567	3.444
3400	66.997	452.220	393.262	200.457	−549.616	−207.507	3.188
3500	66.950	454.161	394.974	207.154	−549.772	−197.443	2.947
3600	66.896	456.047	396.645	213.846	−549.980	−187.373	2.719
3700	66.836	457.879	398.275	220.533	−550.240	−177.298	2.503
3800	66.771	459.660	399.867	227.213	−550.551	−167.214	2.299
3900	66.701	461.394	401.423	233.887	−550.912	−157.122	2.104
4000	66.628	463.082	402.943	240.554	−551.321	−147.019	1.920
4100	66.553	464.726	404.430	247.213	−551.778	−136.906	1.744
4200	66.476	466.329	405.885	253.864	−552.280	−126.781	1.577
4300	66.397	467.892	407.309	260.508	−552.826	−116.644	1.417
4400	66.318	469.418	408.703	267.143	−553.416	−106.494	1.264
4500	66.238	470.907	410.069	273.771	−554.047	−96.329	1.118
4600	66.158	472.362	411.407	280.391	−554.718	−86.150	0.978
4700	66.078	473.784	412.719	287.003	−555.429	−75.957	0.844
4800	65.998	475.174	414.006	293.607	−556.177	−65.747	0.715
4900	65.920	476.534	415.268	300.202	−556.963	−55.522	0.592
5000	65.842	477.865	416.507	306.791	−557.786	−45.280	0.473
5100	65.765	479.168	417.723	313.371	−558.644	−35.021	0.359
5200	65.690	480.445	418.917	319.944	−559.539	−24.746	0.249
5300	65.616	481.695	420.090	326.509	−560.469	−14.452	0.142
5400	65.543	482.921	421.242	333.067	−561.436	−4.141	0.040
5500	65.471	484.123	422.374	339.618	−562.439	6.188	−0.059
5600	65.401	485.302	423.488	346.161	−563.480	16.536	−0.154
5700	65.333	486.459	424.582	352.698	−564.560	26.903	−0.247
5800	65.266	487.595	425.659	359.228	−565.680	37.290	−0.336
5900	65.201	488.710	426.718	365.751	−566.842	47.696	−0.422
6000	65.137	489.805	427.760	372.268	−568.048	58.121	−0.506

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

Iron Chloride ($FeCl_2$) $Cl_2Fe_1(g)$

Dichlorosilane (SiH_2Cl_2) IDEAL GAS $M_r = 101.00738$ Dichlorosilane (SiH_2Cl_2) $Cl_2H_2Si_1(g)$

$S°(298.15\ K) = 286.734 \pm 0.34\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [-313.01 \pm 12.6]\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [-320.49 \pm\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
2224(1)	2237(1)
954(1)	602(1)
527(1)	876(1)
188(1)	590(1)
710(1)	

Ground State Quantum Weight = [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distances: Si–H = 1.480 Å; Si–Cl = 2.033 Å
Bond Angles: H–Si–H = 111.3°; Cl–Si–Cl = 109.72°
Product of the Moments of Inertia: $I_AI_BI_C = 7.53113 \times 10^{-114}\ g^3{\cdot}cm^6$

Enthalpy of Formation

$\Delta_fH°(298.15\ K)$ is estimated from values for $SiCl_4$, $SiHCl_3$, and SiH_4.[1] Data for $SiHCl_3$[1] suggest that $\Delta_fH°$ shows minor deviations from linearity in the chlorosilanes. We assume that $\Delta_fH°$ has a cubic variation with a constant third difference of -1.5 kcal·mol^{-1}. $\Delta_fH°$ values of the chloromethanes yield an almost constant third difference of about -2.5 kcal mol^{-1}.[1-3] This approximation corresonds to Allen's bond additivity scheme involving near–neighbor interactions taken two and three at a time.[2] *Our adopted $\Delta_fH°$ is 1.5 kcal·mol^{-1} more negative than* that estimated by linear interpolation between $SiCl_4$ and SiH_4.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Davis and Gerry[4] for three isotopic forms of dichlorosilane. Structural parameters are essentially substitutional (r_s) values. They are in reasonable agreement with an early electron diffraction study.[5] The principal moments of inertia are $I_A = 5.9928 \times 10^{-39}$, $I_B = 33.0411 \times 10^{-39}$ and $I_C = 38.0343 \times 10^{-39}$ g·cm^2.

Vibrational frequencies are those selected by Shimanouchi[6] from a gas–phase infrared study of SiH_2Cl_2, $SiDHCl_2$ and SiD_2Cl_2 done by Christensen and Nielsen.[7] Assignments are based on band contours and isotopic rules and are supported by theoretical calculations.[4,7] Two frequencies, $\nu_4 = 188$ and infrared inactive $\nu_5 = 710$ cm^{-1}, are from liquid–phase Raman spectra[8] which also support the vibrational assignment. Christensen and Nielsen[7] found a weak infrared band at ~190 cm^{-1} but could not estimate a definite band contour.

We neglect excited states and assume the electronic ground state to be a singlet. A recent vacuum ultraviolet study of Si_2HCl_2[9] is not available to us. We assume that there is little shift in electronic levels between SiH_2Cl_2 and SiH_3Cl,[1] since there is little shift in absorption spectra between CH_2Cl_2 and CH_3Cl.[10] *This implies that contributions from the excited states in SiH_2Cl_2 should be unimportant, just as we* believe them to be in SiH_3Cl.[1]

References

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[10] B. R. Russell, L. O. Edwards and J. W. Raymonda, J. Amer. Chem. Soc. 95, 2129 (1973).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−13.385	−313.013	−313.013	INFINITE
100	38.443	234.601	333.516	−9.892	−315.697	−309.800	161.823
200	49.901	264.436	292.044	−5.522	−318.237	−302.916	79.114
250	56.488	276.287	287.727	−2.860	−319.441	−298.945	62.461
298.15	62.174	286.734	286.734	0.	−320.494	−294.900	51.665
300	62.375	287.119	286.735	0.115	−320.532	−294.741	51.319
350	67.358	297.120	287.514	3.362	−321.488	−290.365	43.335
400	71.521	306.394	289.301	6.837	−322.308	−285.861	37.330
450	75.028	315.027	291.686	10.503	−323.002	−281.263	32.648
500	78.029	323.091	294.427	14.332	−323.585	−276.593	28.895
600	82.940	337.770	300.453	22.390	−324.464	−267.106	23.254
700	86.822	350.858	306.735	30.886	−325.026	−257.498	19.215
800	89.965	362.663	313.001	39.730	−325.343	−247.827	16.181
900	92.536	373.413	319.125	48.860	−325.470	−238.128	13.821
1000	94.653	383.276	325.054	58.222	−325.459	−228.422	11.932
1100	96.406	392.382	330.766	67.778	−325.348	−218.723	10.386
1200	97.864	400.835	336.257	77.494	−325.171	−209.038	9.099
1300	99.084	408.718	341.531	87.343	−324.956	−199.368	8.011
1400	100.112	416.100	346.597	97.304	−324.723	−189.717	7.078
1500	100.983	423.037	351.464	107.360	−324.490	−180.081	6.271
1600	101.726	429.579	356.143	117.497	−324.271	−170.462	5.565
1700	102.363	435.765	360.647	127.702	−374.252	−160.408	4.929
1800	102.912	441.632	364.984	137.966	−373.859	−147.840	4.290
1900	103.389	447.209	369.166	148.282	−373.463	−135.294	3.719
2000	103.805	452.523	373.202	158.642	−373.070	−122.769	3.206
2100	104.169	457.597	377.101	169.041	−372.684	−110.264	2.743
2200	104.490	462.451	380.871	179.474	−372.310	−97.776	2.322
2300	104.775	467.102	384.520	189.938	−371.951	−85.305	1.937
2400	105.027	471.566	388.055	200.428	−371.611	−72.850	1.586
2500	105.252	475.858	391.481	210.942	−371.291	−60.408	1.262
2600	105.454	479.991	394.807	221.478	−370.995	−47.979	0.964
2700	105.635	483.974	398.036	232.032	−370.724	−35.560	0.688
2800	105.799	487.819	401.174	242.604	−370.480	−23.152	0.432
2900	105.947	491.534	404.226	253.192	−370.264	−10.751	0.194
3000	106.081	495.128	407.197	263.793	−370.077	1.643	−0.029
3100	106.203	498.608	410.090	274.408	−369.920	14.031	−0.236
3200	106.315	501.982	412.909	285.034	−369.791	26.414	−0.431
3300	106.417	505.255	415.658	295.670	−369.691	38.794	−0.614
3400	106.510	508.433	418.340	306.317	−369.619	51.171	−0.786
3500	106.596	511.522	420.958	316.972	−369.574	63.547	−0.948
3600	106.676	514.526	423.516	327.636	−753.706	86.382	−1.253
3700	106.749	517.450	426.015	338.307	−753.295	109.712	−1.549
3800	106.816	520.298	428.459	348.985	−752.907	133.031	−1.829
3900	106.879	523.073	430.850	359.670	−752.539	156.341	−2.094
4000	106.937	525.780	433.189	370.361	−752.190	179.641	−2.346
4100	106.991	528.421	435.480	381.057	−751.856	202.933	−2.585
4200	107.042	531.000	437.724	391.759	−751.534	226.216	−2.813
4300	107.089	533.519	439.922	402.466	−751.222	249.492	−3.031
4400	107.133	535.981	442.078	413.177	−750.917	272.761	−3.238
4500	107.174	538.389	444.191	423.892	−750.616	296.023	−3.436
4600	107.212	540.745	446.265	434.611	−750.317	319.278	−3.626
4700	107.249	543.052	448.300	445.334	−750.017	342.527	−3.807
4800	107.283	545.310	450.297	456.061	−749.714	365.770	−3.980
4900	107.314	547.522	452.259	466.791	−749.406	389.006	−4.147
5000	107.345	549.691	454.186	477.524	−749.091	412.235	−4.307
5100	107.373	551.817	456.079	488.260	−748.766	435.459	−4.460
5200	107.400	553.902	457.941	498.998	−748.430	458.676	−4.607
5300	107.425	555.948	459.771	509.740	−748.081	481.886	−4.749
5400	107.449	557.956	461.570	520.483	−747.718	505.090	−4.886
5500	107.472	559.928	463.341	531.229	−747.337	528.286	−5.017
5600	107.493	561.865	465.083	541.978	−746.940	551.476	−5.144
5700	107.514	563.767	466.798	552.728	−746.524	574.658	−5.266
5800	107.533	565.637	468.486	563.480	−746.088	597.833	−5.384
5900	107.552	567.476	470.148	574.235	−745.632	621.000	−5.498
6000	107.569	569.284	471.785	584.991	−745.152	644.159	−5.608

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

Dichlorosilane (SiH_2Cl_2) $Cl_2H_2Si_1(g)$

Mercury Chloride ($HgCl_2$) CRYSTAL M_r = 271.496

$S°$(298.15 K) = [144.494 ± 6.3] J·K^{-1}·mol^{-1}
T_{fus} = 550 K

$\Delta_f H°$(298.15 K) = −230.12 ± 4.2 kJ·mol^{-1}
Δ_{fus}H = 19.414 ± 0.21 kJ·mol^{-1}

Enthalpy of Formation

Taken from.[1]

Heat Capacity and Entropy

$C_p°$ was determined from the enthalpy data of Topol and Ransom[2] and Ewald.[3] Above 550 the curve was smoothly extrapolated. The entropy was estimated by adjusting the value to give the best fit of the melting, sublimation, and vaporization data.

Melting

T_{fus} was taken from.[1] $\Delta_{fus}H$ was given by Topol and Ransom.[2]

References

[1] U. S. Nat. Bur. Stand. Circular 500, (1952).
[2] L. E. Topol and L. D. Ransom, J. Phys. Chem. 64, 1339 (1960).
[3] R. Ewald, Ann. Phys. Chem. (4) 44, 1213 (1914).

Mercury Chloride ($HgCl_2$) $Cl_2Hg_1(cr)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	73.906	144.494	144.494	0.	−230.120	−184.022	32.240
300	73.973	144.952	144.496	0.137	−230.098	−183.736	31.991
400	76.986	166.664	147.436	7.691	−228.779	−168.475	22.001
500	79.224	184.075	153.079	15.498	−227.271	−153.570	16.043
550.000	80.500	191.685	156.247	19.491	--- CRYSTAL <--> LIQUID ---		
600	81.672	198.742	159.498	23.546	−225.569	−138.986	12.100
700	83.948	211.509	166.035	31.832	−282.429	−118.132	8.815
800	85.688	222.830	172.441	40.312	−279.728	−94.844	6.193
900	87.646	233.037	178.615	48.979	−276.859	−71.903	4.173
1000	89.508	242.368	184.531	57.837	−273.816	−49.292	2.575
1100	91.287	250.983	190.185	66.878	−270.604	−26.994	1.282
1200	92.968	258.999	195.589	76.092	−267.231	−4.995	0.217
1300	94.563	266.504	200.759	85.469	−263.704	16.716	−0.672
1400	96.065	273.567	205.710	95.000	−260.034	38.150	−1.423
1500	97.571	280.246	210.458	104.682	−256.221	59.316	−2.066

PREVIOUS: CURRENT: March 1962

Mercury Chloride ($HgCl_2$) LIQUID $M_r = 271.496$ Mercury Chloride ($HgCl_2$) $Cl_2Hg_1(l)$

$S°(298.15\ K) = [164.471]\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{fus} = 550\ K$

$\Delta_f H°(298.15\ K) = [-213.222]\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = 19.414 \pm .21\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(HgCl_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(550\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity was estimated to conform with the bromide and iodide, the value given by Topol and Ransom[1] was discounted. A glass type transition was assumed to be 367 K below which the heat capacity was equal to that of the crystal. The entropy was obtained from $S°(cr)$, the entropy of fusion and the estimated heat capacity.

Fusion and Vaporization

T_{fus} and T_{vap} were taken from NBS Circular 500.[2] $\Delta_{fus} H°$ was given by Topol and Ransom[1] and $\Delta_{vap} H$ was obtained from Prideaux[3] and Johnson;[4] $T_{vap} = 577$ K and $\Delta_{vap} H° = 58.9\ kJ\cdot mol^{-1}$.

References

[1] L. E. Topol and L. D. Ransom, J. Phys. Chem. 64, 1339 (1960).
[2] U. S. Nat. Bur. Stand. Circular 500, (1952).
[3] E. B. R. Prideaux, J. Chem. Soc. (London) 97, 2033 (1910).
[4] F. M. G. Johnson, J. Amer. Chem. Soc. 33, 777 (1911).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	102.090	164.471	164.471	0.	−213.222	−173.080	30.323
300	102.090	165.103	164.473	0.189	−213.148	−172.831	30.093
400	102.090	194.472	168.477	10.398	−209.174	−159.994	20.893
500	102.090	217.253	176.039	20.607	−205.264	−148.152	15.477
550.000	102.090	226.983	180.235	25.711	--- CRYSTAL <--> LIQUID ---		
600	102.090	235.866	184.506	30.816	−201.401	−137.093	11.935
700	102.090	251.603	192.996	41.025	−256.338	−120.107	8.962
800	102.090	265.235	201.193	51.234	−251.907	−100.948	6.591
900	102.090	277.260	208.990	61.443	−247.497	−82.343	4.779
1000	102.090	288.016	216.364	71.652	−243.104	−64.228	3.355
1100	102.090	297.746	223.327	81.861	−238.723	−46.552	2.211
1200	102.090	306.629	229.904	92.070	−234.355	−29.275	1.274
1300	102.090	314.800	236.125	102.278	−229.997	−12.362	0.497
1400	102.090	322.366	242.018	112.487	−225.648	4.216	−0.157
1500	102.090	329.409	247.612	122.696	−221.309	20.484	−0.713

PREVIOUS: CURRENT: March 1962

Mercury Chloride ($HgCl_2$) CRYSTAL-LIQUID M_r = 271.496 Mercury Chloride ($HgCl_2$) $Cl_2Hg_1(cr,l)$

0 to	550 K	crystal
above	550 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	73.906	144.494	144.494	0.	−230.120	−184.022	32.240
300	73.973	144.952	144.496	0.137	−230.098	−183.736	31.991
400	76.986	166.664	147.436	7.691	−228.779	−168.475	22.001
500	79.224	184.075	153.079	15.498	−227.271	−153.570	16.043
550.000	80.500	191.685	156.247	19.491	CRYSTAL <--> LIQUID		
550.000	102.090	226.983	156.247	38.905	TRANSITION		
600	102.090	235.866	162.517	44.009	−205.106	−140.798	12.258
700	102.090	251.603	174.149	54.218	−260.043	−123.811	9.239
800	102.090	265.235	184.701	64.427	−255.612	−104.652	6.833
900	102.090	277.260	194.331	74.636	−251.202	−86.047	4.994
1000	102.090	288.016	203.171	84.845	−246.808	−67.932	3.548
1100	102.090	297.746	211.333	95.054	−242.428	−50.257	2.387
1200	102.090	306.629	218.910	105.263	−238.060	−32.980	1.436
1300	102.090	314.800	225.976	115.472	−233.701	−16.067	0.646
1400	102.090	322.366	232.594	125.681	−229.353	0.511	−0.019
1500	102.090	329.409	238.816	135.890	−225.014	16.779	−0.584

PREVIOUS: CURRENT: March 1962

Mercury Chloride ($HgCl_2$) IDEAL GAS $M_r = 271.496$ Mercury Chloride ($HgCl_2$) $Cl_2Hg_1(g)$

$S^\circ(298.15\ K) = 294.793\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H^\circ(0\ K) = -142.31 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_f H^\circ(298.15\ K) = -146.29 \pm 6.3\ kJ \cdot mol^{-1}$

Vibrational Levels and Multiplicities ν, cm^{-1}
360 (1)
70 (2)
413 (1)

Ground State Quantum Weight: 1
Point Group: $D_{\infty h}$
Bond Distance: Hg–Cl = 2.31 Å
Bond Angle: O–Hg–Cl = 180°
Rotational Constant: $B_0 = 0.044554\ cm^{-1}$

$\sigma = 2$

Enthalply of Formation

The heat of formation of the crystal as given in NBS Circular 500[1] was combined with the 3rd law enthalpy of sublimation at 298.15 K from the data of Niwa and Zhibata,[2] Ruf and Treadwell[3] and Johnson.[4]

Heat Capacity and Entropy

The vibrational constants were given by Klemperer and Lindeman.[5] The bond length is a weighted average of the values given by Braune and Knoke,[6] Gregg *et al.*,[7] Maxwell and Mosely,[8] and Akishin *et al.*[9]

References

[1] U. S. Nat. Bur. Stand. Circular 500, (1952), "Selected Values of Chemical Thermodynamic Properties," (1952).
[2] K. Niwa and Z. Shibata, J. Fac. Sci. Hokkaido Imp. Univ. Ser. III, 2, 183 (1938).
[3] R. Ruf and W. D. Treadwell, Helv. Chim. Acta 37, 1941 (1954).
[4] F. M. G. Johnson, J. Amer. Chem. Soc. 33, 777 (1911).
[5] W. Klemperer and L. Lindeman, J. Chem. Phys. 25, 397 (1956).
[6] H. Braune and S. Knoke, Naturwiss. 21, 349 (1933).
[7] A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton, Trans. Faraday Soc. 33, 852, (1937).
[8] L. R. Maxwell and V. M. Mosley, Phys. Rev. 57, 21 (1940).
[9] P. A. Akishin, V. P. Spiridinov and A. N. Khodchenkov, Zhur. Fiz. Khim. 33, 20 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−14.543	−142.313	−142.313	INFINITE
100	46.437	237.359	343.680	−10.632	−143.019	−144.133	75.287
200	54.452	272.269	300.012	−5.549	−143.559	−145.015	37.874
250	56.690	284.678	295.742	−2.766	−146.092	−145.198	30.338
298.15	58.110	294.793	294.793	0.	−146.294	−145.007	25.405
300	58.154	295.152	294.794	0.108	−146.301	−144.999	25.247
350	59.140	304.196	295.506	3.041	−146.475	−144.768	21.605
400	59.826	312.140	297.099	6.017	−146.627	−144.514	18.872
450	60.319	319.217	299.170	9.021	−146.766	−144.241	16.743
500	60.683	325.592	301.499	12.046	−146.896	−143.954	15.039
600	61.174	336.703	306.467	18.141	−147.147	−143.341	12.479
700	61.478	346.157	311.479	24.275	−206.159	−136.116	10.157
800	61.680	354.381	316.339	30.434	−205.779	−126.136	8.236
900	61.819	361.654	320.977	36.609	−205.403	−116.203	6.744
1000	61.920	368.173	325.376	42.796	−205.031	−106.312	5.553
1100	61.995	374.078	329.540	48.992	−204.663	−96.458	4.580
1200	62.053	379.475	333.479	55.195	−204.301	−86.637	3.771
1300	62.097	384.444	337.211	61.402	−203.945	−76.846	3.088
1400	62.133	389.047	340.751	67.614	−203.593	−67.082	2.503
1500	62.162	393.335	344.115	73.829	−203.248	−57.343	1.997
1600	62.185	397.347	347.318	80.046	−202.909	−47.628	1.555
1700	62.205	401.118	350.373	86.266	−202.577	−37.933	1.166
1800	62.221	404.674	353.292	92.487	−202.252	−28.257	0.820
1900	62.235	408.038	356.086	98.710	−201.935	−18.599	0.511
2000	62.247	411.231	358.764	104.934	−201.626	−8.958	0.234
2100	62.258	414.268	361.335	111.159	−201.328	0.668	−0.017
2200	62.267	417.165	363.808	117.385	−201.041	10.280	−0.244
2300	62.274	419.933	366.188	123.612	−200.767	19.879	−0.451
2400	62.281	422.583	368.483	129.840	−200.507	29.467	−0.641
2500	62.287	425.126	370.698	136.069	−200.262	39.044	−0.816
2600	62.292	427.569	372.839	142.298	−200.033	48.612	−0.977
2700	62.297	429.920	374.910	148.527	−199.822	58.171	−1.125
2800	62.301	432.185	376.915	154.757	−199.630	67.723	−1.263
2900	62.305	434.372	378.859	160.987	−199.457	77.268	−1.392
3000	62.309	436.484	380.745	167.218	−199.302	86.807	−1.511
3100	62.312	438.527	382.576	173.449	−199.167	96.342	−1.623
3200	62.315	440.506	384.355	179.680	−199.050	105.873	−1.728
3300	62.317	442.423	386.086	185.912	−198.951	115.400	−1.827
3400	62.320	444.284	387.771	192.144	−198.868	124.924	−1.919
3500	62.322	446.090	389.411	198.376	−198.801	134.447	−2.007
3600	62.324	447.846	391.010	204.608	−198.746	143.967	−2.089
3700	62.326	449.553	392.569	210.841	−198.702	153.487	−2.167
3800	62.327	451.216	394.091	217.073	−198.667	163.005	−2.241
3900	62.329	452.835	395.577	223.306	−198.639	172.522	−2.311
4000	62.330	454.413	397.028	229.539	−198.615	182.039	−2.377
4100	62.332	455.952	398.446	235.772	−198.592	191.555	−2.440
4200	62.333	457.454	399.833	242.006	−198.568	201.070	−2.501
4300	62.334	458.921	401.191	248.239	−198.540	210.585	−2.558
4400	62.335	460.354	402.519	254.472	−198.506	220.099	−2.613
4500	62.336	461.754	403.820	260.706	−198.464	229.612	−2.665
4600	62.337	463.125	405.094	266.940	−198.411	239.125	−2.715
4700	62.338	464.465	406.343	273.173	−198.346	248.636	−2.763
4800	62.339	465.778	407.568	279.407	−198.265	258.145	−2.809
4900	62.340	467.063	408.769	285.641	−198.168	267.653	−2.853
5000	62.340	468.322	409.947	291.875	−198.053	277.158	−2.895
5100	62.341	469.557	411.104	298.109	−197.918	286.661	−2.936
5200	62.342	470.767	412.240	304.343	−197.762	296.161	−2.975
5300	62.342	471.955	413.355	310.577	−197.584	305.658	−3.012
5400	62.343	473.120	414.451	316.812	−197.384	315.151	−3.048
5500	62.343	474.264	415.529	323.046	−197.160	324.641	−3.083
5600	62.344	475.388	416.588	329.280	−196.911	334.126	−3.117
5700	62.344	476.491	417.629	335.515	−196.639	343.606	−3.149
5800	62.345	477.575	418.653	341.749	−196.341	353.082	−3.180
5900	62.345	478.641	419.661	347.984	−196.019	362.552	−3.210
6000	62.346	479.689	420.653	354.218	−195.672	372.016	−3.239

PREVIOUS. March 1962 (1 atm) CURRENT: March 1962 (1 bar)

Mercury Chloride ($HgCl_2$) $Cl_2Hg_1(g)$

Mercury Chloride (Hg_2Cl_2) CRYSTAL $M_r = 472.086$

$S°(298.15 \text{ K}) = 192.535 \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = -260.537 \pm 0.21 \text{ kJ·mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = -264.927 \pm 0.21 \text{ kJ·mol}^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation is based on the average Gibbs energy of formation, −50.315 kcal·mol^{-1}, as measured by Gerke[1] and Hills and Ives,[2] and the entropy of formation.

Heat Capacity and Entropy

The data of Pollitzer[3] from 22–199 K was treated by Kelley.[4] The heat capacities listed by Kelley were raised by 0.06 to match the entropy data of Gerke.[1] Data above room temperature were obtained by smooth extrapolation. A mean value of the entropy of formation of −46.614 cal·K^{-1}·mol^{-1} was adopted from the cell measurements of Gerke.[1]

Sublimation

The vapor pressure over mercurous chloride reaches 1 atmosphere at 655 K according to Smith and Menzies.[5] At this point the vapor is dissociated into Hg(g) and $HgCl_2$(g).

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Mercury Chloride (Hg_2Cl_2) Cl_2Hg_2(cr)

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−23.476	−260.537	−260.537	INFINITE
100	79.245	92.186	278.165	−18.598	−261.981	−244.855	127.899
200	95.479	153.076	201.673	−9.719	−261.310	−227.924	59.528
298.15	101.968	192.535	192.535	0.	−264.927	−210.485	36.876
300	102.048	193.166	192.537	0.189	−264.904	−210.147	36.590
400	106.023	223.084	196.589	10.598	−263.497	−192.096	25.085
500	109.328	247.106	204.367	21.370	−261.751	−174.442	18.224
600	112.131	267.293	213.217	32.446	−259.735	−157.165	13.682
700	114.558	284.762	222.217	43.781	−375.019	−127.101	9.484
800	116.817	300.210	231.019	55.352	−371.305	−91.936	6.003
900	118.826	314.086	239.491	67.136	−367.399	−57.247	3.323
1000	120.667	326.703	247.591	79.112	−363.317	−23.003	1.202
1100	122.340	338.283	255.316	91.264	−359.072	10.824	−0.514
1200	123.846	348.994	262.682	103.574	−354.680	44.258	−1.926
1300	125.169	358.960	269.709	116.027	−350.158	77.320	−3.107
1400	126.311	368.279	276.421	128.602	−345.521	110.030	−4.105
1500	127.277	377.028	282.839	141.283	−340.788	142.405	−4.959

PREVIOUS: CURRENT: December 1961

$S°(298.15\ K) = [352.864]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -614.43 \pm 4.2\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -617.64 \pm 4.2\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
[219](1)	[104](1)
[108](1)	[184](1)
[180](1)	[100](1)

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: D_{2h}
Bond Distance: Cl–K = [2.932] Å
Bond Angle: Cl–K–Cl = [100.8]°
Product of the Moments of Inertia: $I_A I_B I_C = [2.87407 \times 10^{-112}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

The enthalpy of formation is calculated from that of KCl(g) using $\Delta_r H°(298.15\ K) = 45.0\ kcal{\cdot}mol^{-1}$ for $K_2Cl_2(g) \rightarrow 2\ KCl(g)$ as selected from data analyses summarized below. The three experimental techniques include PVT measurements,[1] combination of total vapor pressure and transpiration data,[2-4] and mass spectrometric studies of the variation of ion intensities with temperature.[5] The results are reasonably consistent, considering the uncertainties inherent in the problem.

The resulting tables were tested by comparison with other data. Calculated total vapor pressures are in satisfactory agreement with the observed values over the range 820–1500 K; however, near the boiling point they are lower by 6–18% [refer to KCl(g)]. Knudsen effusion data and transpiration data over KCl(cr) have been reviewed by Pugh and Barrow.[6] These data suggest negligible dimer formation when combined with the total vapor pressures of Pugh and Barrow[6] but significant dimer formation when combined with the lower (20–30%) total pressures of Dietz.[7] Calculated dimer formation (22 mole percent at 900 K) agrees with the latter combination but calculated total pressures agree with those of Pugh and Barrow.[6] Velocity distribution studies of Miller and Kusch[8] suggest about 10 mole percent of dimer at 900 K. Thus, while minor inconsistencies do exist, it is not apparent that they exceed the combined experimental errors.

Source	Method	Points	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	 3rd law	Drift cal·K^{-1}·mol^{-1}
1	PVT data	15	1310–1404	46.70 ± 2.1	46.01	−0.5 ± 1.6
2	Trans. + Vap. Press.	10	1253–1352	46.24 ± 3.5	44.98	−1.0 ± 2.7
3	Trans. + Vap. Press.	5	1261–1372	43.0 ± 4.5	44.16	0.7 ± 3.4
4	Trans. + Vap. Press.	7	1250–1473	42.54 ± 2.9	45.21	2.2 ± 2.3
5	Mass spectrometry	–	774–1016	41.9 ± 3	—	—

Heat Capacity and Entropy

The structure and vibrational frequencies are those calculated from an ionic model by Berkowitz.[9] The sixth fundamental was arbitrarily lowered from 206 to 100 cm^{-1} since the resulting entropy increase (1.4 cal·K^{-1}·mol^{-1} at 1300 K.) improved the overall agreement with the equilibrium data. Based on electron diffraction studies of the monomer–dimer vapor, Akishin and Rambidi[10] have derived the bond distance and angle to be 2.81 Å and 98°. Interpretation of the diffraction data, however, is complicated by the presence of only about 30 mole percent of dimer at the temperature of measurement. Adoption of this dimer structure would reduce the entropy by 0.23 cal·K^{-1}·mol^{-1}. Principal moments of inertia for the Berkowitz structure are $I_A = 45.3554 \times 10^{-39}$, $I_B = 60.0935 \times 10^{-39}$, and $I_C = 105.4488 \times 10^{-39}\ g{\cdot}cm^2$.

Reference

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−20.133	−614.430	−614.430	INFINITE
100	67.552	269.905	422.606	−15.270	−615.944	−616.913	322.242
200	78.301	321.028	360.199	−7.834	−616.734	−617.550	161.287
250	79.953	338.697	354.191	−3.874	−617.141	−617.708	129.063
298.15	80.865	352.864	352.864	0.	−617.642	−617.774	108.232
300	80.892	353.364	352.866	0.150	−617.665	−617.775	107.564
350	81.473	365.881	353.853	4.210	−623.105	−617.548	92.164
400	81.857	376.787	356.053	8.294	−623.947	−616.696	80.532
450	82.122	386.444	358.903	12.394	−624.751	−615.741	71.473
500	82.314	395.107	362.098	16.505	−625.523	−614.699	64.217
600	82.565	410.139	368.889	24.750	−626.989	−612.395	53.314
700	82.718	422.879	375.715	33.014	−628.388	−609.851	45.508
800	82.817	433.931	382.317	41.292	−629.764	−607.109	39.640
900	82.885	443.690	388.604	49.577	−631.164	−604.194	35.066
1000	82.934	452.425	394.557	57.868	−632.636	−601.119	31.399
1100	82.971	460.332	400.183	66.163	−792.128	−588.672	27.954
1200	82.998	467.552	405.501	74.462	−791.749	−570.192	24.820
1300	83.020	474.197	410.533	82.763	−791.377	−551.745	22.169
1400	83.037	480.350	415.303	91.066	−791.014	−533.325	19.899
1500	83.051	486.079	419.832	99.370	−790.660	−514.931	17.931
1600	83.062	491.439	424.142	107.676	−790.316	−496.560	16.211
1700	83.071	496.475	428.250	115.982	−789.982	−478.211	14.694
1800	83.079	501.224	432.174	124.290	−789.663	−459.881	13.345
1900	83.086	505.716	435.927	132.598	−789.360	−441.568	12.140
2000	83.092	509.978	439.524	140.907	−789.077	−423.270	11.055
2100	83.096	514.032	442.976	149.217	−788.819	−404.986	10.073
2200	83.101	517.898	446.295	157.526	−788.590	−386.714	9.182
2300	83.104	521.592	449.489	165.837	−788.398	−368.452	8.368
2400	83.108	525.129	452.567	174.147	−788.247	−350.197	7.622
2500	83.110	528.521	455.538	182.458	−788.144	−331.947	6.936
2600	83.113	531.781	458.408	190.769	−788.095	−313.700	6.302
2700	83.115	534.918	461.184	199.081	−788.109	−295.454	5.716
2800	83.117	537.941	463.872	207.392	−788.190	−277.206	5.171
2900	83.119	540.857	466.477	215.704	−788.347	−258.954	4.664
3000	83.121	543.675	469.003	224.016	−788.587	−240.695	4.191
3100	83.122	546.401	471.456	232.328	−788.915	−222.427	3.748
3200	83.124	549.040	473.840	240.641	−789.340	−204.147	3.332
3300	83.125	551.598	476.157	248.953	−789.849	−185.853	2.942
3400	83.126	554.079	478.413	257.266	−790.478	−167.541	2.574
3500	83.127	556.489	480.609	265.578	−791.216	−149.209	2.227
3600	83.128	558.831	482.750	273.891	−792.079	−130.854	1.899
3700	83.129	561.108	484.837	282.204	−793.069	−112.474	1.588
3800	83.130	563.325	486.873	290.517	−794.194	−94.065	1.293
3900	83.130	565.484	488.861	298.830	−795.459	−75.624	1.013
4000	83.131	567.589	490.803	307.143	−796.859	−57.150	0.746
4100	83.132	569.642	492.701	315.456	−798.415	−38.639	0.492
4200	83.132	571.645	494.557	323.769	−800.139	−20.087	0.250
4300	83.133	573.601	496.373	332.082	−802.032	−1.493	0.018
4400	83.133	575.512	498.150	340.396	−803.545	17.094	−0.203
4500	83.134	577.381	499.890	348.709	−805.656	35.768	−0.415
4600	83.134	579.208	501.594	357.022	−807.931	54.491	−0.619
4700	83.135	580.996	503.265	365.336	−810.331	73.261	−0.814
4800	83.135	582.746	504.902	373.649	−812.681	92.060	−1.002
4900	83.135	584.460	506.509	381.963	−815.404	110.937	−1.183
5000	83.136	586.140	508.085	390.276	−818.294	129.871	−1.357
5100	83.136	587.786	509.631	398.590	−821.350	148.864	−1.525
5200	83.136	589.400	511.150	406.904	−824.573	167.919	−1.687
5300	83.137	590.984	512.641	415.217	−827.962	187.038	−1.843
5400	83.137	592.538	514.106	423.531	−831.516	206.222	−1.995
5500	83.137	594.064	515.546	431.845	−835.233	225.473	−2.141
5600	83.137	595.562	516.962	440.158	−839.109	244.794	−2.283
5700	83.138	597.033	518.354	448.472	−842.452	264.089	−2.420
5800	83.138	598.479	519.723	456.786	−846.551	283.538	−2.554
5900	83.138	599.900	521.070	465.100	−850.789	303.058	−2.683
6000	83.138	601.298	522.395	473.413	−855.163	322.651	−2.809

PREVIOUS: March 1966 (1 atm) CURRENT· March 1966 (1 bar)

Lithium Chloride ((LiCl)$_2$) IDEAL GAS $M_r = 84.788$ Lithium Chloride ((LiCl)$_2$) $Cl_2Li_2(g)$

$S°(298.15\ K) = [288.767]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -595.61 \pm 12.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -598.55 \pm 12.6\ kJ \cdot mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
[330](1)	[356](1)
[296](1)	335 (1)
[385](1)	460 (1)

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: D_{2h}
Bond Distances: Li–Cl = 2.23 Å; Li–Li = 2.62 Å
Bond Angle: Cl–Li–Cl = 108 ± 4°
Product of the Moments of Inertia: $I_A I_B I_C = 6.41793 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

An enthalpy of sublimation at 298.15 K of 52.1 kcal·mol^{-1} was chosen to fit the vapor pressure data and relative concentrations of monomer, dimer and trimer as described in the table for LiCl(g). This value is in reasonable agreement with the value of 53.5 kcal·mol^{-1} from a 3rd law analysis of the vapor pressure data of Nesmeyanov and Sazonov[1] and the relative concentrations of monomer, dimer, and trimer from the work of Miller and Kusch.[2] Also a value of 54.1 kcal·mol^{-1} was found by Milne and Klein[3] from mass spectrometer studies.

Heat Capacity and Entropy

Klemperer and Norris[4] observed two bands in the infrared spectrum and made tentative assignments. The remaining four frequencies were calculated by Berkowitz[5] from a reasonable model. The bond lengths and angles were determined from the electron diffraction experiments of Bauer *et al.*[6] The principal moments of inertia are: $I_A = 3.9605 \times 10^{-39}$, $I_B = 38.3234 \times 10^{-39}$, and $I_C = 42.2839 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.486	−595.607	−595.607	INFINITE
100	41.503	225.773	345.688	−11.991	−596.014	−598.223	312.479
200	62.653	261.707	295.121	−6.683	−597.427	−599.845	156.663
250	68.505	276.364	289.937	−3.393	−598.012	−600.380	125.443
298.15	72.195	288.767	288.767	0.	−598.546	−600.788	105.256
300	72.309	289.214	288.769	0.134	−598.567	−600.802	104.609
350	74.860	300.565	289.659	3.817	−599.128	−601.130	89.714
400	76.631	310.683	291.666	7.607	−599.765	−601.374	78.531
450	77.902	319.786	294.294	11.472	−600.522	−601.531	69.824
500	78.841	328.045	297.262	15.391	−607.417	−600.983	62.784
600	80.103	342.541	303.634	23.344	−609.063	−599.538	52.194
700	80.885	354.952	310.100	31.396	−610.533	−597.832	44.611
800	81.403	365.789	316.398	39.512	−611.909	−595.923	38.910
900	81.761	375.398	322.430	47.672	−613.252	−593.844	34.466
1000	82.020	384.027	328.166	55.861	−614.572	−591.617	30.903
1100	82.213	391.854	333.605	64.073	−615.872	−589.258	27.982
1200	82.360	399.014	338.762	72.302	−617.157	−586.782	25.542
1300	82.475	405.611	343.654	80.544	−618.431	−584.199	23.473
1400	82.567	411.726	348.300	88.797	−619.693	−581.519	21.697
1500	82.640	417.426	352.721	97.057	−620.939	−578.748	20.154
1600	82.701	422.761	356.933	105.324	−622.170	−575.895	18.801
1700	82.751	427.776	360.955	113.597	−913.861	−558.614	17.164
1800	82.794	432.507	364.800	121.874	−913.562	−537.725	15.604
1900	82.829	436.985	368.482	130.155	−913.271	−516.854	14.209
2000	82.860	441.234	372.014	138.440	−912.992	−495.997	12.954
2100	82.886	445.278	375.408	146.727	−912.726	−475.154	11.819
2200	82.909	449.134	378.672	155.017	−912.477	−454.323	10.787
2300	82.929	452.820	381.816	163.309	−912.250	−433.503	9.845
2400	82.947	456.350	384.849	171.603	−912.047	−412.692	8.982
2500	82.962	459.736	387.777	179.898	−911.874	−391.889	8.188
2600	82.976	462.990	390.607	188.195	−911.735	−371.093	7.455
2700	82.988	466.122	393.347	196.493	−911.635	−350.301	6.777
2800	82.999	469.140	396.000	204.793	−911.576	−329.512	6.147
2900	83.009	472.053	398.573	213.093	−911.565	−308.724	5.561
3000	83.018	474.867	401.069	221.394	−911.603	−287.936	5.013
3100	83.026	477.590	403.494	229.697	−911.695	−267.146	4.501
3200	83.033	480.226	405.851	238.000	−911.843	−246.352	4.021
3300	83.039	482.781	408.143	246.303	−912.049	−225.552	3.570
3400	83.046	485.260	410.375	254.607	−912.316	−204.745	3.146
3500	83.051	487.667	412.549	262.912	−912.646	−183.930	2.745
3600	83.056	490.007	414.669	271.218	−913.039	−163.104	2.367
3700	83.061	492.283	416.736	279.523	−913.496	−142.266	2.008
3800	83.065	494.498	418.753	287.830	−914.019	−121.416	1.669
3900	83.069	496.655	420.723	296.137	−914 607	−100.550	1.347
4000	83.073	498.759	422.648	304.444	−915.262	−79.668	1.040
4100	83.076	500.810	424.529	312.751	−915.983	−58.770	0.749
4200	83.079	502.812	426.369	321.059	−916.771	−37.853	0.471
4300	83.082	504.767	428.170	329.367	−917.627	−16.916	0.205
4400	83.085	506.677	429.933	337.675	−918.509	4.038	−0.048
4500	83.088	508.544	431.659	345.984	−919.481	25.015	−0.290
4600	83 090	510.370	433.350	354.293	−920.524	46.016	−0.523
4700	83.092	512.157	435.008	362.602	−921.634	67.039	−0.745
4800	83.095	513.907	436.634	370.911	−922.811	88.087	−0.959
4900	83.097	515.620	438.228	379.221	−924.057	109.160	−1.164
5000	83.098	517.299	439.793	387.531	−925.373	130.259	−1.361
5100	83.100	518.944	441.329	395.841	−926.748	151.385	−1.550
5200	83.102	520.558	442.837	404.151	−928.206	172.538	−1.733
5300	83.104	522.141	444.318	412.461	−929.737	193.721	−1.909
5400	83.105	523.695	445.774	420.771	−931.345	214.934	−2.079
5500	83.106	525.219	447.205	429.082	−933.032	236.176	−2.243
5600	83.108	526.717	448.611	437.393	−934.799	257.450	−2.401
5700	83.109	528.188	449.994	445.704	−936.650	278.757	−2.555
5800	83.110	529.633	451.355	454.015	−938.587	300.097	−2.703
5900	83.111	531.054	452.694	462.326	−940.612	321.471	−2.846
6000	83.112	532.451	454.011	470.637	−942.727	342.879	−2.985

PREVIOUS: June 1962 (1 atm) CURRENT June 1962 (1 bar)

Lithium Chloride ((LiCl)$_2$) $Cl_2Li_2(g)$

Magnesium Chloride ($MgCl_2$) CRYSTAL $M_r = 95.211$ Magnesium Chloride ($MgCl_2$) $Cl_2Mg_1(cr)$

$S°(298.15\ K) = 89.629\ J·K^{-1}·mol^{-1}$

$T_{fus} = 987\ K$

$\Delta_f H°(0\ K) = -641.196 \pm 0.46\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -641.616 \pm 0.46\ kJ·mol^{-1}$

$\Delta_{fus} H° = 43.095 \pm 0.21\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -153.35 \pm 0.11\ kcal·mol^{-1}$ is from enthalpy of solution measurements reported by Shomate and Huffman.[1] Shomate and Huffman's enthalpy of solution of Mg in 1 M HCL ($\Delta_f H = -111.322 \pm 0.041\ kcal·mol^{-1}$) has been substantiated for calibration purposes by Gunn and Cunningham[2] ($\Delta_f H = -111.3\ kcal·mol^{-1}$) and by Westrum and Eyring[3] ($\Delta_f H = -111.27\ kcal\ mol^{-1}$). Auxiliary enthalpy of dilution and enthalpy of formation data for HCl were taken from Parker[4] and from Wagman *et al.*[5]

Heat Capacity and Entropy

High temperature heat content data by Moore[6] were joined by Shomate correlation with low temperature heat capacity data reported by Kelley and Moore.[7] $C_p°(cr)$ above T_{fus} is a linear extrapolation from 700 K. $S°(298.15\ K)$ is derived from the low temperature data and is based on $S°(53.6\ K) = 2.006\ cal·K^{-1}·mol^{-1}$.

Fusion Data

$\Delta_{fus} H° = 10.30 \pm 0.05\ kcal·mol^{-1}$ is taken from enthalpy measurements of Moore.[6] $T_{fus} = 987$ K is from NBS Circlular 500.[8]

Sublimation Data

The value of $\Delta_{sub} H°(298.15\ K)$ was derived by 2nd and 3rd law analyses of vapor pressure data. Refer to the ideal gas table for details.

References

[1] C. H. Shomate and E. H. Huffman, J. Amer. Chem. Soc. 65, 1625 (1943).

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[5] D. D. Wagman *et al.*, U. S. Nat. Bur. Stand. Technical Note 270-1, (1965).

[6] G. E. Moore, J. Amer. Chem. Soc. 65, 1700 (1943).

[7] K. K. Kelley and G. E. Moore, J. Amer. Chem. Soc. 65, 1264 (1943).

[8] U. S. Nat. Bur. Stand. Circ. 500, (1952).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.759	−641.196	−641.196	INFINITE
100	40.294	25.956	146.771	−12.081	−643.073	−625.817	326.893
200	63.575	62.664	95.923	−6.652	−642.688	−608.599	158.950
298.15	71.379	89.629	89.629	0.	−641.616	−592.087	103.731
300	71.496	90.071	89.630	0.132	−641.593	−591.780	103.038
400	75.709	111.276	92.493	7.513	−640.237	−575.376	75.136
500	78.145	128.451	98.022	15.215	−638.773	−559.328	58.433
600	79.873	142.857	104.326	23.119	−637.269	−543.580	47.323
700	81.253	155.274	110.737	31.176	−635.756	−528.085	39.406
800	82.550	166.209	117.001	39.366	−634.254	−512.806	33.483
900	83.847	176.007	123.022	47.686	−632.773	−497.714	28.887
987.000	84.977	183.795	128.040	55.030	--- CRYSTAL <--> LIQUID ---		
1000	85.144	184.908	128.773	56.135	−639.916	−482.073	25.181
1100	86.417	193.083	134.252	64.714	−638.519	−466.356	22.145
1200	87.662	200.656	139.474	73.418	−637.007	−450.771	19.622
1300	88.880	207.721	144.455	82.245	−635.383	−435.316	17.491
1400	90.071	214.351	149.213	91.193	−761.057	−416.823	15.552
1500	91.235	220.605	153.766	100.258	−757.861	−392.346	13.663
1600	92.372	226.530	158.131	109.439	−754.559	−368.086	12.017
1700	93.482	232.163	162.321	118.732	−751.153	−344.035	10.571
1800	94.565	237.538	166.352	128.135	−747.647	−320.187	9.292
1900	95.621	242.679	170.235	137.644	−744.043	−296.537	8.152
2000	96.650	247.610	173.981	147.258	−740.346	−273.080	7.132

PREVIOUS: December 1960 CURRENT: December 1965

Magnesium Chloride ($MgCl_2$) LIQUID $M_r = 95.211$ Magnesium Chloride ($MgCl_2$) $Cl_2Mg_1(l)$

$S°(298.15\ K) = [129.480]\ J \cdot K^{-1} \cdot mol^{-1}$

$T_{fus} = 987\ K$

$\Delta_f H°(298.15\ K) = [-601.577]\ kJ \cdot mol^{-1}$

$\Delta_{fus}H° = 43.095 \pm 0.21\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(MgCl_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(MgCl_2, cr, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(987\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A constant $C_p°(l) = 22.0\ cal \cdot K^{-1} \cdot mol^{-1}$ over the temperature range 1006–1428 K is from the high temperature enthalpy data of Moore.[1] This constant value was assumed to hold from an assumed glass transition of 660 K to 3000 K. $C_p°(l)$ below 660 K is taken to be that of the crystal. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is calculated as the temperature at which the Gibbs energy change of the reaction $MgCl_2(l) = MgCl_2(g)$ is zero. The difference between $\Delta_f H°$ for $MgCl_2(l)$ and $MgCl_2(g)$ at T_{vap} is $\Delta_{vap}H°$.

Reference

[1] G. E. Moore, J. Amer. Chem. Soc. 65, 1700 (1943).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	71.379	129.480	129.480	0.	−601.577	−563.929	98.798
300	71.496	129.922	129.482	0.132	−601.553	−563.696	98.148
400	75.709	151.128	132.344	7.513	−600.197	−551.276	71.989
500	78.145	168.303	137.873	15.215	−598.733	−539.214	56.331
600	79.873	182.554	144.164	23.034	−597.314	−527.443	45.918
660.000	85.617	190.408	148.013	27.981	GLASS <--> LIQUID TRANSITION		
660.000	92.048	190.415	148.013	27.985			
700	92.048	195.831	150.592	31.667	−595.225	−515.943	38.500
800	92.048	208.122	157.032	40.872	−592.708	−504.791	32.959
900	92.048	218.964	163.323	50.077	−590.342	−493.945	28.668
987.000	92.048	227.458	168.608	58.085	--- CRYSTAL <--> LIQUID ---		
1000	92.048	228.662	169.381	59.282	−596.730	−482.642	25.211
1100	92.048	237.435	175.175	68.486	−594.706	−471.331	22.382
1200	92.048	245.444	180.702	77.691	−592.694	−460.204	20.032
1300	92.048	252.812	185.969	86.896	−590.692	−449.244	18.051
1400	92.048	259.634	190.990	96.101	−716.109	−435.271	16.240
1500	92.048	265.984	195.781	105.306	−712.774	−415.328	14.463
1600	92.048	271.925	200.356	114.510	−709.448	−395.607	12.915
1700	92.048	277.505	204.732	123.715	−706.130	−376.093	11.556
1800	92.048	282.767	208.922	132.920	−702.822	−356.775	10.353
1900	92.048	287.744	212.941	142.125	−699.523	−337.640	9.282
2000	92.048	292.465	216.800	151.330	−696.234	−318.679	8.323
2100	92.048	296.956	220.511	160.534	−692.957	−299.881	7.459
2200	92.048	301.238	224.084	169.739	−689.692	−281.240	6.677
2300	92.048	305.330	227.528	178.944	−686.441	−262.747	5.967
2400	92.048	309.247	230.852	188.149	−683.206	−244.395	5.319
2500	92.048	313.005	234.063	197.354	−679.988	−226.177	4.726

PREVIOUS: December 1960 CURRENT: December 1965

Magnesium Chloride ($MgCl_2$) CRYSTAL-LIQUID

0 to 987 K crystal
above 987 K liquid

Refer to the individual tables for details.

M_r = 95.211 Magnesium Chloride ($MgCl_2$) $Cl_2Mg_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−13.759	−641.196	−641.196	INFINITE
100	40.294	25.956	146.771	−12.081	−643.073	−625.817	326.893
200	63.575	62.664	95.923	−6.652	−642.688	−608.599	158.950
298.15	71.379	89.629	89.629	0.	−641.616	−592.087	103.731
300	71.496	90.071	89.630	0.132	−641.593	−591.780	103.038
400	75.709	111.276	92.493	7.513	−640.237	−575.376	75.136
500	78.145	128.451	98.022	15.215	−638.773	−559.328	58.433
600	79.873	142.857	104.326	23.119	−637.269	−543.580	47.323
700	81.253	155.274	110.737	31.176	−635.756	−528.085	39.406
800	82.550	166.209	117.001	39.366	−634.254	−512.806	33.483
900	83.847	176.007	123.022	47.686	−632.773	−497.714	28.887
987.000	84.977	183.795	128.040	55.030	____ CRYSTAL <--> LIQUID ____		
987.000	92.048	227.458	128.040	98.125	TRANSITION		
1000	92.048	228.662	129.341	99.321	−596.730	−482.642	25.211
1100	92.048	237.435	138.775	108.526	−594.706	−471.331	22.382
1200	92.048	245.444	147.335	117.731	−592.694	−460.204	20.032
1300	92.048	252.812	155.169	126.936	−590.692	−449.244	18.051
1400	92.048	259.634	162.390	136.141	−716.109	−435.271	16.240
1500	92.048	265.984	169.087	145.345	−712.774	−415.328	14.463
1600	92.048	271.925	175.331	154.550	−709.448	−395.607	12.915
1700	92.048	277.505	181.179	163.755	−706.130	−376.093	11.556
1800	92.048	282.767	186.678	172.960	−702.822	−356.775	10.353
1900	92.048	287.744	191.867	182.165	−699.523	−337.640	9.282
2000	92.048	292.465	196.780	191.369	−696.234	−318.679	8.323
2100	92.048	296.956	201.444	200.574	−692.957	−299.881	7.459
2200	92.048	301.238	205.884	209.779	−689.692	−281.240	6.677
2300	92.048	305.330	210.119	218.984	−686.441	−262.747	5.967
2400	92.048	309.247	214.169	228.189	−683.206	−244.395	5.319
2500	92.048	313.005	218.048	237.393	−679.988	−226.177	4.726

PREVIOUS: CURRENT: December 1965

Magnesium Chloride ($MgCl_2$) IDEAL GAS $M_r = 95.211$

$S°(298.15\ K) = 277.027 \pm 2.1\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -392.57 \pm 2.1\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -392.46 \pm 2.1\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
590 (1)
88 (2)
[273](1)

Ground State Quantum Weight: 1
Point Group: $D_{\infty h}$
Bond Distance: Mg–Cl = 2.18 Å
Bond Angle: Cl–Mg–Cl = 180°
Rotational Constant: $B_0 = 0.050027\ cm^{-1}$

$\sigma = 2$

Enthalpy of Formation

Analysis of vapor pressure data on $MgCl_2$ is clouded by conflicting evidence for the amount of dimer in the vapor. Berkowitz and Marquart[1] by mass spectrometer studies found about 2% dimer at 920 K and derived $\Delta_{dim}H = -39.2\ kcal{\cdot}mol^{-1}$ and $\Delta_{dim}S = -29.9\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. Schrier and Clark[2] from gas transpiration data calculated about 30% dimer in the saturated vapor at 1300 K with $\Delta_{dim}H = -32.0\ kcal{\cdot}mol^{-1}$ and $\Delta_{dim}S = -18.8\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. Thermodynamic functions for the gaseous monomer adopted here are clearly not compatible with large amounts of dimer and it is assumed for the present that the mass spectrometer results are correct.

Several vapor pressure studies have been published and third law analyses are given below. Berkowitz and Marquart[1] gave a single point while the remaining publications gave only equations but not individual points. Total pressures calculated from the equations were corrected for dimer.

Source	Method	T/K	$\Delta_{sub}H°(298.15\ K)$ kcal·mol^{-1} 3rd law
Berkowitz and Marquart[1]	Mass spectrometer	920	58.1
Schrier and Clark[2]	Boiling Point	1208–1413	59.55–59.68
Hildenbrand *et al.*[3]	Torsion–effusion	802–985	59.55–59.19
Hildenbrand *et al.*[4]	Torsion–effusion	800-970	59.53–59.38
Fischer *et al.*[5] (total vapor pressures)	"Bell" method	1136–1435	59.30–59.56

The selected value for $\Delta_{sub}H°(298.15\ K)$ is 59.55 kcal·mol^{-1} which is combined with $\Delta_f H°(298.15\ K)$ of the crystal to give $\Delta_f H°(g, 298.15\ K) = -93.80\ kcal{\cdot}mol^{-1}$.

Heat Capacity and Entropy

White *et al.*[6] by matrix infrared spectroscopy determined the molecule to be linear with the asymmetric stretching frequency at 590 cm^{-1} and the doubly degenerate bending frequency at 88 cm^{-1}. The symmetric stretching frequency was estimated as 273 cm^{-1}. The asymmetric stretching was observed by Buchler and Klemperer[7] at 597 cm^{-1} and by Randall *et al.*[8] at 598 cm^{-1}, both by infrared spectroscopy of the vapor at high temperature. Electric deflection experiments by Klemperer and co–workers as summarized by Hayes[9] and the electron diffraction data of Akishin and Spiridonov[10] agree with the linear structure within their error limits of about 20. The Mg–Cl bond length was determined as 2.18 Å by Akishin and Spiridonov.[10]

References

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[2] E. E. Schrier and H. M. Clark, J. Phys. Chem. 67, 1259 (1963).
[3] D. L. Hildenbrand, W. F. Hall, F. Ju, and N. D. Potter, J. Chem. Phys. 40, 2882 (1964).
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Magnesium Chloride ($MgCl_2$) $Cl_2Mg_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−14.285	−392.565	−392.565	INFINITE
100	46.426	220.299	325.112	−10.481	−392.316	−394.494	206.063
200	53.484	254.921	282.150	−5.446	−392.325	−396.688	103.604
250	55.615	267.097	277.959	−2.715	−392.384	−397.772	83.110
298.15	57.097	277.027	277.027	0.	−392.459	−398.803	69.869
300	57.145	277.380	277.028	0.106	−392.462	−398.842	69.445
350	58.249	286.277	277.728	2.992	−392.557	−399.898	59.682
400	59.057	294.110	279.296	5.926	−392.668	−400.940	52.357
450	59.658	301.102	281.337	8.894	−392.796	−401.966	46.659
500	60.116	307.413	283.635	11.889	−392.942	−402.977	42.099
600	60.747	318.434	288.542	17.935	−393.296	−404.953	35.254
700	61.150	327.830	293.500	24.031	−393.744	−406.862	30.360
800	61.420	336.014	298.314	30.160	−394.302	−408.699	26.685
900	61.610	343.260	302.913	36.312	−394.989	−410.459	23.822
1000	61.748	349.759	307.278	42.481	−404.413	−411.422	21.490
1100	61.851	355.649	311.412	48.661	−405.414	−412.074	19.568
1200	61.931	361.035	315.326	54.850	−406.418	−412.636	17.962
1300	61.993	365.994	319.035	61.046	−407.424	−413.113	16.599
1400	62.042	370.590	322.556	67.248	−535.845	−410.346	15.310
1500	62.082	374.872	325.902	73.455	−535.508	−401.393	13.978
1600	62.115	378.880	329.090	79.665	−535.176	−392.463	12.813
1700	62.143	382.647	332.130	85.878	−534.850	−383.553	11.785
1800	62.166	386.199	335.036	92.093	−534.531	−374.663	10.872
1900	62.185	389.561	337.819	98.311	−534.220	−365.790	10.056
2000	62.202	392.751	340.486	104.530	−533.916	−356.933	9.322
2100	62.217	395.786	343.048	110.751	−533.623	−348.091	8.658
2200	62.229	398.681	345.511	116.973	−533.341	−339.263	8.055
2300	62.240	401.447	347.884	123.197	−533.071	−330.447	7.505
2400	62.250	404.096	350.171	129.421	−532.816	−321.643	7.000
2500	62.258	406.638	352.379	135.647	−532.577	−312.849	6.537
2600	62.266	409.080	354.513	141.873	−532.357	−304.064	6.109
2700	62.272	411.430	356.578	148.100	−532.156	−295.288	5.713
2800	62.278	413.695	358.578	154.327	−531.976	−286.518	5.345
2900	62.284	415.880	360.516	160.555	−531.820	−277.755	5.003
3000	62.288	417.992	362.397	166.784	−531.687	−268.996	4.684
3100	62.293	420.034	364.224	173.013	−531.580	−260.242	4.385
3200	62.297	422.012	365.999	179.242	−531.499	−251.490	4.105
3300	62.301	423.929	367.725	185.472	−531.445	−242.741	3.842
3400	62.304	425.789	369.406	191.703	−531.419	−233.993	3.595
3500	62.307	427.595	371.043	197.933	−531.421	−225.245	3.362
3600	62.310	429.350	372.638	204.164	−531.450	−216.496	3.141
3700	62.312	431.058	374.194	210.395	−531.508	−207.747	2.933
3800	62.315	432.719	375.712	216.626	−531.593	−198.996	2.735
3900	62.317	434.338	377.195	222.858	−531.707	−190.242	2.548
4000	62.319	435.916	378.643	229.090	−531.847	−181.484	2.370
4100	62.321	437.455	380.059	235.322	−532.015	−172.723	2.201
4200	62.323	438.956	381.444	241.554	−532.211	−163.958	2.039
4300	62.324	440.423	382.798	247.786	−532.432	−155.187	1.885
4400	62.326	441.856	384.124	254 019	−532.681	−146.411	1.738
4500	62.327	443.256	385.423	260.251	−532.955	−137.630	1.598
4600	62.328	444.626	386.695	266.484	−533.255	−128.841	1.463
4700	62.330	445.967	387.942	272.717	−533.582	−120.046	1.334
4800	62.331	447.279	389.164	278.950	−533.935	−111.244	1.211
4900	62.332	448.564	390.364	285.183	−534.313	−102.434	1.092
5000	62.333	449.823	391.540	291.416	−534.718	−93.616	0.978
5100	62.334	451.058	392.695	297.650	−535.149	−84.790	0.868
5200	62.335	452.268	393.829	303.883	−535.608	−75.955	0.763
5300	62.336	453.456	394.943	310.117	−536.092	−67.111	0.661
5400	62.337	454.621	396.037	316.350	−536.605	−58.257	0.564
5500	62.337	455.765	397.113	322.584	−537.144	−49.394	0.469
5600	62.338	456.888	398.170	328.818	−537.713	−40.521	0.378
5700	62.339	457.991	399.210	335.052	−538.311	−31.637	0.290
5800	62.339	459.075	400.233	341.286	−538.939	−22.743	0.205
5900	62.340	460.141	401.239	347.520	−539.597	−13.837	0.123
6000	62.341	461.189	402.230	353.754	−540.287	−4.920	0.043

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

Molybdenum Chloride Oxide (MoO_2Cl_2) IDEAL GAS $M_r = 198.8448$ Molybdenum Chloride Oxide (MoO_2Cl_2) $Cl_2Mo_1O_2(g)$

$\Delta_f H°(0\text{ K}) = -628.99 \pm 14.6$ kJ·mol^{-1}

$S°(298.15\text{ K}) = 337.787 \pm 5.44$ J·K^{-1}·mol^{-1} $\Delta_f H°(298.15\text{ K}) = -633.04 \pm 14.6$ kJ·mol^{-1}

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
972 (1)	134 (1)	156 (1)
453 (1)	233 (1)	437 (1)
347 (1)	996 (1)	287 (1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2v}

Bond Distances: Mo–O = 1.75 ± 0.10 Å; Mo–Cl = 2.28 ± 0.03 Å

Bond Angles: O–Mo–O = 109.5°; Cl–Mo–Cl = 113°

O–Mo–O plane perpendicular to Cl–Mo–Cl plane

Product of Moments of Inertia: $I_AI_BI_C = 1.09994 \times 10^{-112}$ g^3·cm^6

Enthalpy of Formation

Graham and Hepler[1] determined calorimetrically $\Delta_r H° = -65.3 \pm 0.5$ kcal·mol^{-1} for the reaction:

$$MoO_2Cl_2(cr) + 4\ NaOH(\infty H_2O) \rightarrow Na_2MoO_4(\infty H_2O) + 2\ NaCl(\infty H_2O) + 2\ H_2O(l).$$

Combining this result with the following enthalpy of formation data; $\Delta_f H°(Na_2MoO_4, \infty H_2O) = -353 \pm 0.4$ kcal·mol^{-1};[2] $\Delta_f H°(NaCl, \infty H_2O) = -97.33 \pm 0.09$ kcal·mol^{-1}.[3,4] $\Delta_f H°(NaOH, \infty H_2O) = -112.46 \pm 0.1$ kcal·mol^{-1};[3,4] $\Delta_f H°(H_2O, l) = -68.315$ kcal·mol^{-1};[5] we derive $\Delta_f H°(MoO_2Cl_2, cr) = -169.6 \pm 1.0$ kcal·mol^{-1}.

Shchukarev *et al.*[6] measured the heats of solution of $MoO_3(cr)$, $MoO_2Cl_2(cr)$ and $NaCl(cr)$ in NaOH(aq) and derived $\Delta_r H° = -45.56 \pm 0.5$ kcal·mol^{-1} for the reaction $MoO_2Cl_2(cr) + 2\ NaOH{\cdot}77\ H_2O \rightarrow MoO_3(cr) + 2\ NaCl(cr) + H_2O(l)$. Using JANAF auxiliary data,[3,4] we obtain $\Delta_f H°(MoO_2Cl_2, cr, 298.15\text{ K}) = -172.86 \pm 1.0$ kcal·mol^{-1}.

The two investigations differ only in the heat of solution of $MoO_2Cl_2(cr)$, both samples were better than 99.9% pure, and multiple determinations on two different samples were employed in each case. We adopt an average of the two values, -171.2 ± 1.7 kcal·mol^{-1} for $\Delta_f H°(MoO_2Cl_2, cr, 298.15\text{ K})$. Shchukarev *et al.*[8] reported an equation for the vapor pressure over the solid from which we have calcualted a 2nd law $\Delta_{sub}H°(298.15\text{ K}) = 19.9$ kcal·mol^{-1} with an estimated uncertainty of ±2 kcal·mol^{-1}, a ΔC_p correction of -4.1 cal·K^{-1}·mol^{-1} was used.[3] Thus, our adopted value is $\Delta_f H°(MoO_2Cl_2, g, 298.15\text{ K}) = -151.3 \pm 3.5$ kcal·mol^{-1}.

Shchukarev *et al.*[7] reported equilibrium constants for the reaction $MoO_2Cl_2(g) + 0.5\ O_2(g) = MoO_3(cr) + Cl_2(g)$. Shchukarev *et al.*[8] and Hultgren and Brewer[9] reported equilibrium data for the reaction $MoO_3(cr) + 2\ HCl(g) = MoO_2Cl_2(g) + H_2O(g)$. 2nd and 3rd law analysis of these equilibrium data give the following results:

Source	Data Points	$\Delta_r H°(298.15\text{ K})$, kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{-1}	$-\Delta_f H°(298.15\text{ K})$ kcal·mol^{-1}
[7]	7	−15.6	−30.11 ± 2.0	−15.0	148.0 ± 3.0
[8]	Eqn	12.1	13.8 ± 1.0	2.95	150.6 ± 1.2
[9] Set I	5	27.2	15.2 ± 1.7	−21.37	149.2 ± 2.0
Set II	5	26.5	15.4 ± 3.2	−21.75	149.4 ± 3.5

These equilbrium data are in agreement with the adopted enthalpy of formation but are suspect because of the significant drifts and because the range of validity of the equation[8] is estimated.

Heat Capacity and Entropy

The molecular structural data are from the compilation of Sutton.[10] Infrared data[11-13] for vapor phase MoO_2Cl_2 have indicated that the molecule possesses a distorted tetrahedral structure by reason of the similarity of its spectra to that of CrO_2Cl_2. Principal moments of inertia are $I_A = 32.2143 \times 10^{-39}$, $I_B = 53.4145 \times 10^{-39}$, and $I_C = 63.9238 \times 10^{-39}$ g·cm^2.

The vibrational frequencies 972, 996, 453, and 437 have been observed in the infrared vapor phase spectra of MoO_2Cl_2 by Barraclough and Stals.[11] These frequencies were assigned to the symmetric and asymmetric Mo–O and Mo–Cl stretches, respectively. Similar infrared data for these four frequencies have been reported by Iorns and Stafford[12] and Ward and Stafford.[13] The rest of the frequencies are from the infrared and Raman studies of crystalline MoO_2Cl_2 by Adams and Churchill.[14] Assignments are made by comparison with data reported for $CrO_2Cl_2(l)$ by Miller *et al.*[15]

Continued on page 938

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−18.400	−628.990	−628.990	INFINITE
100	53.401	261.666	405.432	−14.377	−631.275	−620.507	324.120
200	74.277	305.899	345.270	−7.874	−632.563	−609.158	159.096
250	80.563	323.183	339.165	−3.996	−632.879	−603.266	126.046
298.15	85.220	337.787	337.787	0.	−633.039	−597.546	104.688
300	85.378	338.315	337.789	0.158	−633.043	−597.326	104.004
350	89.169	351.772	338.843	4.525	−633.085	−591.368	88.257
400	92.191	363.883	341.228	9.062	−633.036	−585.411	76.447
450	94.615	374.887	344.366	13.734	−632.921	−579.465	67.262
500	96.572	384.960	347.929	18.516	−632.761	−573.533	59.917
600	99.467	402.841	355.629	28.327	−632.357	−561.724	48.902
700	101.440	418.331	363.505	38.378	−631.905	−549.987	41.041
800	102.829	431.973	371.228	48.596	−631.446	−538.316	35.148
900	103.835	444.145	378.666	58.932	−631.002	−526.702	30.569
1000	104.585	455.126	385.772	69.354	−630.591	−515.136	26.908
1100	105.156	465.122	392.538	79.843	−630.224	−503.608	23.914
1200	105.600	474.291	398.974	90.381	−629.915	−492.112	21.421
1300	105.952	482.758	405.097	100.960	−629.673	−480.638	19.312
1400	106.235	490.621	410.929	111.569	−629.508	−469.181	17.505
1500	106.465	497.959	416.489	122.205	−629.430	−457.732	15.940
1600	106.656	504.836	421.798	132.861	−629.448	−446.286	14.570
1700	106.815	511.307	426.875	143.535	−629.570	−434.835	13.361
1800	106.949	517.416	431.737	154.223	−629.806	−423.374	12.286
1900	107.064	523.202	436.400	164.924	−630.167	−411.896	11.324
2000	107.161	528.696	440.878	175.635	−630.661	−400.396	10.457
2100	107.246	533.926	445.186	186.356	−631.302	−388.868	9.673
2200	107.320	538.917	449.334	197.084	−632.098	−377.305	8.958
2300	107.384	543.689	453.333	207.820	−633.062	−365.703	8.305
2400	107.441	548.261	457.194	218.561	−634.206	−354.055	7.706
2500	107.491	552.648	460.925	229.307	−635.542	−342.355	7.153
2600	107.535	556.864	464.534	240.059	−637.094	−330.598	6.642
2700	107.575	560.924	468.029	250.814	−638.903	−318.776	6.167
2800	107.610	564.837	471.417	261.574	−641.032	−306.881	5.725
2900	107.643	568.613	474.704	272.336	−679.446	−294.855	5.311
3000	107.671	572.263	477.896	283.102	−680.420	−281.577	4.903
3100	107.698	575.794	480.997	293.871	−681.430	−268.265	4.520
3200	107.721	579.214	484.013	304.642	−682.475	−254.921	4.161
3300	107.743	582.529	486.949	315.415	−683.552	−241.543	3.823
3400	107.763	585.745	489.807	326.190	−684.660	−228.132	3.505
3500	107.781	588.870	492.593	336.967	−685.798	−214.689	3.204
3600	107.798	591.906	495.310	347.746	−686.963	−201.212	2.920
3700	107.813	594.860	497.961	358.527	−688.152	−187.703	2.650
3800	107.827	597.735	500.549	369.309	−689.363	−174.160	2.394
3900	107.840	600.536	503.077	380.092	−690.593	−160.586	2.151
4000	107.852	603.267	505.547	390.877	−691.839	−146.981	1.919
4100	107.864	605.930	507.963	401.663	−693.098	−133.344	1.699
4200	107.874	608.529	510.327	412.450	−694.367	−119.676	1.488
4300	107.884	611.068	512.640	423.237	−695.644	−105.977	1.287
4400	107.893	613.548	514.906	434.026	−696.926	−92.250	1.095
4500	107.902	615.973	517.125	444.816	−698.210	−78.493	0.911
4600	107.910	618.345	519.300	455.607	−699.495	−64.708	0.735
4700	107.917	620.665	521.432	466.398	−700.777	−50.894	0.566
4800	107.924	622.937	523.523	477.190	−702.056	−37.053	0.403
4900	107.931	625.163	525.574	487.983	−703.329	−23.185	0.247
5000	107.937	627.343	527.588	498.776	−1295.980	−3.561	0.037
5100	107.943	629.481	529.565	509.570	−1298.917	22.317	−0.229
5200	107.948	631.577	531.507	520.365	−1301.991	48.252	−0.485
5300	107.953	633.633	533.414	531.160	−1305.199	74.250	−0.732
5400	107.958	635.651	535.289	541.955	−1308.540	100.308	−0.970
5500	107.963	637.632	537.132	552.751	−1312.010	126.429	−1.201
5600	107.967	639.577	538.944	563.548	−1315.607	152.615	−1.424
5700	107.971	641.488	540.726	574.345	−1319.328	178.866	−1.639
5800	107.975	643.366	542.480	585.142	−1323.171	205.184	−1.848
5900	107.979	645.212	544.205	595.940	−1327.131	231.567	−2.050
6000	107.983	647.027	545.904	606.738	−1331.210	258.020	−2.246

PREVIOUS: June 1970 (1 atm) CURRENT June 1970 (1 bar)

Sodium Chloride ((NaCl)$_2$) IDEAL GAS $M_r = 116.88554$ Sodium Chloride ((NaCl)$_2$) $Cl_2Na_2(g)$

$S°(298.15\ K) = [325.432]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -562.47 \pm 8.4\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -566.10 \pm 8.4\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
[265](1)	[155](1)
[159](1)	[222](1)
[226](1)	[260](1)

Ground State Quantum Weight = 1
Point Group: D_{2h} $\sigma = 4$
Bond Distance: Cl–Na = [2.624] Å
Bond Angle: Cl–Na–Cl = [108.4]°
Product of the Moments of Inertia: $I_A I_B I_C = [6.84195 \times 10^{-113}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

An analysis is given below of the more extensive measurements relating to the dimer dissociation, $(NaCl)_2(g) \rightarrow 2\ NaCl(g)$. The mass spectrometric studies suggest that higher polymeric species may be neglected. Velocity distribution analyses are consistent with this procedure. When reduced to 298.15 K, the observed heats of dissociation of the dimer show a range of more than 7 kcal·mol^{-1}, reflecting the considerable uncertainty involved in such measurements. A value of $\Delta_r H°(298.15\ K) = 48.6$ kcal·mol^{-1} was selected for the dissociation; combining this with $\Delta_{sub}H°(298.15\ K) = 54.9$ kcal·mol^{-1} for sublimation to the monomer leads to $\Delta_{sub}H°(298.15\ K) = 61.2$ kcal·mol^{-1} for sublimation to the dimer.

Source	Method	T/K	$\Delta_r H°(T)$ kcal·mol^{-1}	$\Delta_r H°$(298.15 K)kcal·mol^{-1} 2nd law	3rd law
1	Molecular weight from vapor pressures	1350	51.0	52.8	52.0
2	Molecular weight from P-V-T measurements	1337	50.6	52.4	54.1
3	Double oven effusion with mass spectrometer	1002	47.4	48.6	—
4	Knudsen effusion with mass spectrometer	870	47.3	48.3	—
5	Knudsen effusion with mass spectrometer	930	44.5	45.6	—
6	Velocity distribution analysis	940	49.8	50.9	—
7	Velocity distribution analysis	980	46.6	47.8	—

Heat Capacity and Entropy

The structure and vibrational frequencies are those calculated from an ionic model by Berkowitz.[8] Electron diffraction studies by Akishin and Rambidi[9] gave a similar bond angle (108°) and a slightly shorter bond distance (2.50 Å); however, interpretation of the diffraction pattern was complicated by uncertainty in the monomer-dimer ratio for the vapor. Principal moments of inertia for the Berkowitz structure are $I_A = 17.9886 \times 10^{-39}$, $I_B = 53.3306 \times 10^{-39}$, and $I_C = 71.3192 \times 10^{-39}\ g{\cdot}cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.446	−562.467	−562.467	INFINITE
100	57.464	248.550	391.674	−14.312	−563.924	−565.116	295.186
200	74.137	294.802	332.524	−7.544	−565.105	−565.794	147.770
250	77.102	311.696	326.720	−3.756	−565.585	−565.911	118.241
298.15	78.786	325.432	325.432	0.	−566.095	−565.929	99.148
300	78.836	325.919	325.433	0.146	−566.116	−565.928	98.537
350	79.928	338.160	326.397	4.117	−566.770	−565.847	84.448
400	80.656	348.883	328.552	8.133	−572.843	−565.251	73.814
450	81.163	358.414	331.350	12.179	−573.698	−564.250	65.496
500	81.531	366.986	334.492	16.247	−574.503	−563.156	58.833
600	82.016	381.897	341.187	24.426	−575.988	−560.745	48.817
700	82.312	394.564	347.930	32.644	−577.346	−558.096	41.646
800	82.505	405.569	354.462	40.885	−578.623	−555.258	36.255
900	82.639	415.295	360.692	49.143	−579.860	−552.263	32.053
1000	82.734	424.007	366.595	57.412	−581.102	−549.130	28.684
1100	82.805	431.896	372.179	65.689	−582.392	−545.871	25.921
1200	82.859	439.103	377.460	73.972	−777.291	−537.611	23.402
1300	82.901	445.737	382.460	82.260	−776.933	−517.653	20.800
1400	82.934	451.882	387.202	90.552	−776.580	−497.721	18.570
1500	82.961	457.605	391.707	98.847	−776.233	−477.815	16.639
1600	82.983	462.960	395.995	107.144	−775.893	−457.931	14.950
1700	83.002	467.991	400.083	115.443	−775.560	−438.069	13.460
1800	83.017	472.736	403.989	123.744	−775.235	−418.226	12.137
1900	83.030	477.225	407.726	132.047	−774.919	−398.401	10.953
2000	83.041	481.484	411.309	140.350	−774.613	−378.592	9.888
2100	83.051	485.536	414.748	148.655	−774.319	−358.799	8.925
2200	83.059	489.399	418.054	156.960	−774.039	−339.018	8.049
2300	83.066	493.092	421.237	165.267	−773.775	−319.251	7.250
2400	83.073	496.627	424.305	173.574	−773.531	−299.494	6.518
2500	83.078	500.018	427.266	181.881	−773.309	−279.747	5.845
2600	83.083	503.277	430.127	190.189	−773.113	−260.009	5.224
2700	83.088	506.413	432.895	198.498	−772.944	−240.277	4.648
2800	83.092	509.434	435.575	206.807	−772.808	−220.551	4.114
2900	83.095	512.350	438.172	215.116	−772.706	−200.830	3.617
3000	83.098	515.167	440.692	223.426	−772.641	−181.111	3.153
3100	83.101	517.892	443.139	231.736	−772.617	−161.394	2.719
3200	83.104	520.531	445.516	240.046	−772.637	−141.677	2.313
3300	83.106	523.088	447.828	248.356	−772.700	−121.959	1.930
3400	83.108	525.569	450.078	256.667	−772.812	−102.238	1.571
3500	83.110	527.978	452.270	264.978	−772.974	−82.513	1.231
3600	83.112	530.319	454.406	273.289	−773.187	−62.782	0.911
3700	83.114	532.597	456.488	281.601	−773.455	−43.045	0.608
3800	83.116	534.813	458.520	289.912	−773.779	−23.301	0.320
3900	83.117	536.972	460.504	298.224	−774.162	−3.546	0.047
4000	83.118	539.076	462.443	306.536	−774.605	16.219	−0.212
4100	83.120	541.129	464.337	314.847	−775.111	35.996	−0.459
4200	83.121	543.132	466.189	323.159	−775.679	55.785	−0.694
4300	83.122	545.088	468.001	331.472	−776.319	75.589	−0.918
4400	83.123	546.999	469.775	339.784	−776.945	95.402	−1.133
4500	83.124	548.867	471.512	348.096	−777.685	115.235	−1.338
4600	83.125	550.694	473.214	356.409	−778.512	135.087	−1.534
4700	83.125	552.481	474.881	364.721	−779.415	154.957	−1.722
4800	83.126	554.231	476.516	373.034	−780.395	174.847	−1.903
4900	83.127	555.945	478.120	381.346	−781.457	194.759	−2.076
5000	83.128	557.625	479.693	389.659	−782.589	214.692	−2.243
5100	83.128	559.271	481.237	397.972	−783.821	234.650	−2.403
5200	83.129	560.885	482.754	406.285	−785.145	254.632	−2.558
5300	83.129	562.469	484.243	414.598	−786.566	274.642	−2.707
5400	83.130	564.022	485.706	422.911	−788.086	294.678	−2.850
5500	83.130	565.548	487.144	431.224	−789.711	314.745	−2.989
5600	83.131	567.046	488.557	439.537	−791.444	334.841	−3.123
5700	83.131	568.517	489.947	447.850	−793.288	354.969	−3.253
5800	83.132	569.963	491.314	456.163	−795.249	375.131	−3.378
5900	83.132	571.384	492.659	464.476	−797.328	395.328	−3.500
6000	83.133	572.781	493.983	472.789	−799.214	415.524	−3.617

PREVIOUS: December 1964 (1 atm)   CURRENT: December 1964 (1 bar)

Nickel Chloride ($NiCl_2$) CRYSTAL $M_r = 129.596$ Nickel Chloride ($NiCl_2$) $Cl_2Ni_1(cr)$

$S°(298.15\ K) = 98.157 \pm 0.21\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 1304 \pm 4\ K,\ p\ 2.5\ atm$

$\Delta_f H°(0\ K) = -305.389 \pm 0.21\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -304.930 \pm 0.21\ kJ{\cdot}mol^{-1}$
$\Delta_{fus} H° = 77.170 \pm 0.84\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ of $-72.88 \pm 0.5\ kcal{\cdot}mol^{-1}$ is based on our 3rd law analysis of equilibrium data for the reaction $NiCl_2(cr) + H_2(g) \rightarrow Ni(cr) + 2HCl(g)$ of Busey and Giauque.[1] This value is selected from the studies shown below mainly because of the attention to purity of the sample, assurance of equilibrium, and correction for diffusion of hydrogen through pyrex by these authors. The results of Busey and Giauque[1] show excellent agreement between 2nd and 3rd law values with a consequent low drift. Our analysis of the other studies is given below and the large drifts for some of the studies indicate a lack of equilibrium which is attained very slowly in this system; this is certainly the case for Shchukarev *et al.*[2] and possibly also for others.[3-5] The emf results of Egan[6] and Gee and Shelton[7] are about 0.5 kcal·mol^{-1} more negative than the adopted value and we increase the uncertainty in the event that these results prove to be more accurate.

Source	Reaction	Method	Data Points	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Giauque and Busey[1]	A	static	15	630 – 738	28.86 ± 0.05	28.75 ± 0.02	−0.16 ± 0.08	72.88 ± 0.1
Sano[3]	A	static	5	661 – 792	29.96 ± 0.38	29.26 ± 0.13	−0.96 ± 0.52	73.39 ± 0.1
Egan[6]	B	emf	2	673, 723	−69.73	−73.32 ± 0.36	−5.13	73.32 ± 0.4
Shchukarev *et al.*[2]	A	circulation	7	573 –823	26.52 ± 0.13	28.90 ± 0.58	3.35 ± 0.19	73.03 ± 0.6
Jellinek and Uloth[4]	A	dynamic	3	573 – 723	31.50 ± 3.09	29.81 ± 0.84	−2.64 ± 4.80	73.94 ± 0.8
Berger and Crut[5]	A	static	16	583 – 718	31.84 ± 0.44	29.57 ± 0.46	−3.52 ± 0.67	73.70 ± 0.5
Gee and Shelton[7]	C	emf	Equation	470 – 750	−0.97	−1.20 ± 0.08	−0.39	73.50 ± 0.3
Gee and Shelton[7]	D	emf	Equation	530 – 800	−7.35	−8.34 ± 0.31	−1.51	73.36 ± 0.3

[a]Reactions: A) $NiCl_2(cr) + H_2(g) \rightarrow Ni(cr) + 2HCl(g)$ C) $Co(cr) + NiCl_2(g) \rightarrow CoCl_2(cr) + Ni(cr)$
B) $Ni(cr) + Cl_2(g) \rightarrow NiCl_2(cr)$ D) $Fe(cr) + NiCl_2(g) \rightarrow FeCl_2(cr) + Ni(cr)$

Heat Capacity and Entropy

Heat capacity data below 300 K are based on the measurements of Kostryokova[8] (2–30 K) and Busey and Giauque[9] (14.14–336.36 K). The two sets of data are joined smoothly via a least squares procedure; Kostryokova's values[8] are higher than those of Busey and Giaugue[9] by 5.3% at 15 K and 0.3% at 30 K. The results of Busey and Giauque[9] indicate a sharp lambda peak at 52.35 K which is apparently associated with the cooperative ordering of the magnetic moments of the nickel ions. $C_p°$ near the maximum is 6.74 cal·K^{-1}·mol^{-1} and the enthalpy associated with this transition is of the order of a few calories. The only other measurements in this temperature region are by Trapeznikowa *et al.*[10] (13–129 K) who report three peaks in $C_p°$ at 49.55 K, 57–58 K, and 60–61 K. We put no weight on these results since the authors apparently suffered from an impure sample among other experimental problems;[9] their results range from 4 to 13% higher than those of Busey and Giauque over the temperature range 40–130 K. Earlier results by Kostryokova[11] below 16 K are in good agreement with the adopted $C_p°$ values. $S°(298\ 15\ K)$ is obtained from integration of the adopted $C_p°$'s and is based on $C_p°(2\ K) = 0.0055$.

$C_p°$ data above 300 K are based on the high temperature enthalpy data of Coughlin[12] (376–1282 K). These data are corrected to IPTS 68[13] and then joined smoothly with the low temperature $C_p°$ data of Busey and Giauque[9] to yield the adopted $C_p°$ values. Data above 1300 K are extrapolated. The high temperature enthalpy data of Krestovnikov and Karetinkov[14] range from 2 to 11% higher than those of Coughlin and are believed to be of lower accuracy.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$T_{sub} = \sim 1245$ K is calculated as the temperature at which $\Delta_r G = 0$ for $NiCl_2(cr) \rightarrow NiCl_2(g)$.[15] See the enthalpy of formation section of the $NiCl_2(g)$ table[15] for the derivation of the adopted enthalpy of sublimation.

References

[1] R. H. Busey and W. F Giauque, J. Amer. Chem. Soc. 75, 1791 (1953).
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[5] E. Berger and G. Crut, Compt. Rend. 173, 977 (1921).
[6] J. J. Egan, U S. Atomic Energy Commission Rept. BNL9343, (1965).
[7] R. Gee and R. A. J. Shelton, Trans. Inst. Min. Metall., Sect. C 85, C208 (1976).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.426	−305.389	−305.389	INFINITE
52.350	28.361	11.674	278.918	−13.990	C_p LAMBDA MAXIMUM TRANSITION		
52.350	29.122	11.674	278.918	−13.990			
100	43.878	32.394	156.473	−12.408	−306.791	−290.384	151.681
200	64.890	70.800	104.534	−6.747	−306.057	−274.184	71.610
298.15	71.660	98.157	98.157	0.	−304.930	−258.779	45.337
300	71.747	98.601	98.159	0.133	−304.908	−258.492	45.008
400	76.289	119.910	101.033	7.551	−303.688	−243.202	31.759
500	78.898	137.244	106.597	15.324	−302.454	−228.225	23.842
600	79.881	151.724	112.945	23.267	−301.421	−213.481	18.585
700	80.313	164.068	119.389	31.275	−300.407	−198.895	14.842
800	80.900	174.824	125.660	39.331	−299.137	−184.480	12.045
900	82.067	184.412	131.664	47.473	−297.846	−170.225	9.880
1000	84.072	193.153	137.382	55.771	−296.473	−156.117	8.155
1100	87.077	201.298	142.826	64.320	−294.932	−142.155	6.750
1200	91.186	209.043	148.024	73.223	−293.120	−128.343	5.587
1300	96.469	216.542	153.007	82.596	−290.929	−114.698	4.609
1304.000	96.705	216.839	153.202	82.982	--- CRYSTAL <--> LIQUID ---		
1400	102.973	223.922	157.809	92.558	−288.244	−101.239	3.777
1500	110.733	231.284	162.462	103.232	−284.946	−87.992	3.064
1600	119.771	238.712	166.995	114.747	−280.911	−74.989	2.448
1700	130.107	246.276	171.435	127.230	−276.016	−62.264	1.913
1800	141.752	254.036	175.808	140.812	−287.283	−49.140	1.426

PREVIOUS: CURRENT: September 1977

Nickel Chloride (NiCl$_2$) LIQUID M_r = 129.596 Nickel Chloride (NiCl$_2$) Cl$_2$Ni$_1$(l)

$S°(298.15\ K) = [151.810]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(298.15) = [-233.516]\ kJ{\cdot}mol^{-1}$

$T_{fus} = 1304 \pm 4\ K,\ p \cong 2.5\ atm$

$\Delta_{fus}H° = 77\ 170 \pm 0.84\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(NiCl$_2$, l, 298.15 K) is calculated from that of the crystal by addition of $\Delta_{fus}H°$ and the difference in enthalpy, $H°$(1304 K)–$H°$(298.15 K), between the crystal and liquid.[1]

Heat Capacity and Entropy

The adopted values of $C_p°$ are obtained from our analysis of the high temperature enthalpy data of Coughlin[2] (1305–1337 K) after correction to IPTS 68.[3] The constant $C_p°$ value obtained from these data is assumed to be valid above an assumed glass transition temperature at 880 K. The assumption of a constant $C_p°$ over such a broad range based on data over a very short range leads to a rather large uncertainty in the thermal functions. Below the glass transition at 880 K, $C_p°$ is assumed to be that of the crystal.

$S°$(298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The temperature and heat of melting are obtained from our analysis of Coughlin's[2] measurements after correction to IPTS 68.[3] He observed pre-melting beginning at 1288 K and continuing to 1305 K where the enthalpy change again becomes regular. We adopt a melting point near the upper end of this range, T_{fus} = 1304 ± 4 K. The adopted enthalpy of melting is 18.444 ± 0.2 kcal·mol^{-1} at T_{fus}.

Phase Data

NiCl$_2$(l) will not exist as a stable phase at 1 bar pressure according to calculations from our tables.[1] We calculate sublimation at ~1245 K in good agreement with the measured value of 1241 ± 3 K at 730 torr.[4] The adopted melting point of 1304 ± 4 K is from Coughlin's work which was conducted at 2–3.5 atm in the presence of inert gas. These pressures are high enough to increase the sublimation point above the melting point and a relatively short liquid range will be observed. Information on the enthalpy of sublimation is in the enthalpy of formation section of the ideal gas table.[1]

References

[1] JANAF Thermochemical Tables: NiCl$_2$(cr), NiCl$_2$(g), 9–30–77.

[2] J. P. Coughlin, J. Amer. Chem. Soc. 73, 5314 (1951).

[3] T B. Douglas, J. Res. Nat. Bur. Stand. 73A, 451 (1969).

[4] H. Schaefer, Z. anorg. allg. Chem. 278, 300 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	71.659	151.810	151.810	0.	−233.517	−203.362	35.628
300	71.747	152.253	151.811	0.133	−233.495	−203.175	35.376
400	76.289	173.562	154.685	7.551	−232.275	−193.250	25.236
500	78.898	190.896	160.249	15.324	−231.041	−183.638	19.184
600	79.881	205.376	166.597	23.267	−230.007	−174.259	15.171
700	80.313	217.720	173.041	31.275	−228.993	−165.038	12.315
800	80.900	228.476	179.312	39.331	−227.724	−155.989	10.185
880.000	81.773	236.225	184.139	45.836	GLASS <−−> LIQUID TRANSITION		
880.000	101.186	236.225	184.139	45.836			
900	101.186	238.499	185.322	47.860	−226.045	−147.103	8.538
1000	101.186	249.160	191.182	57.978	−222.853	−138.504	7.235
1100	101.186	258.804	196.898	68.097	−219.741	−130.220	6.184
1200	101.186	267.608	202.429	78.215	−216.714	−122.216	5.320
1300	101.186	275.708	207.758	88.334	−213.778	−114.461	4.599
1304.000	101.186	276.018	207.967	88.739	−−− CRYSTAL <−−> LIQUID −−−		
1400	101.186	283.206	212.883	98.453	−210.936	−106.929	3.990
1500	101.186	290.187	217.807	108.571	−208.194	−99.596	3.468
1600	101.186	296.718	222.537	118.690	−205.555	−92.443	3.018
1700	101.186	302.852	227.082	128.808	−203.024	−85.451	2.626
1800	101.186	308.636	231.454	138.927	−217.755	−77.891	2.260

PREVIOUS: CURRENT September 1977

Nickel Chloride (NiCl$_2$) Cl$_2$Ni$_1$(l)

Nickel Chloride ($NiCl_2$) CRYSTAL-LIQUID

0 to 1304 K crystal
above 1304 K liquid

Refer to the individual tables for details.

M_r = 129.596 Nickel Chloride ($NiCl_2$) $Cl_2Ni_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−14.426	−305.389	−305.389	INFINITE
52.350	28.361	11.674	278.918	−13.990	C_p LAMBDA MAXIMUM TRANSITION		
52.350	29.122	11.674	278.918	−13.990			
100	43.878	32.394	156.473	−12.408	−306.791	−290.384	151.681
200	64.890	70.800	104.534	−6.747	−306.057	−274.184	71.610
298.15	71.660	98.157	98.157	0.	−304.930	−258.779	45.337
300	71.747	98.601	98.159	0.133	−304.908	−258.492	45.008
400	76.289	119.910	101.033	7.551	−303.688	−243.202	31.759
500	78.898	137.244	106.597	15.324	−302.454	−228.225	23.842
600	79.881	151.724	112.945	23.267	−301.421	−213.481	18.585
700	80.313	164.068	119.389	31.275	−300.407	−198.895	14.842
800	80.900	174.824	125.660	39.331	−299.137	−184.480	12.045
900	82.067	184.412	131.664	47.473	−297.846	−170.225	9.880
1000	84.072	193.153	137.382	55.771	−296.473	−156.117	8.155
1100	87.077	201.298	142.826	64.320	−294.932	−142.155	6.750
1200	91.186	209.043	148.024	73.223	−293.120	−128.343	5.587
1300	96.469	216.542	153.007	82.596	−290.929	−114.698	4.609
1304.000	96.705	216.839	153.202	82.982	CRYSTAL <--> LIQUID TRANSITION		
1304.000	101.186	276.018	153.202	160.152			
1400	101.186	283.206	161.873	169.866	−210.936	−106.929	3.990
1500	101.186	290.187	170.198	179.984	−208.194	−99.596	3.468
1600	101.186	296.718	177.903	190.103	−205.555	−92.443	3.018
1700	101.186	302.852	185.075	200.222	−203.024	−85.451	2.626
1800	101.186	308.636	191.780	210.340	−217.755	−77.891	2.260

PREVIOUS: CURRENT: September 1977

Nickel Chloride ($NiCl_2$) IDEAL GAS $M_r = 129.596$ Nickel Chloride ($NiCl_2$) $Cl_2Ni_1(g)$

$S°(298.15\ K) = 294.233 \pm 8.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -74.17 \pm 0.25\ kJ{\cdot}mol^{-1}$
$(298.15\ K) = -73.932 \pm 0.25\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i,cm^{-1}	g_i	State	ϵ_i,cm^{-1}	g_i
$^3\Pi_g$	0	6	$^1\Delta_g$	15466	2
$^3\Sigma_g^-$	[879]	3	$^1\Delta_g$	18236	2
$^3\Delta_g$	2454	6	$^3\Sigma_g^-$	21701	3
$^3\Phi_g$	5853	6	$^1\Pi_g$	[26740]	2
$^1\Sigma_g^+$	10601	1	$^1\Sigma_g^+$	[27234]	1
$^1\Pi_g$	11727	2	$^1\Gamma_g$	[28825]	2
$^3\Pi_g$	12984	6	$^1\Sigma_g^+$	[55433]	1
$^1\Phi_g$	14717	2			

Vibrational Frequencies and Degeneracies
ν, cm^{-1}

360 (1)
87 (2)
523 (1)

Point Group: $D_{\infty h}$ $\sigma = [2]$
Bond Distance: Ni–Cl = [2.09] Å
Bond Angle: Cl–Ni–Cl = 180°
Rotational Constant: $B_0 = [0.054428]\ cm^{-1}$

Enthalpy of Formation

The adopted value of $\Delta_f H°(298.15\ K)$ is calculated from $\Delta_{sub} H°(298.15\ K) = 55.21 \pm 0.3\ kcal{\cdot}mol^{-1}$ by addition of $\Delta_f H°(NiCl_2, cr, 298.15\ K)$.[1] The adopted value is an average derived from our 3rd law analysis of the sublimation data of Ratkovskii *et al.*,[2] McCreary and Thorn,[3] Schaefer *et al.*,[4] and Hildenbrand.[5] The data of Maier[6] are rejected because there is an apparent temperature dependent error at the high temperature end of his data.

Source	Method	T/K	Data Points	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Ratkovskii *et al.*[2]	Knudsen	973 – 1203	Equation	57.14	55.36 ± 0.29	−1.6	−17.52 ± 0.8
McCreary and Thorn[3]	Torsional Recoil	823 – 881	Equation	55.68	55.01 ± 0.03	−0.80	−17.87 ± 0.5
McCreary and Thorn[3]	Mass Effusion	823 – 881	Equation	54.85	55.08 ± 0.01	0.27	−17.80 ± 0.5
Schaefer *et al.*[4]	Transpiration	973 – 1056	10	55.25 ± 1.50	55.62 ± 0.23	0.36 ± 1.47	−17.26 ± 0.7
Maier[6]	Static (pure sample)	1047 – 1236	18	54.00 ± 0.89	55.39 ± 0.42	1.19 ± 0.75	−17.49 ± 0.7
Hildenbrand[5]	Torsion Effusion	706 – 771	19	55.14 ± 0.34	54.99 ± 0.08	−0.19 ± 0.46	−17.89 ± 0.5

Schoonmaker *et al.*[7] observed no dimers in their Knudsen–mass spectroscopic study while Schaefer and Binnewies[8] observed dimerization to the extent of 0.15% at 796 K by a similar technique. We have not corrected for this small dimerization effect. Of more importance may be the observation of significant quantities of $SiCl_4(g)$ and $Si_2Cl_6(g)$ by Schoonmaker *et al.*[7] indicating reaction between $NiCl_2(g)$ and the quartz liner in their experiment. Schaefer and Binnewies[8] make no mention of Si_xCl_y species even though their Knudsen cell contains a quartz crucible. Therefore we ignore this effect while recognizing the need for further work in the characterization of the vapor over $NiCl_2$.

Heat Capacity and Entropy

The adopted gas phase values of $\nu_2 = 87\ cm^{-1}$ and $\nu_3 = 523\ cm^{-1}$ are from the matrix isolation work of Thompson and Carlson,[9] we have added 2 cm^{-1} to the observed values to account for the matrix effect. The symmetric stretching frequency, ν_1, has not been observed in the infrared spectrum and this is one of the major indications that the molecule is linear. The adopted value of ν_1 (360 cm^{-1}) is from the observed vibrational spacing of the fluorescence spectrum by Gruen *et al.*[10] and is in good agreement with the value of 351 cm^{-1} calculated by Milligan *et al.*[11]

The rotational constant is calculated assuming the molecule is linear with the bond distance estimated to be 2.09 Å in accordance with Brewer *et al.*[12] Further support for a linear structure comes from the molecular beam work of Buchler *et al.*[13] which indicates a zero dipole moment for a number of transition metal difluorides including NiF_2.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.206	−74.171	−74.171	INFINITE
100	45.245	237.999	342.346	−10.435	−73.819	−77.973	40.729
200	53.251	271.980	299.409	−5.486	−73.797	−82.160	21.458
250	56.051	284.178	295.178	−2.750	−73.854	−84.245	17.602
298.15	58.077	294.233	294.233	0.	−73.931	−86.240	15.109
300	58.144	294.592	294.234	0.108	−73.935	−86.316	15.029
350	59.697	303.677	294.948	3.055	−74.039	−88.372	13.189
400	60.859	311.728	296.552	6.071	−74.170	−90.411	11.806
450	61.749	318.950	298.646	9.137	−74.331	−92.432	10.729
500	62.451	325.494	301.009	12.243	−74.536	−94.432	9.865
600	63.502	336.979	306.073	18.543	−75.146	−98.359	8.563
700	64.265	346.828	311.208	24.933	−75.750	−102.170	7.624
800	64.839	355.448	316.211	31.390	−76.080	−105.922	6.916
900	65.270	363.111	321.004	37.897	−76.423	−109.632	6.363
1000	65.590	370.006	325.565	44.440	−76.805	−113.302	5.918
1100	65.824	376.269	329.894	51.012	−77.241	−116.931	5.553
1200	65.993	382.004	334.001	57.603	−77.741	−120.518	5.246
1300	66.114	387.291	337.900	64.209	−78.317	−124 060	4.985
1400	66.200	392.194	341.605	70.825	−78.979	−127.554	4.759
1500	66.260	396.763	345.132	77.448	−79.732	−130.998	4.562
1600	66.300	401.041	348.494	84.076	−80.583	−134.388	4.387
1700	66.327	405.061	351.704	90.707	−81.540	−137.723	4.232
1800	66.344	408.853	354.775	97.341	−99.755	−140.282	4.071
1900	66.354	412.440	357.716	103.976	−100.838	−142.504	3.918
2000	66.360	415.844	360.538	110.612	−101.931	−144.669	3.778
2100	66.363	419.082	363.250	117.248	−103.035	−146.779	3.651
2200	66.365	422.169	365.858	123.884	−104.150	−148.836	3.534
2300	66.367	425.119	368.371	130.521	−105.279	−150.842	3.426
2400	66.370	427.944	370.795	137.158	−106.422	−152.798	3.326
2500	66.374	430.653	373.135	143.795	−107.581	−154.707	3.232
2600	66.380	433.257	375.398	150.433	−108.756	−156.569	3.146
2700	66.389	435.762	377.587	157.071	−109.949	−158.385	3.064
2800	66.400	438.177	379.709	163.710	−111.159	−160.157	2.988
2900	66.413	440.507	381.765	170.351	−112.388	−161.885	2.916
3000	66.428	442.759	383.761	176.993	−113.635	−163.571	2.848
3100	66.445	444.937	385.699	183.637	−114.900	−165.215	2.784
3200	66.465	447.047	387.584	190.282	−493.016	−161.629	2.638
3300	66.486	449.092	389.417	196.930	−492.660	−151.278	2.395
3400	66.509	451.078	391.201	203.580	−492.318	−140.939	2.165
3500	66.532	453.006	392.940	210.232	−491.988	−130.609	1.949
3600	66.557	454.880	394.634	216.886	−491.670	−120.288	1.745
3700	66.583	456.704	396.287	223.543	−491.361	−109.976	1.553
3800	66.609	458.480	397.901	230.203	−491.061	−99.673	1.370
3900	66.635	460.211	399.476	236.865	−490 768	−89 377	1.197
4000	66.661	461.898	401.016	243.530	−490.481	−79.088	1.033
4100	66.687	463.545	402.521	250.197	−490.196	−68.807	0.877
4200	66.712	465.152	403.993	256.867	−489.914	−58.533	0.728
4300	66.737	466.722	405.434	263.539	−489.632	−48.265	0.586
4400	66.762	468.257	406.844	270.214	−489.348	−38.004	0.451
4500	66.785	469.757	408.226	276.892	−489.062	−27.750	0.322
4600	66.808	471.225	409.579	283.571	−488.771	−17.501	0.199
4700	66.829	472.662	410.906	290.253	−488.475	−7.260	0.081
4800	66.850	474.069	412.208	296.937	−488.173	2.976	−0.032
4900	66.869	475.448	413.484	303.623	−487.863	13.205	−0.141
5000	66.887	476.799	414.737	310.311	−487.546	23.428	−0.245
5100	66.904	478.124	415.967	317.000	−487.221	33.644	−0.345
5200	66.919	479.423	417.175	323.692	−486.888	43.854	−0.441
5300	66.933	480.698	418.361	330.384	−486.546	54.057	−0.533
5400	66.945	481.949	419.527	337.078	−486.196	64.254	−0.622
5500	66.956	483.178	420.674	343.773	−485.838	74.444	−0.707
5600	66.966	484.384	421.800	350.469	−485.474	84.628	−0.789
5700	66.975	485.570	422.909	357.166	−485.102	94.805	−0.869
5800	66.982	486.734	423.999	363.864	−484.725	104.976	−0.945
5900	66.987	487.880	425.072	370.563	−484.343	115.139	−1.019
6000	66.992	489.005	426.129	377.262	−483.959	125.297	−1.091

PREVIOUS: September 1977 (1 atm) CURRENT. September 1977 (1 bar)

Dichlorine Oxide (ClOCl) IDEAL GAS $M_r = 86.9048$ Chlorine Oxide (ClOCl) $Cl_2O_1(g)$

$\Delta_{at}H°(0\ K) = 428.3 \pm 2\ kJ\cdot mol^{-1}$
$S°(298.15\ K) = 271.72 \pm 1.5\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 82.8 \pm 2\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 81.0 \pm 2\ kJ\cdot mol^{-1}$

Electroninc Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
X^1A	0.0	1

Vibrational Levels and Degeneracies ν, (cm^{-1})
638 (1)
298 (1)
678 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Cl-O = 1.9697Å
Bond Angle: Cl-O-Cl = 110.893°
Product of the Moments of Inertia: $I_A I_B I_C = 2.824188 \times 10^{-114}\ g^3\cdot cm^6$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(298.15\ K)$, was measured by reaction gas phase calorimetry at 298 K. Alqasmi *et al.*[1] measured the enthalpy of the reaction:

$$ClNO + Cl_2O \rightarrow ClNO_2 + Cl_2$$

The value of $\Delta_f H°(298.15K)$ is calculated using auxiliary information from JANAF Thermochemical Tables.[2]

Kustodina *et al.*[3] derived the enthalpy of formation of Cl_2O dissolved in CCl_4 from solution calorimetry at 278, 283, 288 and 308 K. The enthalpy of formation in CCl_4 was interpolated to 285 K. Yost and Felt[4] measured the partial vapor pressure of Cl_2O above its CCl_4 solution at 273 and 298 K which yielded the heat of solution of $-6.59\ kcal\cdot mol^{-1}$ at 285 K. Wallace and Goodeve[5] obtained the heat of explosion of $Cl_2O(g)$· their measured data gave $\Delta_f H°(Cl_2O,g,298.15\ K) = 21.4\ kcal\cdot mol^{-1}$ which is in very good agreement with the above. Also Gunther and Wekua[6] measured the enthalpy of explosion; their data gave $\Delta_f H°(Cl_2O,g,298.15\ K) = 24.7\ kcal\cdot mol^{-1}$.

Source	Reaction	T/K	$\Delta_r H(T)$ $kcal\cdot mol^{-1}$	$\Delta_f H(298.15\ K)$ $kcal\cdot mol^{-1}$
Kustodina et al.[3]	$Cl_2(g) + 1/2O_2(g) \rightarrow Cl_2O(in\ CCl_4)$	285	60.16	–
Yost and Felt[4]	$Cl_2O(in\ CCl_4) \rightarrow Cl_2O(g)$	285	27.57	87.86
Wallace and Goodeve[5]	$Cl_2O(g) \rightarrow Cl_2(g) + 1/2\ O_2(g)$	298	−89.54	89.54
Gunther and Wekua[6]	$Cl_2O(g) \rightarrow Cl_2(g) + 1/2O_2(g)$	298	−103.34	103.34

Heat Capacity and Entropy

The inertial parameters come from the microwave spectrum of Cl_2O which has been measured by several investigators.[7,8,9] The results of Nakata, et. al.[7] obtained for the $^{35}Cl_2{}^{16}O$ isotopic species are used to compute moments of inertia of the naturally occurring isotopic species. The principle moments of inertia (in $g\cdot cm^2$) are: $I_A = 2.7054 \times 10^{-39}$, $I_B = 30.9855 \times 10^{-39}$, $I_C = 33.6908 \times 10^{-39}$.

The stretching fundamentals, ν_1 and ν_3 have been observed in the infrared gas phase spectrum by Rochkind and Pimentel.[10] Raman spectra of all the fundamentals have been observed in an argon matrix by Chi and Andrews.[11] Their spectrum and assignment, which is given above, is in agreement with earlier results on the Raman spectrum of liquid Cl_2O obtained by Gardiner.[12]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−11.714	82.809	82.809	INFINITE
100	35.535	227.019	310.387	−8.337	81.821	86.686	−45.280
200	42.350	253.700	275.941	−4.448	81.217	91.818	−23.980
250	45.468	263.496	272.497	−2.250	81.067	94.488	−19.742
298.15	47.910	271.721	271.721	.000	81.000	97.080	−17.008
300	47.992	272.018	271.722	.089	80.999	97.179	−16.920
350	49.953	279.570	272.314	2.539	80.993	99.877	−14.906
400	51.458	286.343	273.652	5.076	81.031	102.573	−13.395
450	52.617	292.473	275.408	7.680	81.099	105.262	−12.219
500	53.519	298.066	277.398	10.334	81.188	107.942	−11.277
600	54.796	307.945	281.688	15.754	81.396	113.274	−9.861
700	55.626	316.459	286.061	21.278	81.621	118.569	−8.848
800	56.192	323.926	290.337	26.871	81.845	123.832	−8.085
900	56.593	330.569	294.445	32.511	82.063	129.068	−7.491
1000	56.886	336.547	298.361	38.186	82.270	134.279	−7.014
1100	57.107	341.980	302.083	43.886	82.465	139.471	−6.623
1200	57.277	346.956	305.618	49.606	82.649	144.645	−6.296
1300	57.410	351.546	308.977	55.340	82.819	149.804	−6.019
1400	57.517	355.805	312.172	61.087	82.977	154.951	−5.781
1500	57.604	359.776	315.214	66.843	83.122	160.086	−5.575
1600	57.675	363.496	318.117	72.607	83.253	165.213	−5.394
1700	57.734	366.995	320.890	78.378	83.369	170.332	−5.234
1800	57.784	370.296	323.544	84.154	83.469	175.444	−5.091
1900	57.826	373.422	326.088	89.934	83.553	180.552	−4.964
2000	57.862	376.389	328.529	95.719	83.619	185.655	−4.849
2100	57.894	379.212	330.876	101.506	83.665	190.756	−4.745
2200	57.921	381.906	333.135	107.297	83.691	195.855	−4.650
2300	57.945	384.482	335.312	113.090	83.695	200.953	−4.564
2400	57.965	386.948	337.412	118.886	83.675	206.051	−4.485
2500	57.984	389.315	339.441	124.683	83.630	211.151	−4.412
2600	58.000	391.589	341.404	130.483	83.560	216.253	−4.345
2700	58.015	393.778	343.303	136.283	83.462	221.359	−4.282
2800	58.028	395.889	345.144	142.086	83.336	226.468	−4.225
2900	58.039	397.925	346.929	147.889	83.182	231.582	−4.171
3000	58.050	399.893	348.662	153.693	83.000	236.703	−4.121
3100	58.060	401.796	350.345	159.499	82.791	241.830	−4.075
3200	58.068	403.640	351.982	165.305	82.555	246.963	−4.031
3300	58.076	405.427	353.575	171.113	82.292	252.105	−3.990
3400	58.083	407.161	355.125	176.921	82.006	257.255	−3.952
3500	58.090	408.845	356.636	182.729	81.697	262.414	−3.916
3600	58.096	410.481	358.109	188.539	81.368	267.582	−3.883
3700	58.102	412.073	359.546	194.348	81.021	272.759	−3.851
3800	58.107	413.622	360.949	200.159	80.658	277.947	−3.821
3900	58.112	415.132	362.319	205.970	80.283	283.143	−3.792
4000	58.116	416.603	363.658	211.781	79.897	288.350	−3.765
4100	58.120	418.038	364.967	217.593	79.504	293.566	−3.740
4200	58.124	419.439	366.247	223.405	79.106	298.792	−3.716
4300	58.128	420.807	367.500	229.218	78.706	304.027	−3.693
4400	58.131	422.143	368.727	235.031	78.307	309.272	−3.672
4500	58.134	423.449	369.929	240.844	77.910	314.525	−3.651
4600	58.137	424.727	371.106	246.658	77.520	319.788	−3.631
4700	58.140	425.977	372.260	252.471	77.137	325.058	−3.613
4800	58.142	427.202	373.392	258.285	76.763	330.337	−3.595
4900	58.145	428.400	374.503	264.100	76.401	335.624	−3.578
5000	58.147	429.575	375.592	269.914	76.053	340.918	−3.562
5100	58.149	430.727	376.662	275.729	75.718	346.219	−3.546
5200	58.151	431.856	377.713	281.544	75.400	351.525	−3.531
5300	58.153	432.963	378.745	287.359	75.099	356.839	−3.517
5400	58.155	434.050	379.759	293.175	74.815	362.157	−3.503
5500	58.156	435.118	380.756	298.990	74.549	367.481	−3.490
5600	58.158	436.165	381.736	304.806	74.303	372.809	−3.477
5700	58.159	437.195	382.700	310.622	74.075	378.141	−3.465
5800	58.161	438.206	383.648	316.438	73.867	383.478	−3.454
5900	58.162	439.201	384.581	322.254	73.678	388.817	−3.442
6000	58 164	440.178	385.500	328.070	73.509	394.160	−3.431

PREVIOUS: December 1965 (1 bar) CURRENT December 1992 (1 bar)

Chlorosyl Chloride (ClClO) IDEAL GAS $M_r = 86.9048$ Chlorosyl Chloride (ClClO) $Cl_2O_1(g)$

$S°(298.15\ K) = 278.81 \pm 2\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 91 \pm 30\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 90 \pm 30\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^3A''$	0.0	3

Vibrational Levels and Degeneracies ν, (cm^{-1})
961.8 (1)
239.4 (1)
375.1 (1)

Point Group: C_s $\sigma = 1$
Bond Distances: Cl-O = [1.587]Å; Cl-Cl = [2.268] Å
Bond Angle: O-Cl-O = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.6917819 \times 10^{-114}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

Browett *et al.*[1] estimated that D_0(OCl-Cl) = ~130 kJ·mol through an interpretation of the infrared spectrum; this implied $\Delta_f H$ = ~91 kJ·mol.

Dekock *et al.*[2] performed molecular orbital calculations using the MNDO method and reported that the enthalpy of formation of ClClO was 175 kJ·mol less stable than ClOCl. However, on an absolute basis, the numbers appeared to be approximately 50 kJ·mol too large in comparison with experimental data for ClOCl. Lee,[3] using a comparative coupled cluster study, calculated that ClClO is less stable than ClOCl by 62.3 ± 3.8 kJ·mol. Luke[4] calculated the energies of the two isomers (ClOCl and ClClO) at the G2 and G2(MP2) levels and concluded that ClClO was less stable that ClOCl by 71 kJ·mol and 68 kJ·mol respectively. In contrast, Luke referred to a Density Functional Theory (DFT) result, which suggested a difference in stability of 22 kJ·mol. This adopted value suggests that this species is less stable (by ~9 kJ·mol^{-1}) than ClOCl(g).

Heat Capacity and Entropy

Jacox[5] has summarized the IR studies on the three fundamental frequencies.[6-8] The matrix isolated infrared spectrum of this species formed by the photolysis of Cl_2O or the reaction of Cl + O_3 has been observed by several workers.[6,8] Chi and Andrews[8] have observed the argon matrix isolated Raman spectrum of all the isotopic species involving ^{35}Cl, ^{37}Cl, ^{16}O and ^{18}O. The observations of Rochkind and Pimentel[6] are consistent with the more complete results of Chi and Andrews.[8] Chi and Andrews have fitted the results of all the isotopic species to a force field using the estimated bond distances and angle given above. The vibrational frequencies given by Chi and Andrews[8] for the $^{35}Cl_2{}^{16}O$ are used for the thermodynamic calculations. In determining the UV and IR intensities of the ClClO molecule, Johnsson *et al.*[9] reported ν values (961.9, 240.2, 374.2 cm^{-1}) which agree closely with our adopted values. Lee,[3] Luke[4] and Morris and Bhatia[10] have calculated the three vibrational frequencies which are in good agreement with the experimental values.

The bond distances and angles used by Chi and Andrews in their normal coordinate treatment have been used to compute the moments of inertia for naturally occurring isotopic species. The principle moments of inertia (in g·cm^2) are: $I_A = [2.5010 \times 10^{-39}]$, $I_B = [24.7879 \times 10^{-39}]$, $I_C = [27.2889 \times 10^{-39}]$ In comparison, Lee[3] calculated (CCSD[*T*]) a bond angle of 114.2° and *r*(Cl-Cl) = 2.232 Å and *r*(Cl-O) = 1.545 Å; Luke[4] calculated (MP2/6-31G(D)) a bond angle of 116.7° and *r*(Cl-Cl) = 2.366 Å and *r*(Cl-O) = 1.524 Å; Morris and Bhatia[10] calculated (HF/6-31G) a bond angle of 111.3° and *r*(Cl-Cl) = 2.040 Å and *r*(Cl-O) = 1.528 Å. The latter results agree with the calculations of Luke[4] who also used this level of calculation.

The reactive scattering work of Browett *et al.*[1] concluded that the bent molecule has a $^3A''$ symmetry.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−12.223	91.300	91.300	INFINITE
100	37.727	231.482	319.302	−8.782	90.376	94.794	−49.515
200	44.869	260.094	283.158	−4.613	90.052	99.375	−25.954
250	47.105	270.357	279.602	−2.311	90.006	101.712	−21.251
298.15	48.841	278.807	278.807	.000	90.000	103.967	−18.215
300	48.901	279.109	278.808	.090	90.000	104.054	−18.117
350	50.370	286.761	279.409	2.573	90.026	106.394	−15.878
400	51.573	293.569	280.761	5.123	90.077	108.729	−14.199
450	52.555	299.702	282.530	7.727	90.147	111.057	−12.891
500	53.358	305.282	284.531	10.376	90.229	113.376	−11.844
600	54.559	315.123	288.831	15.775	90.417	117.988	−10.272
700	55.385	323.600	293.207	21.275	90.618	122.567	−9.146
800	55.970	331.035	297.480	26.844	90.819	127.118	−8.300
900	56.395	337.654	301.583	32.464	91.015	131.643	−7.640
1000	56.712	343.613	305.493	38.120	91.204	136.147	−7.112
1100	56.954	349.030	309.208	43.804	91.383	140.633	−6.678
1200	57.143	353.994	312.736	49.509	91.552	145.103	−6.316
1300	57.292	358.574	316.089	55.231	91.710	149.559	−6.009
1400	57.412	362.824	319.277	60.966	91.857	154.003	−5.746
1500	57.511	366.789	322.314	66.713	91.992	158.437	−5.517
1600	57.592	370.503	325.211	72.468	92.113	162.863	−5.317
1700	57.659	373.997	327.979	78.230	92.222	167.282	−5.140
1800	57.717	377.294	330.628	83.999	92.315	171.694	−4.982
1900	57.765	380.416	333.167	89.773	92.392	176.102	−4.841
2000	57.807	383.380	335.604	95.552	92.452	180.506	−4.714
2100	57.843	386.201	337.947	101.335	92.493	184.908	−4.599
2200	57.874	388.893	340.202	107.121	92.514	189.308	−4.495
2300	57.902	391.466	342.375	112.909	92.514	193.708	−4.399
2400	57.926	393.931	344.472	118.701	92.490	198.107	−4.312
2500	57.947	396.296	346.498	124.494	92.441	202.509	−4.231
2600	57.966	398.569	348.457	130.290	92.367	206.913	−4.157
2700	57.983	400.757	350.354	136.088	92.266	211.321	−4.088
2800	57.998	402.866	352.192	141.887	92.137	215.733	−4.025
2900	58.012	404.901	353.975	147.687	91.981	220.149	−3.965
3000	58.024	406.868	355.705	153.489	91.796	224.572	−3.910
3100	58.035	408.771	357.387	159.292	91.584	229.002	−3.859
3200	58.046	410.614	359.021	165.096	91.345	233.438	−3.810
3300	58.055	412.400	360.612	170.901	91.081	237.882	−3.765
3400	58.063	414.133	362.161	176.707	90.793	242.335	−3.723
3500	58.071	415.817	363.670	182.514	90.482	246.796	−3.683
3600	58.078	417.453	365.141	188.321	90.151	251.267	−3.646
3700	58.085	419.044	366.577	194.129	89.802	255.747	−3.611
3800	58.091	420.593	367.978	199.938	89.437	260.238	−3.577
3900	58.096	422.102	369.346	205.747	89.060	264.737	−3.546
4000	58.101	423.573	370.684	211.557	88.673	269.247	−3.516
4100	58.106	425.008	371.991	217.368	88.278	273.766	−3.488
4200	58.111	426.408	373.270	223.178	87.879	278.295	−3.461
4300	58.115	427.775	374.522	228.990	87.478	282.834	−3.436
4400	58.119	429.111	375.748	234.801	87.077	287.381	−3.412
4500	58.122	430.418	376.948	240.614	86.680	291.938	−3.389
4600	58.126	431.695	378.124	246.426	86.288	296.503	−3.367
4700	58.129	432.945	379.277	252.239	85.904	301.077	−3.346
4800	58.132	434.169	380.408	258.052	85.529	305.659	−3.326
4900	58.135	435.368	381.518	263.865	85.167	310.250	−3.307
5000	58.137	436.542	382.607	269.679	84.817	314.846	−3.289
5100	58.140	437.694	383.675	275.492	84.482	319.451	−3.272
5200	58.142	438.823	384.725	281.307	84.162	324.060	−3.255
5300	58.144	439.930	385.756	287.121	83.860	328.677	−3.239
5400	58.146	441.017	386.770	292.935	83.575	333.299	−3.224
5500	58.148	442.084	387.766	298.750	83.309	337.926	−3.209
5600	58.150	443.132	388.745	304.565	83.062	342.558	−3.195
5700	58.152	444.161	389.708	310.380	82.834	347.193	−3.182
5800	58.154	445.172	390.656	316.196	82.625	351.834	−3.169
5900	58.155	446.166	391.588	322.011	82.435	356.476	−3.156
6000	58.157	447.144	392.506	327.827	82.265	361.122	−3.144

PREVIOUS: CURRENT December 1995 (1bar)

Chlorosyl Chloride (ClClO) $Cl_2O_1(g)$

Titanium Chloride Oxide ($TiOCl_2$) IDEAL GAS $M_r = 134.7854$ Titanium Chloride Oxide ($TiOCl_2$) $Cl_2O_1Ti_1(g)$

$S°(298.15\ K) = [321.001]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [-543.909]\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [-545.552]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
[455](1)	[250](1)
[849](1)	[250](1)
[120](1)	[180](1)

Ground State Quantum Weights: [1] $\sigma = 2$
Point Group: [C_{2v}]
Bond Distances: O–Ti = [1.62] Å; Ti–Cl = [2.20] Å
Bond Angle: O–Ti–Cl = [120]°
Product of the Moments of Inertia: $I_AI_BI_C = [4.63214 \times 10^{-113}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

$\Delta_fH°(0\ K)$ was estimated as −130 kcal·mol⁻¹ by Gordon.[1] $\Delta_fH°(298.15\ K)$ was then calculated.

Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1] Principal moments of inertia are: $I_A = 17.8783 \times 10^{-39}$, $I_B = 42.7411 \times 10^{-39}$, and $I_C = 60.6194 \times 10^{-39}\ g{\cdot}cm^2$.

Reference

[1] J. S. Gordon, Astrosystems, Inc., Caldwell Twp., N. J., personal communication, (January 10, 1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−16.710	−543.909	−543.909	INFINITE
100	51.425	252.861	380.084	−12.722	−544.846	−541.740	282.976
200	65.445	293.526	327.402	−6.775	−545.309	−538.428	140.623
250	69.250	308.562	322.172	−3.403	−545.448	−536.691	112.135
298 15	71.952	321.001	321.001	0.	−545.552	−534.994	93.729
300	72.041	321.447	321.003	0.133	−545.555	−534.929	93.139
350	74.138	332.717	321.888	3.790	−545.643	−533.150	79.568
400	75.739	342.726	323.879	7.539	−545.719	−531.360	69.389
450	76.976	351.721	326.481	11.358	−545.792	−529.561	61.470
500	77.945	359.883	329.420	15.232	−545.867	−527.754	55.134
600	79.330	374.226	335.725	23.101	−546.035	−524.116	45.628
700	80.243	386.528	342.125	31.082	−546.241	−520.447	38.836
800	80.870	397.286	348.362	39.140	−546.476	−516.747	33.740
900	81.318	406.839	354.338	47.250	−546.780	−513.013	29.775
1000	81.647	415.424	360.025	55.399	−547.219	−509.240	26.600
1100	81.896	423.218	365.421	63.577	−547.862	−505.412	24.000
1200	82.088	430.353	370.539	71.777	−552.693	−501.397	21.825
1300	82.240	436.930	375.396	79.993	−553.020	−497.110	19.974
1400	82.361	443.029	380.012	88.224	−553.438	−492.794	18.386
1500	82.459	448 715	384 405	96.465	−553.958	−488.445	17.009
1600	82.541	454.039	388.592	104.715	−554.596	−484.057	15.803
1700	82.608	459.045	392.591	112.973	−555.366	−479.626	14.737
1800	82.665	463.769	396.415	121.236	−556.281	−475.145	13.788
1900	82.714	468.239	400.079	129.505	−557.357	−470.609	12.938
2000	82.755	472.483	403.594	137.779	−573.294	−465.558	12.159
2100	82.791	476.522	406.971	146.056	−575.482	−460.118	11.445
2200	82.822	480.374	410.221	154.337	−577.690	−454.572	10.793
2300	82.849	484.056	413.351	162.620	−579.919	−448.926	10.195
2400	82.873	487.582	416.371	170.907	−582.172	−443.183	9.646
2500	82.894	490.966	419.288	179.195	−584.450	−437.345	9.138
2600	82.913	494.217	422.108	187.485	−586.753	−431.415	8.667
2700	82.929	497.347	424.837	195.777	−589.084	−425.396	8.230
2800	82.944	500.363	427.481	204.071	−591.441	−419.291	7.822
2900	82.958	503.274	430.044	212.366	−593.827	−413.101	7.441
3000	82.970	506.087	432.532	220.663	−596.241	−406.828	7.084
3100	82.981	508.807	434.949	228.960	−598.682	−400.473	6.748
3200	82.991	511.442	437.299	237.259	−601.150	−394.041	6.432
3300	83.000	513.996	439.584	245.558	−603.643	−387.530	6.134
3400	83.008	516.474	441.810	253.859	−606.161	−380.943	5.852
3500	83.016	518.880	443.977	262.160	−608.701	−374.283	5.586
3600	83.023	521.219	446.091	270.462	−611.261	−367.549	5.333
3700	83.029	523.494	448.152	278.764	−1022.938	−352.955	4.983
3800	83.035	525.708	450.164	287.068	−1024.297	−334.829	4.603
3900	83.041	527.865	452.129	295.371	−1025.725	−316.667	4.241
4000	83.046	529.968	454.049	303.676	−1027.217	−298.467	3.898
4100	83.051	532.018	455.925	311.981	−1028.768	−280.229	3.570
4200	83.055	534.020	457.761	320.286	−1030.375	−261.953	3.258
4300	83.059	535.974	459.557	328.592	−1032.034	−243.637	2.960
4400	83.063	537.883	461.316	336.898	−1033.739	−225.283	2.674
4500	83.066	539.750	463.038	345.204	−1035.487	−206.890	2.402
4600	83.070	541.576	464.726	353.511	−1037.273	−188.457	2.140
4700	83.073	543.362	466.380	361.818	−1039.093	−169.985	1.889
4800	83.076	545.111	468.002	370.126	−1040.943	−151.474	1.648
4900	83.079	546.824	469.593	378.433	−1042.819	−132.923	1.417
5000	83.081	548.503	471.155	386.741	−1044.718	−114.335	1.194
5100	83.084	550.148	472.687	395.049	−1046.636	−95.708	0.980
5200	83.086	551.761	474.193	403.358	−1048.570	−77.044	0.774
5300	83.088	553.344	475.671	411.667	−1050.516	−58.342	0.575
5400	83.090	554.897	477.124	419.976	−1052.473	−39.603	0.383
5500	83.092	556.422	478.552	428.285	−1054.437	−20.829	0.198
5600	83.094	557.919	479.956	436.594	−1056.406	−2.018	0.019
5700	83.096	559.390	481.337	444.903	−1058.379	16.828	−0.154
5800	83.097	560.835	482.695	453.213	−1060.352	35.709	−0.322
5900	83.099	562.256	484.031	461.523	−1062.325	54.623	−0.484
6000	83.100	563.652	485.347	469.833	−1064.296	73.571	−0.640

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

Titanium Chloride Oxide ($TiOCl_2$) $Cl_2O_1Ti_1(g)$

Chlorine Oxide (ClOOCl) IDEAL GAS $M_r = 102.9042$ Chlorine Oxide (ClO_2Cl) $Cl_2O_2(g)$

$S(298.15\ K) = 300.98 \pm 5\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 136.5 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 133.0 \pm 8\ kJ \cdot mol^{-1}$

Vibrational Levels and Degeneracies

ν, cm^{-1}	ν, cm^{-1}
765 (1)	649.9 (1)
647.6 (1)	[440] (1)
[320] (1)	127 (1)

Ground State Quantum Weight = [1] $\sigma = 1$
Point Group: C_2
Bond Distances: Cl–O = 1.7044 ± 0.001 Å; O–O = 1.4259 ± 0.0021 Å
Bond Angles: ClOO = 110.07 ± 0.1°; dihedral angle = 81.03 ± 0.8°
Product of the Moments of Inertia: $I_A I_B I_C = 8.996135 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation has been obtained from kinetic and equilibrium measurements of the rate of self reaction of ClO and the decomposition of the dimer to form the monomer unit. The results of these studies, as summarized by Cox and Hayman[1] indicate the dimer is bound by 17 kcal·mol^{-1} relative to the monomeric ClO. The $\Delta_r H$ and $\Delta_r S$, as determined by a lnK vs $1/T$ plot in the temperature range of 203–300 K, of the reaction of two monomeric units to form the dimer is -72.5 ± 3.0 kJ·mol^{-1} and -144 ± 11 J·K^{-1}·mol^{-1} respectively.[1] In this study, optical cross sections of the chlorine oxide species were used to determine the equilibrium constants as a function of temperature, from which the thermodynamic properties of the reaction of ClO to form $(ClO)_2$ were determined. These results are in agreement with previous results within combined experimental errors for the enthalpy of this reaction.[2] The cross sections measured by Cox and Hayman[1] are in agreement with recent results of Burkholder *et al.*[3] who measured the ultraviolet cross sections between 210 and 410 nm for $(ClO)_2$. These authors[3] also measured the infrared spectrum of $(ClO)_2$ and Cl_2O_3 in the region of 500 to 2000 cm^{-1} using a Fourier transform infrared spectrometer. Using the enthalpy of reaction given by Cox and Hayman[1] and the dissociation energy of ClO as determined by Coxon and Ramsay,[4] and the $^2\Pi_{1/2}$–$^2\Pi_{3/2}$ splitting A = 320 cm^{-1},[5] gives the value of 133 kJ·mol^{-1} at 298.15 K for the enthalpy of formation of $(ClO)_2$ with an estimated uncertainty of 8 kJ·mol^{-1}.

Heat Capacity and Entropy

The microwave spectrum of this species had been obtained by Birk *et al.*[6] The observered microwave spectrum is in substantial agreement with the earlier theoretical calculations which gave estimates of both the vibrational frequencies and molecular dimensions of the ClO dimer.[7] The molecular dimensions were used to compute the inertial parameters for the normally occuring isotopic species. The computed entropy for the $(ClO)_2$ species at 298.15 K is 300.98 J·K^{-1}·mol^{-1}. The measured entropy for the dimerization of ClO combined with the entropy of formation for ClO gave an $S°$(298.15 K) of 305.92 ± 11 J·mol^{-1}·K^{-1}. The major uncertainty in the computed entropy are the estimated frequencies 320 and 440 cm^{-1}. Lowering these estimated frequencies to 250 and 350 cm^{-1} increases the comuted $S°$(298.15 K) by 3.18 J·K^{-1}·mol^{-1}. This would decrease the calculated $\Delta_r S$, for the dimerization of ClO from −149 to −146 J·K^{-1}·mol^{-1} compared to the measured $\Delta_r S$ of −144 ± 11 J·K^{-1}·mol^{-1}.[1]

The vibrational spectrum of this species in the infrared region of 500 to 2000 cm^{-1} has been observed by Burkholder *et al.*[3] They observed three features that they could assign to $(ClO)_2$ at 750, 653 and 560 cm^{-1}. The two higher frequency absorptions correspond to the 750, 649, and 647 cm^{-1} found by Cheng and Lee[7] in the matrix isolated infrared spectra of the products of the reactions described below. These workers observed the three stretching modes by trapping the molecules formed, in a discharge system, by the reactions: Cl + O_3, Cl + OClO, O + OClO, Cl + ClOCl, and O + ClOCl in an argon matrix at 12 K. They obtained the Cl–O, (649.9 and 647.6 cm^{-1}) and O–O (752.6 cm^{-1}) stretching fundamentals, which have appropriate ^{35}Cl–^{37}Cl isotope shifts. The torsional mode, 127 cm^{-1}, estimated from the microwave measurements,[6] is in excellent agreement with the 119 cm^{-1} obtained in the quantum mechanical calculation.[7] The bending modes, 320 and 440 cm^{-1}, are obtained from the quantum mechanical calculation.[7]

Others have studied the infrared spectrum of the self reaction of ClO by reacting Cl with O_3, Cl_2O, or OClO in a flow system.[8] These workers observed the Cl–O and O–O stretching modes in addition to absorptions in the 1000 to 1250 cm^{-1} region, which they ascribed to $(ClO)_2$. Later workers suggest these bands are due to Cl_2O_3 produced from the termolecular reaction of OClO with ClO, including Burkholder et al.[3] and Cheng and Lee[6] and supported by quantum mechanical calculations of the frequencies of the $-ClO_2$ moiety.[6] Earlier workers who studied the infrared spectrum formed by reacting Cl + O_3 in a matrix have observed other absorptions which are probably due to other chlorine oxygen species.[9-12]

The principle moments of inertia (in g·cm^2) are: $I_A = 6.4270 \times 10^{-39}$, $I_B = 35.2686 \times 10^{-39}$, and $I_C = 39.6879 \times 10^{-39}$.

References

[1] R. A. Cox and G. D. Hayman, Nature **332**, 796 (1988).
[2] N. Basco and J. E. Hunt, Int. J. Chem. Kinetics **11**, 649 (1979).

Continued on page 939

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−14.410	136.454	136.454	INFINITE
100	42.140	244.047	351.478	−10.743	134.305	146.131	−76.331
200	54.797	277.119	306.612	−5.899	133.200	158.466	−41.387
250	60.367	289.965	302.025	−3.015	133.007	164.809	−34.435
298.15	64.703	300.983	300.983	.000	133.000	170.938	−29.948
300	64.850	301.384	300.984	.120	133.003	171.173	−29.804
350	68.331	311.653	301.787	3.453	133.141	177.525	−26.494
400	71.010	320.960	303.611	6.940	133.381	183.851	−24 008
450	73.080	329.449	306.018	10.544	133.693	190.141	−22.071
500	74.694	337.235	308.756	14.240	134.052	196.395	−20.517
600	76.985	351.072	314.684	21.832	134.852	208.789	−18.177
700	78.481	363.059	320.758	29.611	135.704	221.045	−16.495
800	79.502	373.610	326.718	37.513	136.570	233.178	−15.225
900	80.226	383.018	332.461	45.501	137.432	245.202	−14.231
1000	80.757	391.499	337.947	53.552	138.284	257.130	−13.431
1100	81.157	399.216	343.172	61.648	139.121	268.975	−12.773
1200	81.465	406.291	348.141	69.780	139.943	280.743	−12.220
1300	81.707	412.822	352.869	77.939	140.746	292.444	−11.751
1400	81.901	418.884	357.370	86.120	141.532	304.083	−11.345
1500	82.058	424.540	361.662	94.318	142.298	315.667	−10.992
1600	82.187	429.840	365.759	102.531	143.043	327.200	−10.682
1700	82.295	434.826	369.676	110.755	143.767	338.688	−10.407
1800	82.386	439.533	373.428	118.989	144.468	350.133	−10.161
1900	82.463	443.989	377.025	127.231	145.144	361.541	−9.939
2000	82.528	448.221	380.480	135.481	145.793	372.913	−9.739
2100	82.585	452.249	383.803	143.737	146.415	384.254	−9.558
2200	82.634	456.092	387.002	151.998	147.007	395.566	−9.392
2300	82.677	459.766	390.086	160.264	147.568	406.851	−9.240
2400	82.715	463.286	393.063	168.533	148.096	418.112	−9.100
2500	82.749	466.663	395.940	176.806	148.590	429.353	−8.971
2600	82.779	469.909	398.723	185.083	149.048	440.574	−8.851
2700	82.805	473.034	401.418	193.362	149.470	451.779	−8.740
2800	82.829	476.045	404.030	201.644	149.855	462.969	−8.637
2900	82.850	478.952	406.563	209.928	150.203	474.144	−8.540
3000	82.869	481.761	409.024	218.214	150.514	485.310	−8.450
3100	82.887	484.479	411.414	226.502	150.789	496.466	−8.365
3200	82.903	487.111	413.739	234.791	151.029	507.612	−8.286
3300	82.917	489.662	416.001	243.082	151.235	518.752	−8.211
3400	82.930	492.138	418.204	251.374	151.409	529.886	−8.141
3500	82.942	494.542	420.351	259.668	151.553	541.015	−8.074
3600	82.953	496.878	422.444	267.963	151.670	552.141	−8.011
3700	82.963	499.151	424.487	276.259	151.762	563.264	−7.952
3800	82.973	501.364	426.481	284.555	151.831	574.385	−7.895
3900	82.982	503.519	428.429	292.853	151.881	585.505	−7.842
4000	82.990	505.620	430.332	301.152	151.915	596.622	−7.791
4100	82.997	507.670	432.194	309.451	151.935	607.740	−7.743
4200	83.004	509.670	434.015	317.751	151.944	618.857	−7.697
4300	83.011	511.623	435.797	326.052	151.946	629.974	−7.653
4400	83.017	513.531	437.542	334.353	151.942	641.090	−7.611
4500	83.022	515.397	439.252	342.655	151.935	652.207	−7.571
4600	83.027	517.222	440.927	350.958	151.929	663.324	−7.532
4700	83.032	519.008	442.569	359.261	151.923	674.442	−7.496
4800	83.037	520.756	444.180	367.564	151.922	685.559	−7.460
4900	83.041	522.468	445.760	375.868	151.926	696.677	−7.427
5000	83.046	524.146	447.311	384.172	151.936	707.794	−7.394
5100	83.049	525.790	448.834	392.477	151.955	718.912	−7.363
5200	83.053	527.403	450.329	400.782	151.982	730.027	−7.333
5300	83.056	528.985	451.799	409.088	152.020	741.144	−7.304
5400	83.060	530.537	453.242	417.394	152.067	752.259	−7.277
5500	83.063	532.062	454.662	425.700	152.125	763.373	−7.250
5600	83.066	533.558	456.057	434.006	152.194	774.486	−7.224
5700	83.068	535.029	457.430	442.313	152.272	785.598	−7.199
5800	83.071	536.473	458.780	450.620	152.362	796.709	−7.175
5900	83.074	537.893	460.109	458.927	152.460	807.816	−7.152
6000	83.076	539.290	461.417	467.234	152.568	818.923	−7.129

PREVIOUS: CURRENT. December 1992 (1 bar)

Chloryl Chloride (ClOClO) IDEAL GAS $M_r = 102.9042$ Chloryl Chloride (ClOClO) Cl_2O_2(g)

$S°(298.15\ K) = 309.17 \pm 2.0\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 178.8 \pm 10\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = 176.4 \pm 15\ kJ{\cdot}mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
952(1)
648(1)
403(1)
341(1)
236(1)
90(1)

Ground State Quantum Weight = [1]
Point Group: C_1
Bond Distances: Cl-O = 1.726 Å; O-Cl' = 1.814 Å; Cl'-O' = 1.532 Å
Bond Angles: ClOCl' = 111.0°; OCl'O' = 113.5°; dihedral angle: = 75.7°
Product of the Moments of Inertia: $I_AI_BI_C = 8.362433 \times 10^{-114}\ g^3{\cdot}cm^6$

Enthalpy of Formation

The enthalpy of formation has been calculated, by numerous quantum mechanical methods, by McGrath, *et al.*[1,2] and Lee.[3] These calculations suggested that the ClOClO isomer is less stable than the ClOOCl isomer by 31 to 42 $kJ{\cdot}mol^{-1}$. We adopt the results of Lee[3] which stated that the ClOClO isomer was 10.1 $kcal{\cdot}mol^{-1}$ or 42.3 $kJ{\cdot}mol^{-1}$ higher in energy than the ClOOCl isomer at $T/K = 0$.

Heat Capacity and Entropy

The structure and harmonic vibrational frequencies of ClOClO have been calculated, by numerous quantum mechanical methods, by McGrath, *et al.*,[1,2] Lee,[3] and Rendell and Lee.[4] We adopt the results of Lee.[3] The structures (bond distances and bond angles), as presented in these above mentioned studies are in fair agreement: within 5%, except for the dihedral angle where the difference is approximately 11%. The principal moments of inertia are (in $g{\cdot}cm^2$): $I_A = 6.2905 \times 10^{-39}$, $I_B = 34.7070 \times 10^{-39}$, and $I_C = 38.3028 \times 10^{-39}$.

References

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[4] A. P. Rendell and T. J. Lee, J. Chem. Phys. 94, 6219 (1991).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	S° (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_fH°$ (kJ·mol⁻¹)	$\Delta_fG°$ (kJ·mol⁻¹)	log K_f
0	.000	.000	INFINITE	−15.476	178.754	178.754	INFINITE
100	46.365	247.309	363.316	−11.601	176.813	188.313	−98.365
200	59.481	283.809	315.103	−6.259	176.206	200.134	−52.270
250	64.001	297.588	310.257	−3.167	176.221	206.117	−43.066
298.15	67.416	309.165	309.165	.000	176.366	211.864	−37.118
300	67.532	309.583	309.166	.125	176.374	212.084	−36.927
350	70.293	320.209	309.999	3.573	176.627	218.017	−32.537
400	72.460	329.742	311.882	7.144	176.952	223.909	−29.239
450	74.169	338.379	314.353	10.812	177.326	229.756	−26.669
500	75.529	346.267	317.156	14.555	177.733	235.560	−24.609
600	77.505	360.225	323.201	22.214	178.600	247.045	−21.507
700	78.828	372.278	329.371	30.035	179.494	258.382	−19.281
800	79.748	382.868	335.410	37.966	180.389	269.591	−17.602
900	80.408	392.301	341.217	45.976	181.273	280.688	−16.291
1000	80.897	400.799	346.757	54.042	182.141	291.687	−15.236
1100	81.267	408.528	352.026	62.151	182.990	302.601	−14.369
1200	81.554	415.612	357.034	70.293	183.821	313.437	−13.644
1300	81.781	422.149	361.795	78.460	184.633	324.206	−13.027
1400	81.963	428.216	366.325	86.648	185.425	334.912	−12.496
1500	82.111	433.876	370.642	94.852	186.197	345.562	−12.034
1600	82.233	439.180	374.762	103.069	186.948	356.162	−11.628
1700	82.335	444.168	378.699	111.298	187.676	366.716	−11.268
1800	82.421	448.877	382.468	119.535	188.380	377.227	−10.947
1900	82.494	453.335	386.082	127.781	189.060	387.700	−10.659
2000	82.556	457.568	389.551	136.034	189.712	398.137	−10.398
2100	82.610	461.597	392.887	144.292	190.337	408.543	−10.162
2200	82.657	465.442	396.098	152.556	190.931	418.921	−9.946
2300	82.698	469.117	399.193	160.823	191.494	429.271	−9.749
2400	82.734	472.637	402.181	169.095	192.024	439.597	−9.568
2500	82.766	476.015	405.067	177.370	192.519	449.902	−9.400
2600	82.794	479.262	407.859	185.648	192.979	460.188	−9.245
2700	82.820	482.387	410.561	193.929	193.403	470.458	−9.102
2800	82.842	485.399	413.181	202.212	193.789	480.712	−8.968
2900	82.863	488.307	415.721	210.497	194.139	490.952	−8.843
3000	82.881	491.116	418.188	218.785	194.451	501.182	−8.726
3100	82.898	493.834	420.585	227.074	194.727	511.402	−8.617
3200	82.913	496.466	422.915	235.364	194.968	521.613	−8.514
3300	82.927	499.018	425.183	243.656	195.175	531.817	−8.418
3400	82.939	501.494	427.391	251.949	195.350	542.016	−8.327
3500	82.951	503.898	429.543	260.244	195.495	552.210	−8.241
3600	82.961	506.235	431.641	268.539	195.613	562.400	−8.160
3700	82.971	508.508	433.688	276.836	195.705	572.587	−8.083
3800	82.980	510.721	435.686	285.134	195.775	582.773	−8.011
3900	82.988	512.877	437.638	293.432	195.826	592.956	−7.942
4000	82.996	514.978	439.545	301.731	195.860	603.138	−7.876
4100	83.003	517.027	441.410	310.031	195.881	613.320	−7.814
4200	83.010	519.027	443.234	318.332	195.891	623.501	−7.754
4300	83.016	520.981	445.020	326.633	195.893	633.683	−7.698
4400	83.022	522.889	446.768	334.935	195.890	643.864	−7.644
4500	83.027	524.755	448.480	343.238	195.884	654.044	−7.592
4600	83.032	526.580	450.158	351.541	195.877	664.226	−7.543
4700	83.037	528.366	451.803	359.844	195.873	674.407	−7.495
4800	83.042	530.114	453.417	368.148	195.872	684.589	−7.450
4900	83.046	531.826	454.999	376.452	195.876	694.771	−7.406
5000	83.050	533.504	456.553	384.757	195.887	704.952	−7.365
5100	83.053	535.149	458.078	393.062	195.906	715.134	−7.324
5200	83.057	536.762	459.575	401.368	195.934	725.314	−7.286
5300	83.060	538.344	461.047	409.674	195.972	735.495	−7.249
5400	83.063	539.896	462.493	417.980	196.019	745.673	−7.213
5500	83.066	541.420	463.914	426.286	196.078	755.851	−7.178
5600	83.069	542.917	465.311	434.593	196.147	766.029	−7.145
5700	83.072	544.388	466.686	442.900	196.226	776.204	−7.113
5800	83.074	545.832	468.038	451.207	196.315	786.380	−7.082
5900	83.076	547.252	469.369	459.515	196.414	796.551	−7.052
6000	83.079	548.649	470.678	467.823	196.522	806.722	−7.023

PREVIOUS. CURRENT: December 1992 (1 bar)

Chloryl Chloride (ClOClO) Cl_2O_2(g)

Chlorine Chlorite ($ClClO_2$) IDEAL GAS $M_r = 102.9042$ Chlorine Chlorite ($ClClO_2$) $Cl_2O_4(g)$

$S°(298.15 K) = 294.41 \pm 2.0 J·K^{-1}·mol^{-1}$

$\Delta_f H°(0 K) = 140.7 \pm 12 kJ·mol^{-1}$
$\Delta_f H°(298.15 K) = 136.6 \pm 16 kJ·mol^{-1}$

Vibrational Levels and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1041.5(1)	271.4(1)
522.7(1)	1281.2(1)
440.5(1)	251.4(1)

Ground State Quantum Weight = [1]
Point Group: C_s
Bond Distances: Cl-O = 1.440 ± 0.005 Å; Cl-Cl = 2.22 ± 0.06 Å
Bond Angles: $\angle$(ClClO) = 103.5 ± 1°; $\angle$(OClO) = 116.0 ± 0.5°
Product of the Moments of Inertia: $I_A I_B I_C = 6614.3322 \times 10^{-117}$ $g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation has been calculated, by numerous quantum mechanical methods, by McGrath, *et al.*[1,2], Lee *et al.*,[3] Jensen and Oddershede,[4] and Stanton, *et al.*[5] These calculations suggested that the $ClClO_2$ isomer is less stable than the ClOOCl isomer by 4.2 to 32 $kJ·mol^{-1}$. We adopt the results of Lee[3] which stated that the $ClClO_2$ isomer was 4.2 $kJ·mol^{-1}$ higher in energy than the ClOOCl isomer at $T/K = 0$.

Heat Capacity and Entropy

The vibrational frequencies (ν_1, ν_2, ν_3, and ν_5) are taken from the gas phase infared studies of Müller and Willner,[6,7] while ν_4 and ν_6 are taken from the Ne martrix infrared studies of Müller and Willner.[6,8] The same authors also provided values for all vibrational frequencies in Ne matrices, as well as values for ν_1 and ν_5 in Ar matrices.

The structure is that estimated by Müller and Willner.[6] The results were based on a combination of: use of product rules in the symmetry class A" with vibrational frequencies of four independent isotopomers, in conjunction with expermental and ab initio results of related compounds. The principal moments of inertia are (in $g·cm^2$): $I_A = 9.0179 \times 10^{-39}$, $I_B = 23.8814 \times 10^{-39}$, and $I_C = 30.7121 \times 10^{-39}$.

References

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[2] M. P. McGrath, K. C. Clemitshaw, F. S. Rowland, and W. J. Hehre, J. Phys. Chem. 94, 6126 (1990).
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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−13.762	140.652	140.652	INFINITE
100	39.852	239.842	342.580	−10.274	138.324	150.571	−78.650
150	47.043	257.397	311.376	−8.097	137.558	156.873	−54.628
200	52.769	271.751	299.727	−5.595	137.054	163.393	−42.674
250	57.214	284.022	295.388	−2.841	136.731	170.019	−35.523
298.15	60.703	294.407	294.407	.000	136.550	176.448	−30.913
300	60.825	294.783	294.408	.112	136.545	176.696	−30.765
350	63.852	304.393	295.160	3.231	136.469	183.395	−27.370
400	66.416	313.092	296.867	6.490	136.482	190.099	−24.824
450	68.589	321.043	299.118	9.867	136.565	196.796	−22.844
500	70.429	328.368	301.681	13.343	136.705	203.482	−21.258
600	73.306	341.477	307.247	20.538	137.108	216.802	−18.874
700	75.381	352.942	312.973	27.978	137.621	230.045	−17.166
800	76.901	363.112	318.617	35.596	138.203	243.209	−15.880
900	78.036	372.238	324.077	43.345	138.826	256.297	−14.875
1000	78.898	380.507	329.313	51.194	139.476	269.315	−14.068
1100	79.566	388.059	334.315	59.118	140.142	282.267	−13.404
1200	80.092	395.006	339.087	67.102	140.815	295.158	−12.848
1300	80.513	401.434	343.639	75.133	141.491	307.992	−12.375
1400	80.854	407.413	347.983	83.202	142.164	320.775	−11.968
1500	81.133	413.001	352.133	91.302	142.832	333.509	−11.614
1600	81.366	418.245	356.103	99.427	143.490	346.200	−11.302
1700	81.560	423.184	359.905	107.574	144.136	358.849	−11.026
1800	81.725	427.851	363.552	115.738	144.767	371.461	−10.780
1900	81.866	432.273	367.053	123.918	145.380	384.038	−10.558
2000	81.987	436.476	370.420	132.111	145.973	396.584	−10.358
2100	82.092	440.478	373.662	140.315	146.543	409.100	−10.176
2200	82.183	444.299	376.786	148.529	147.088	421.591	−10.010
2300	82.263	447.954	379.802	156.751	147.606	434.056	−9.858
2400	82.333	451.457	382.715	164.981	148.094	446.499	−9.718
2500	82.396	454.819	385.532	173.218	148.551	458.923	−9.589
2600	82.451	458.052	388.260	181.460	148.975	471.330	−9.469
2700	82.501	461.165	390.902	189.708	149.365	483.721	−9.358
2800	82.545	464.166	393.466	197.960	149.721	496.098	−9.255
2900	82.585	467.063	395.954	206.217	150.042	508.462	−9.158
3000	82.622	469.863	398.371	214.477	150.327	520.817	−9.068
3100	82.654	472.573	400.721	222.741	150.578	533.163	−8.984
3200	82.684	475.198	403.008	231.008	150.796	545.500	−8.904
3300	82.711	477.743	405.234	239.278	150.981	557.831	−8.830
3400	82.736	480.212	407.403	247.550	151.135	570.158	−8.759
3500	82.759	482.611	409.518	255.825	151.260	582.480	−8.693
3600	82.780	484.942	411.581	264.102	151.359	594.799	−8.630
3700	82.799	487.211	413.594	272.381	151.434	607.116	−8.571
3800	82.817	489.419	415.561	280.662	151.487	619.431	−8.515
3900	82.834	491.571	417.482	288.944	151.522	631.746	−8.461
4000	82.849	493.668	419.361	297.228	151.541	644.058	−8.411
4100	82.863	495.714	421.198	305.514	151.548	656.371	−8.362
4200	82.876	497.711	422.996	313.801	151.544	668.684	−8.316
4300	82.888	499.661	424.757	322.089	151.533	680.997	−8.272
4400	82.900	501.567	426.481	330.378	151.517	693.310	−8.231
4500	82.911	503.430	428.170	338.669	151.499	705.623	−8.191
4600	82.921	505.252	429.826	346.961	151.481	717.937	−8.152
4700	82.930	507.036	431.450	355.253	151.466	730.252	−8.116
4800	82.939	508.782	433.043	363.547	151.454	742.567	−8.081
4900	82.947	510.492	434.606	371.841	151.448	754.882	−8.047
5000	82.955	512.168	436.141	380.136	151.450	767.197	−8.015
5100	82.962	513.811	437.648	388.432	151.459	779.512	−7.984
5200	82.969	515.422	439.128	396.728	151.479	791.826	−7.954
5300	82.976	517.002	440.582	405.026	151.508	804.141	−7.925
5400	82.982	518.553	442.012	413.324	151.547	816.454	−7.898
5500	82.988	520.076	443.417	421.622	151.598	828.766	−7.871
5600	82.993	521.571	444.800	429.921	151.659	841.078	−7.845
5700	82.999	523.040	446.159	438.221	151.730	853.388	−7.820
5800	83.004	524.484	447.497	446.521	151.813	865.698	−7.796
5900	83.008	525.903	448.814	454.821	151.905	878.004	−7.773

PREVIOUS.   CURRENT. December 1992 (1 bar)

Sulfuryl Chloride (SO_2Cl_2) IDEAL GAS $M_r = 134.9648$ Sulfuryl Chloride (SO_2Cl_2) $Cl_2O_2S_1(g)$

$\Delta_f H°(0\ K) = -348.56 \pm 2.1\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = 311.095 \pm 0.4\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -354.80 \pm 2.1\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies (ω, cm^{-1}, all singly degenerate)								
1205	577	406	209	208	1434	388	586	363

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: C_{2v}

Bond Distances: S–O = 1.404 ± 0.004 Å; S–Cl = 2.011 ± 0.005 Å

Bond Angles: O–S–O = 123.5 ± 0.8°; Cl–S–Cl = 100.0 ± 0.7°

Product of the Moments of Inertia: $I_A I_B I_C = 3.80579 \times 10^{-113}\ g^3\cdot cm^6$

Enthalpy of Formation

The adopted $\Delta_f H° = -84.8 \pm 0.5\ kcal\cdot mol^{-1}$ is based on K_p for dissociation to SO_2 and Cl_2 (see below). The relatively thorough study of Arii[2] gave similar values of K_p near the pressure of SO_2Cl_2 and at reduced pressures. The entropy discrepancy is large ($\delta S = -11\ cal\cdot K^{-1}\cdot mol^{-1}$), but this may be due to the small temperature range and to uncertainties in absorption on the activated charcoal catalyst. Absorption uncertainties probably exist in all of the K_p studies, but the high– temperature data of Trautz[3] have an additional uncertainty; i.e., K_p is very sensitive to small systematic errors in the data since the SO_2Cl_2 is almost completely decomposed. Exclusion of data[3] above 416 K yields a 3rd law $\Delta_r H°$ which agrees satisfactorily with Arii.[2] Data of Londergan[1] yield a 3rd law $\Delta_r H°$ which is smaller by about 0.4 $kcal\cdot mol^{-1}$; these data yield almost no entropy discrepancy, but the experimental method[1] appears to be less satisfactory.

The adopted $\Delta_f H°$ is consistent with old calorimetric data of Thomsen[5] for hydrolysis of the liquid but inconsistent with recent data of Neale and Williams,[4] on which the selections of NBS 270–3[6] are probably based. Consistency tests require $\Delta_v H$, thus, we note that in the absence of a catalyst $SO_2Cl_2(g)$ persists to well above the boiling point even though it is unstable with respect to SO_2 and Cl_2. Evidence for this conclusion includes studies of catalysts,[3 7] vapor densities,[8] boiling point and vapor pressures.[9 10 7] The boiling point (69.5 ± 0.3 °C) and $\Delta_{vap}S$ (20.8 $cal\cdot K^{-1}\cdot mol^{-1}$) are almost exactly those predicted by comparison with SO_2ClF (7.3 °C and 20.6 $cal\cdot K^{-1}\cdot mol^{-1}$) and SO_2F_2 (−55.3°C and 21.1 $cal\cdot K^{-1}\cdot mol^{-1}$), which have normal vapors. Vapor pressure data[9] for SO_2Cl_2 yield $\Delta_v H = 7.1\ kcal\cdot mol^{-1}$ at 69.5 °C and $\Delta_v H° = 7.8\ kcal\cdot mol^{-1}$ at 25°C. Trautz *et al.*[10] used a condensation method to measure $\Delta_{vap}H = 6.67\ kcal\cdot mol^{-1}$ near Tb, but we dismiss this value since the resulting $\Delta_{vap}S$ (19.5 $cal\cdot K^{-1}\cdot mol^{-1}$) is too small for normal vapor and much too small for dissociating vapor.

Source	Data	Reaction[a]	T/K	$\Delta_r H°$(298.15 K), $kcal\cdot mol^{-1}$ 2nd law	3rd law	δS, $cal\cdot K^{-1}mol^{-1}$	$\Delta_f H°$(298.15 K), kcal·mol[b] gas	liquid
[1]	K_p	A	340–373	13.08 ± 0.05	13.41 ± 0.3	−0.9 ± 0.1	−84.36	(−92.1)
[2]	K_p	A	303–323	10.41 ± 0.13	13.84 ± 0.2	−10.9 ± 0.4	−84.79	(−92.6)
[3]	K_p	A	375–464	6.33 ± 0.51	14.2 ± 1.1	−19.2 ± 1.2	−85.2	(−93.0)
			375–416	—	13.91 ± 0.4	—	−84.86	(−92.7)
[4]	$\Delta_r H$	B	295–296	—	−63.4 ± 0.5[c]	—	(−86.1)	−93.9
[5]	$\Delta_r H$	B	291–293	—	−63.6 ± 0.5			
[6]	4?	B?	298?	—	−63.1	—	−87.0	−94.2

[a] A) $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$; B) $SO_2Cl_2(l) + 2\ H_2O(l) \rightarrow [H_2SO_4 + 2HCl](nH_2O)$

[b] Values in parentheses calculated from $\Delta_{vap}H° = 7.8\ kcal\cdot mol^{-1}$ at 25°C.

[c] Calorimetric $\Delta_r H$ adjusted to 25°C.

Heat Capacity and Entropy

Bond lengths and bond angles are those derived from new electron–diffraction data by Hargittai.[11] These differ significantly from early results of Palmer.[12] Microwave spectra were reported by Abbar,[13] but structural parameters were not derived from the data. The adopted structure has an O–S–Cl angle of 107.7° and principal moments of inertia of $I_A = 24.0520 \times 10^{-39}$, $I_B = 36.0706 \times 10^{-39}$, and $I_C = 43.8672 \times 10^{-39}\ g\cdot cm^2$.

The vibrational assignment is from force–constant calculations of Toyuki and Shimizu.[14] Pfeiffer's assignment[15] is only slightly different and results in negligible change in the thermodynamic functions. Spectral data were summarized by Gillespie and Robinson[16] in their study of the liquid–phase Raman spectra. Only those frequencies above 500 cm^{-1} are based on gas–phase spectra. Trautz *et al.*[10] found $C_p = 15.4 \pm 0.3\ J\cdot K^{-1}\cdot mol^{-1}$ by calorimetry at 43 mmHg and 16 to 99°C; this C_p is too low, like $\Delta_{vap}H$,[10] and the error is almost 20%.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	S° (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−16.028	−348.555	−348.555	INFINITE
100	43.179	245.860	370.394	−12.453	−351.487	−338.589	176.861
200	64.505	282.771	317.789	−7.004	−353.628	−324.765	84.820
250	71.750	297.982	312.336	−3.589	−354.309	−317.466	66.331
298.15	77.095	311.095	311.095	0.	−354.803	−310.323	54.367
300	77.276	311.573	311.097	0.143	−354.820	−310.047	53.984
350	81.651	323.826	312.055	4.120	−355.204	−302.553	45.154
400	85.216	334.969	314.233	8.294	−357.706	−294.923	38.513
450	88.175	345.182	317.112	12.631	−358.588	−287.030	33.318
500	90.655	354.604	320.396	17.104	−359.455	−279.030	29.150
600	94.520	371.494	327.538	26.373	−360.562	−262.831	22.881
700	97.321	386.286	334.896	35.973	−361.236	−246.485	18.393
800	99.387	399.423	342.156	45.813	−361.643	−230.062	15.021
900	100.940	411.223	349.186	55.833	−415.006	−212.518	12.334
1000	102.128	421.922	355.933	65.989	−413.905	−190.078	9.929
1100	103.052	431.701	362.383	76.250	−412.775	−167.749	7.966
1200	103.783	440.700	368.539	86.593	−411.629	−145.525	6.335
1300	104.370	449.031	374.414	97.002	−410.478	−123.396	4.958
1400	104.847	456.784	380.024	107.463	−409.330	−101.356	3.782
1500	105.240	464.031	385.386	117.968	−408.190	−79.398	2.765
1600	105.566	470.834	390.516	128.509	−407.065	−57.515	1.878
1700	105.840	477.242	395.431	139.080	−405.957	−35.702	1.097
1800	106.073	483.299	400.146	149.676	−404.871	−13.954	0.405
1900	106.271	489.039	404.675	160.293	−403.810	7.735	−0.213
2000	106.442	494.495	409.030	170.929	−402.775	29.368	−0.767
2100	106.590	499.692	413.225	181.581	−401.770	50.950	−1.267
2200	106.719	504.653	417.269	192.246	−400.796	72.486	−1.721
2300	106.833	509.400	421.172	202.924	−399.855	93.977	−2.134
2400	106.933	513.949	424.944	213.613	−398.949	115.428	−2.512
2500	107.021	518.316	428.592	224.310	−398.080	136.843	−2.859
2600	107.100	522.515	432.124	235.016	−397.247	158.223	−3.179
2700	107.170	526.558	435.547	245.730	−396.453	179.573	−3.474
2800	107.233	530.457	438.867	256.450	−395.697	200.893	−3.748
2900	107.290	534.221	442.091	267.176	−394.980	222.186	−4.002
3000	107.342	537.859	445.223	277.908	−394.302	243.457	−4.239
3100	107.388	541.379	448.268	288.645	−393.662	264.705	−4.460
3200	107.431	544.790	451.232	299.386	−393.058	285.932	−4.667
3300	107.469	548.096	454.117	310.131	−392.490	307.142	−4.862
3400	107.505	551.305	456.929	320.879	−391.956	328.335	−5.044
3500	107.537	554.422	459.670	331.632	−391.454	349.512	−5.216
3600	107.567	557.451	462.344	342.387	−390.981	370.676	−5.378
3700	107.594	560.399	464.955	353.145	−390.535	391.827	−5.532
3800	107.620	563.269	467.504	363.906	−390.115	412.967	−5.677
3900	107.643	566.065	469.996	374.669	−389.716	434.095	−5.814
4000	107.665	568.790	472.432	385.434	−389.338	455.214	−5.944
4100	107.685	571.449	474.814	396.202	−388.976	476.323	−6.068
4200	107.704	574.044	477.146	406.971	−388.628	497.423	−6.186
4300	107.721	576.579	479.429	417.742	−388.293	518.516	−6.299
4400	107.738	579.055	481.665	428.515	−387.966	539.601	−6.406
4500	107.753	581.477	483.857	439.290	−387.647	560.678	−6.508
4600	107.767	583.845	486.005	450.066	−387.333	581.748	−6.606
4700	107.781	586.163	488.111	460.843	−387.023	602.812	−6.699
4800	107.793	588.432	490.178	471.622	−386.714	623.869	−6.789
4900	107.805	590.655	492.205	482.402	−386.406	644.920	−6.875
5000	107.816	592.833	494.196	493.183	−386.096	665.964	−6.957
5100	107.827	594.968	496.151	503.965	−385.784	687.003	−7.036
5200	107.836	597.062	498.072	514.748	−385.470	708.034	−7.112
5300	107.846	599.116	499.959	525.532	−385.152	729.060	−7.185
5400	107.855	601.132	501.814	536.317	−384.831	750.080	−7.256
5500	107.863	603.111	503.638	547.103	−384.506	771.093	−7.323
5600	107.871	605.055	505.432	557.890	−384.177	792.102	−7.388
5700	107.878	606.964	507.196	568.678	−383.845	813.104	−7.451
5800	107.885	608.840	508.933	579.466	−383.509	834.101	−7.512
5900	107.892	610.685	510.642	590.255	−383.171	855.089	−7.570
6000	107.899	612.498	512.324	601.044	−382.832	876.075	−7.627

PREVIOUS June 1971 (1 atm) CURRENT: June 1971 (1 bar)

Tungsten Chloride Oxide (WO_2Cl_2) CRYSTAL M_r = 286.7548 Tungsten Chloride Oxide (WO_2Cl_2) $Cl_2O_2W_1(cr)$

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = [200.832]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = -780.32 \pm 5.9\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Shchukarev *et al* [1] measured calorimetrically the enthalpies of reaction (1) and (2) at 298.15 K at −67.3 ± 0.2 and −13.6 ± 0.11 kcal·mol^{-1}, respectively. The reactions are given as follows: (1) $WO_2Cl_2(cr) + 4\ NaOH(aq,\ 16.3\ H_2O) \rightarrow Na_2WO_4(aq,\ 80000\ H_2O) + 2\ NaCl(aq,\ 40000\ H_2O) + 2\ H_2O(l)$ and (2) $H_2WO_4(cr) + 2\ NaOH(aq,\ 16.3\ H_2O) \rightarrow Na_2WO_4(aq,\ 20000\ H_2O) + 2\ H_2O(l)$.

Based on these data and the enthalpies of dilution for NaOH(aq), NaCl(aq) and Na_2WO_4(aq), we obtain $\Delta_r H°(298.15\ K) = 53.77 \pm 1.0$ kcal·mol^{-1} for $WO_2Cl_2(cr) + 2\ OH^-(aq,\ \infty) \rightarrow H_2WO_4(cr) + 2\ Cl^-(aq,\infty)$. This leads to $\Delta_f H°(WO_2Cl_2,\ cr,\ 298.15\ K) = -186.5$ kcal·mol^{-1} using $\Delta_f H°(H_2WO_4,\ cr,\ 298.15\ K) = -270.5 \pm 0.4$ kcal·mol^{-1}.

Heat Capacity and Entropy

$C_p°(300) = 25.0$ cal·K^{-1}·mol^{-1} is estimated using Kopp's rule. Heat capacities at higher temperature are estimated from those of WO_2(cr), WO_3(cr), WCl_6(cr). The entropy $S°(298.15\ K) = 48.0$ cal·K^{-1}·mol^{-1} is calculated from $\Delta S°(598.6\ K) = 32.27 \pm 1.3$ cal·K^{-1}·mol^{-1} for $WO_2Cl_2(cr) \rightarrow WO_2Cl_2(g)$. The value of $\Delta S°(598.6\ K)$ is obtained from the 2nd law analysis of the vapor pressure data given by Shchukarev and Suvorov.[4]

Decomposition Data

Shchukarev and Suvorov[4] found that WO_2Cl_2(cr) does not melt but decomposes. The saturated vapor over WO_2Cl_2(cr) consists mainly of $WOCl_4$(g) which will disproportionate to form WO_2Cl_2(g) and WCl_6(g). The estimated $T_{dcm} = 642$ K is derived by interpolation to one atmosphere in the total pressures of $WOCl_4$(g), WO_2Cl_2(g) reported by Shchukarev and Suvorov.[4]

References

[1] S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov, Zh. Neorg. Khim. 3, 2642 (1958).
[2] V. B. Parker, U. S. Nat. Bur. Stand., NSRDS-NBS 2, (1965).
[3] We have assumed $\Delta_{dil}H° = 0$ for $Na_2WO_4(aq,\ 20000\ H_2O) \rightarrow Na_2WO_4(aq,\ 80000\ H_2O)$.
[4] S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. I Khim., No. 1, 87 (1961). Earlier data reported by Shchukarev *et al.*, Zh. Neorg. Khim. 3, 2630 (1958); 5, 1650 (1960), have been revised and they are not used here.
[5] JANAF Thermochemical Tables: H_2WO_4(cr), 3–31–67.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	104.408	200.832	200.832	0.	−780.316	−702.781	123.124
300	104.600	201.478	200.834	0.193	−780.285	−702.300	122.281
400	115.060	233.003	205.062	11.176	−778.207	−676.597	88.354
500	125.520	259.809	213.391	23.209	−775.319	−651.511	68.063
600	135.562	283.597	223.145	36.272	−771.605	−627.085	54.593
700	144.557	305.202	233.347	50.298	−767.106	−603.344	45.022
800	151.042	324.947	243.581	65.092	−761.993	−580.292	37.889
900	155.854	343.031	253.641	80.451	−756.449	−557.909	32.380
1000	158.992	359.629	263.422	96.207	−750.625	−536.159	28.006

PREVIOUS: September 1962 CURRENT: March 1967

Tungsten Chloride Oxide (WO_2Cl_2) IDEAL GAS $M_r = 286.7548$ Tungsten Chloride Oxide (WO_2Cl_2) $Cl_2O_2W_1(g)$

$S°(298.15\ K) = [353.927]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -668.2 \pm 25\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -671.5 \pm 25\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
984 (1)	[400](1)	[150](1)
972 (1)	[300](1)	[100](1)
[400](1)	[300](1)	[100](1)

Ground State Quantum Weight: 1 $\sigma = [2]$
Point Group: $[C_{2v}]$
Bond Distances: W–Cl = [2.26] Å; W–O = [1.81] Å
Bond Angles: Cl–W–Cl = [113]°; O–W–O = [109.47]°; O–W–Cl = [90]°
Product of the Moments of Inertia: $I_AI_BI_C = [1.16512 \times 10^{-112}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

$\Delta_fH°(WO_2Cl_2, g, 298.15\ K) = -160.5\ kcal{\cdot}mol^{-1}$ is obtained from $\Delta_rH°(298.15\ K) = 26.0\ kcal{\cdot}mol^{-1}$ for $WO_2Cl_2(cr) \rightarrow WO_2Cl_2(g)$. The latter is calculated by the 3rd law method from the partial pressures of $WO_2Cl_2(g)$ given by Shchukarev and Suvorov.[6] 2nd law analysis gives $\Delta_rH°(598.6\ K) = 24.1 \pm 0.8\ kcal{\cdot}mol^{-1}$ $\Delta_rH°(298.15\ K) = 26.0\ kcal{\cdot}mol^{-1}$. These reported partial vapor pressures of $WO_2Cl_2(g)$ were derived by the optical tensimetric method from total pressures over $WO_2Cl_2(cr)$ considering the species $WOCl_4(g)$, $WO_2Cl_2(g)$ and $WCl_6(g)$. Since the decomposition of $WO_2Cl_2(cr)$ was very complicated, we tentatively assign 6 kcal·mol^{-1} uncertainty to the adopted enthalpy of formation.

Shchukarev and Suvorov[6] have also derived a log K_p equation for the disproportionation process, $2\ WOCl_4(g) = WO_2Cl_2(g) + WCl_6(g)$. 3rd law analysis gives $\Delta_rH°(298.15\ K) = 10.3\ kcal{\cdot}mol^{-1}$ for the above process. This leads to $\Delta_fH°(WO_2Cl_2, g, 298.15\ K) = -145.7 \pm 16\ kcal{\cdot}mol^{-1}$. The 2nd law $\Delta_rH°(590\ K)$ is 11.0 kcal·mol^{-1} $\Delta_rH°(298.15\ K) = 10.1\ kcal{\cdot}mol^{-1}$. The drift in the 3rd law analysis is 0.3 cal·K^{-1}·mol^{-1}.

Heat Capacity and Entropy

The molecular configuration is assumed to be a distorted tetrahedron of C_{2v} symmetry, similar to that of $MoO_2Cl_2(g)$,[1] and $CrO_2Cl_2(g)$.[2] The bond distances W–O and W–Cl are estimated to be the same as those in $WO_3(g)$ and $WCl_6(g)$, respectively The bond angles are assumed to be the same as those in $MoO_2Cl_2(g)$.[1] The principal moments of inertia are: $I_A = 33.9761 \times 10^{-39}$, $I_B = 53.4238 \times 10^{-39}$, and $I_C = 64.1894 \times 10^{-39}\ g{\cdot}cm^2$.[2]

The vibrational frequencies, 984 cm^{-1} and 972 cm^{-1}, were observed in the infrared spectra Barraclough and Stals.[3] They tentatively assigned these two as the symmetric and asymmetric W–O stretching frequencies. The rest of the frequencies are estimated by comparison with those observed in the infrared and Raman spectra for $CrO_2Cl_2(g)$.[4,5] They are not listed in point group order.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−19.504	−668.198	−668.198	INFINITE
100	59.017	273.602	424.320	−15.072	−670.235	−660.403	344.959
200	77.605	320.992	361.629	−8.127	−671.247	−650.101	169.789
250	83.093	338.927	355.341	−4.104	−671.457	−644.787	134.721
298.15	87.199	353.927	353.927	0.	−671.532	−639.642	112.063
300	87.339	354.467	353.929	0.161	−671.533	−639.445	111.337
350	90.723	368.194	355.006	4.616	−671.497	−634.098	94.634
400	93.447	380.493	357.436	9.223	−671.376	−628.762	82.108
450	95.648	391.631	360.627	13.952	−671.192	−623.446	72.368
500	97.435	401.804	364.243	18.781	−670.963	−618.153	64.578
600	100.093	419.820	372.043	28.666	−670.427	−607.640	52.900
700	101.913	435.394	380.006	38.772	−669.848	−597.221	44.565
800	103.198	449.092	387.803	49.031	−669.271	−586.886	38.320
900	104.131	461.303	395.304	59.400	−668.717	−576.621	33.466
1000	104.827	472.312	402.463	69.849	−668.199	−566.417	29.587
1100	105.358	482.329	409.275	80.360	−667.727	−556.261	26.415
1200	105.771	491.515	415.751	90.917	−667.305	−546.147	23.773
1300	106.098	499.995	421.909	101.511	−666.937	−536.066	21.539
1400	106.361	507.867	427.771	112.134	−666.625	−526.011	19.626
1500	106.576	515.213	433.359	122.781	−666.372	−515.977	17.968
1600	106.753	522.097	438.692	133.448	−666.182	−505.957	16.518
1700	106.902	528.574	443.791	144.131	−666.057	−495.947	15.239
1800	107.027	534.688	448.672	154.828	−665.998	−485.943	14.102
1900	107.133	540.477	453.353	165.536	−666.009	−475.940	13.084
2000	107.224	545.975	457.848	176.254	−666.092	−465.934	12.169
2100	107.303	551.208	462.170	186.980	−666.249	−455.923	11.340
2200	107.371	556.201	466.331	197.714	−666.484	−445.901	10.587
2300	107.431	560.976	470.343	208.454	−666.797	−435.869	9.899
2400	107.484	565.549	474.216	219.200	−667.191	−425.821	9.268
2500	107.531	569.938	477.957	229.951	−667.668	−415.754	8.687
2600	107.572	574.156	481.577	240.706	−668.227	−405.666	8.150
2700	107.609	578.217	485.081	251.465	−668.894	−395.555	7.652
2800	107.643	582.131	488.478	262.228	−669.707	−385.417	7.190
2900	107.672	585.909	491.773	272.994	−670.703	−375.248	6.759
3000	107.699	589.559	494.972	283.762	−671.911	−365.039	6.356
3100	107.724	593.091	498.080	294.533	−673.373	−354.786	5.978
3200	107.746	596.512	501.103	305.307	−675.119	−344.483	5.623
3300	107.766	599.827	504.045	316.083	−677.174	−334.120	5.289
3400	107.785	603.045	506.909	326.860	−679.570	−323.689	4.973
3500	107.802	606.169	509.701	337.639	−682.371	−313.182	4.674
3600	107.817	609.207	512.423	348.420	−685.669	−302.589	4.390
3700	107.832	612.161	515.079	359.203	−724.329	−291.705	4 118
3800	107.845	615.037	517.672	369.987	−725.329	−279.999	3 849
3900	107.857	617.838	520.204	380.772	−726.348	−268.266	3.593
4000	107.868	620.569	522.679	391.558	−727.383	−256.507	3.350
4100	107.879	623.233	525.100	402.345	−728.431	−244.722	3.118
4200	107.889	625.832	527.467	413.134	−729.490	−232.912	2.897
4300	107.898	628.371	529.784	423.923	−730.556	−221.076	2.686
4400	107.906	630.852	532.053	434.713	−731.628	−209.215	2.484
4500	107.914	633.277	534.276	445.504	−732.701	−197.331	2.291
4600	107.922	635.649	536.454	456.296	−733.775	−185.422	2.106
4700	107.928	637.970	538.589	467.089	−734.847	−173.490	1.928
4800	107.935	640.242	540.683	477.882	−735.916	−161.534	1.758
4900	107.941	642.468	542.738	488.676	−736.978	−149.556	1.594
5000	107.947	644.649	544.755	499.470	−738.034	−137.558	1.437
5100	107.952	646.786	546.734	510.265	−739.082	−125.537	1.286
5200	107.957	648.882	548.679	521.060	−740.120	−113.498	1.140
5300	107.962	650.939	550.589	531.856	−741.149	−101.437	1.000
5400	107.967	652.957	552.466	542.653	−742.167	−89.358	0.864
5500	107.971	654.938	554.311	553.450	−743.175	−77.260	0.734
5600	107.975	656.884	556.125	564.247	−744.172	−65.142	0.608
5700	107.979	658.795	557.910	575.045	−745.158	−53.008	0.486
5800	107.983	660.673	559.665	585.843	−746.134	−40.856	0.368
5900	107.986	662.519	561.393	596.641	−747.101	−28.690	0.254
6000	107.990	664.334	563.094	607.440	−748.058	−16.504	0.144

PREVIOUS. March 1967 (1 atm) CURRENT. March 1967 (1 bar)

Lead Chloride (PbCl$_2$) CRYSTAL $M_r = 278.106$ Lead Chloride (PbCl$_2$) Cl$_2$Pb$_1$(cr)

$\Delta_f H°(0\ \mathrm{K})$ = Unknown

$S°(298.15\ \mathrm{K}) = 135.98 \pm 2.1\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ $\Delta_f H°(298.15\ \mathrm{K}) = -359.4 \pm 0.8\ \mathrm{kJ{\cdot}mol^{-1}}$

$T_{\mathrm{fus}} = 774\ \mathrm{K}$ $\Delta_{\mathrm{fus}} H° = 21.88 \pm 0.84\ \mathrm{kJ{\cdot}mol^{-1}}$

Enthalpy of Formation

$\Delta_f H°$ of $-85.9 \pm 0.2\ \mathrm{kcal{\cdot}mol^{-1}}$ is obtained from a 3rd law analysis of six sets of electromotive force data[3,4,6,7] for three different reactions, namely, (A) Pb(cr) + 2 AgCl(cr) = 2 Ag(cr) + PbCl$_2$(cr), (B) Pb(cr) + Hg$_2$Cl$_2$(cr) = 2 Hg(l) + PbCl$_2$(cr), and (C) Pb(l) + Cl$_2$(g) = PbCl$_2$(cr). Seven other sets of similar data[1,2,5] give $\Delta_f H°$ values which are within ± 0.2 kcal·mol^{-1}of adopted value, while one set of emf data[7] for (D) 2CuCl(cr) + Pb(cr) = PbCl$_2$(cr) + 2 Cu(cr) gives a $\Delta_f H°$ value of -85.4 kcal·mol^{-1}. A $\Delta_f H°$ value can be obtained also from a 3rd law analysis of equilibrium data[8] for (E) PbCl$_2$(cr) + H$_2$(g) = Pb(l) + 2 HCl(g). Auxiliary enthalpies of formation used in our analysis are $\Delta_f H°(298.15\ \mathrm{K})$, kcal·mol^{-1}: AgCl, cr, = -30.370,[9] CuCl, cr = -33.0 ± 0.4,[10] Pb, l = 1.025,[10] Hg$_2$Cl$_2$, cr = -63.319 ± 0.05[10] and HCl, g = -22.063 ± 0.05.[10] We assign an uncertainty of ± 0.2 kcal·mol^{-1} to $\Delta_f H°$ to reflect the estimated error in the adopted value for $S°(298.15\ \mathrm{K})$.

Source	Reaction	Data Points	T/K	$-\Delta_f H°(298.15\ \mathrm{K})$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ \mathrm{K})$ kcal·mol^{-1}
[1]	A	5	273–298	24.5	25.06 ± 0.04	−1.8 ± 0.3	85.8 ± 0.1
	B	7	273–298	22.0	22.34 ± 0.03	−1.3 ± 0.3	85.7 ± 0.1
[2] Set I	A	5	273–294	24.8	25.26 ± 0.03	−1.7 ± 0.1	86.0 ± 0.1
Set II	A	5	273–294	24.9	25.25 ± 0.03	−1.4 ± 0.2	86.0 ± 0.1
Set I	B	5	273–298	22.2	22.36 ± 0.02	−0.7 ± 0.1	85.7 ± 0.1
Set II	B	5	273–296	22.2	22.36 ± 0.02	−0.7 ± 0.3	85.7 ± 0.1
[3]	A	5	278–318	25.1	25.17 ± 0.03	−0.1 ± 0.5	85.9 ± 0.1
Set I	B	5	278–318	22.7	22.54 ± 0.04	0.4 ± 0.7	85.9 ± 0.1
Set II	B	5	288–308	22.7	25.54 ± 0.04	0.5 ± 0.7	85.9 ± 0.1
[4]	A	3	288–308	25.2	25.17 ± 0.02	0.2 ± 0.9	85.9 ± 0.1
[5]	C	Eqn	673–771	82.1	86.87 ± 0.55	−6.6	85.8 ± 0.6
[6]	C	2	723–773	86.8	86.98 ± 0.02	−0.2	85.9 ± 0.1
[7]	D	Eqn	363–553	19.8	19.44 ± 0.13	0.9	85.4 ± 1.0
	A	Eqn	293–573	24.9	25.20 ± 0.80	−0.7	85.9 ± 0.9
[8]	E	3	633–773	23.3	33.7 ± 2.4	14.7 ± 7.8	76.8 ± 2.5

Heat Capacity and Entropy

$C_p°$ data below 298.15 K have been reported by Nerst (15.6–87.7 K),[11] Eucken (106.5–290.7 K),[12] and Bronsted (283 K).[13] We combine these results with $C_p° = 18.52\ \mathrm{cal{\cdot}K^{-1}{\cdot}mol^{-1}}$ [14] at 330 K and obtain $S°(298.15\ \mathrm{K}) = 33.7\ \mathrm{cal{\cdot}K^{-1}{\cdot}mol^{-1}}$ based on $S°(15.6\ \mathrm{K}) = 0.9\ \mathrm{cal{\cdot}K^{-1}{\cdot}mol^{-1}}$. Kelley and King[15] analyzed the same $C_p°$'s and found $S°(298.15\ \mathrm{K}) = 34.0 \pm 1.0\ \mathrm{cal{\cdot}K^{-1}{\cdot}mol^{-1}}$. Data obtained from cell measurements on both the crystal and liquid allow independent calculations of $S°(298.15\ \mathrm{K})$. Thirteen of the 23 sets of emf data htat we have analyzed are more compatible with a value for $S°(298.15\ \mathrm{K})$ which is at least one cal·K^{-1}·mol^{-1} less than that determined from the low temperature data. Since the cell measurements are judged to be more reliable, we adopt $S°(298.15\ \mathrm{K}) = 32.5 \pm 0.5\ \mathrm{cal{\cdot}K^{-1}{\cdot}mol^{-1}}$ and omit the $C_p°$ data below 298.25 K.

$C_p°$'s above 300 K are based on the smoothed relative enthalpies of Alim *et al.*[16] Their measurements were made in an isothermal diphenyl ether calorimeter over the temperature range 400 to 950 K. The PbCl$_2$ was reported to have a purity of 99.96%, and samples of this material were sealed in platinum capsules for the drop experiments. Their enthalpies are fitted to a polynomial which represents the data to within ± 0.4%. The calculated $C_p°$'s above 300 K are joined graphically with those of Eucken[12] at 298.15 K by comparison with the $C_p°$–T curve for BaCl$_2$(cr).[10] Our adopted enthalpies are in reasonable agreement with those of Kelley.[17] His results are based on the enthalpy measurements of Krestovnikov and Karetnikov,[18] and most of the points agree with ours to better than a percent but show a maximum deviation of −1.3% at 500 K. Other enthalpy data that have been recently reported are those of Bloom and Tricklebank (693–773 K),[19] and Thompson and Flengas (577–745 K).[20] Both of these studies show rather poor agreement with our adopted results. Deviations from our values are −4.2% at 673 K to −5.0% at 773 K for Bloom and Tricklebank,[19] 0.1% at 680 K and −6.2% at 745 K for Thompson and Flengas.[20] Both drop investigations were conducted with quartz capsules which might have been slowly attacked by the PbCl$_2$ at the higher temperatures. The earlier enthalpy measurements of Goodwin and Kalmus[21] are considered less reliable and not included in our analysis.

Modestova[22] has reported the existence of a transition for PbCl$_2$ at 695 K based on differential thermal analysis and x-ray studies. This transition has not been observed by other workers, and we prefer not to include it. However, if it does exist, we speculate that the enthalpy associated with it is quite small; thus, our functions would be only slightly altered.

Fusion Data

$T_{\mathrm{fus}} = 774$ K is from the enthalpy study of Alim *et al.*[16] Other values reported for T_{fus} based on enthalpy measurements are 771,[21] 774,[18] 774[19] and 772.[20] DTA measurements[24] gave T_{fus} equal to 774 K, while cryoscopic studies[23] yielded 768 K. $\Delta_{\mathrm{fus}} H°$ is calculated to be 5.23 kcal·mol^{-1} from the adopted enthalpies for the crystal and liquid at T_{fus}. Published values (all in kcal·mol^{-1}) include 5.15,[21] 5.70,[23] 2.98,[18] 5.3,[19] 5.56,[20] and 5.03.[24]

Continued on page 939

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	77.073	135.980	135.980	0.	−359.406	−314.121	55.033
300	77.170	136.457	135.981	0.143	−359.375	−313.840	54.644
400	80.094	159.059	139.043	8.006	−357.711	−298.911	39.034
500	82.985	177.242	144.922	16.160	−355.942	−284.413	29.712
600	85.881	192.628	151.622	24.603	−354.020	−270.285	23.530
700	88.772	206.083	158.460	33.336	−356.781	−255.694	19.080
774.000	90.915	215.110	163.451	39.984	--- CRYSTAL <--> LIQUID ---		
800	91.667	218.126	165.179	42.358	−354.476	−241.407	15.762
900	94.558	229.090	171.680	51.669	−351.870	−227.427	13.200
1000	97.454	239.203	177.933	61.270	−348.961	−213.753	11.165
1100	100.345	248.626	183.936	71.160	−345.746	−200.385	9.516
1200	103.240	257.482	189.699	81.339	−342.222	−187.324	8.154
1300	106.131	265.860	195.238	91.808	−338.397	−174.569	7.014
1400	109.027	273.831	200.570	102.566	−334.283	−162.119	6.049
1500	111.918	281.451	205.710	113.613	−329.891	−149.973	5.223

PREVIOUS: March 1962 CURRENT: June 1973

Lead Chloride (PbCl$_2$) LIQUID $M_r = 278.106$ Lead Chloride (PbCl$_2$) Cl$_2$Pb$_1$(l)

$S°(298.15\ \text{K}) = [153.396]\ \text{J·K}^{-1}\text{·mol}^{-1}$
$T_{fus} = 774\ \text{K}$

$\Delta_f H°(298.15\ \text{K}) = [-344.251]\ \text{kJ·mol}^{-1}$
$\Delta_{fus}H° = 21.88 \pm 0.84\ \text{kJ·mol}^{-1}$

	Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa		
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	77.073	153.396	153.396	0.	−344.251	−304.160	53.288
300	77.170	153.873	153.398	0.143	−344.221	−303.911	52.916
400	80.094	176.475	156.460	8.006	−342.557	−290.723	37.965
500	82.985	194.659	162.338	16.160	−340.787	−277.967	29.039
500.000	82.985	194.659	162.338	16.160	GLASS <--> LIQUID		
500.000	111.504	194.659	162.338	16.160	TRANSITION		
600	111.504	214.988	169.470	27.311	−336.158	−265.840	23.143
700	111.504	232.177	177.232	38.461	−336.502	−253.680	18.930
774.000	111.504	243.382	183.030	46.712	--- CRYSTAL <--> LIQUID ---		
800	111.504	247.066	185.051	49.611	−332.068	−242.151	15.811
900	111.504	260.199	192.686	60.762	−327.623	−231.178	13.417
1000	111.504	271.947	200.035	71.912	−323.164	−220.701	11.528
1100	111.504	282.575	207.063	83.063	−318.689	−210.671	10.004
1200	111.504	292.277	213.766	94.213	−314.194	−201.050	8.751
1300	111.504	301.202	220.153	105.363	−309.687	−191.804	7.707
1400	111.504	309.465	226.241	116.514	−305.181	−182.905	6.824
1500	111.504	317.158	232.049	127.664	−300.686	−174.328	6.071
1600	111.504	324.354	237.595	138.814	−296.207	−166.050	5.421
1700	111.504	331.114	242.900	149.965	−291.751	−158.052	4.856
1800	111.504	337.488	247.979	161.115	−287.320	−150.315	4.362
1900	111.504	343.516	252.850	172.265	−282.917	−142.824	3.927
2000	111.504	349.236	257.528	183.416	−278.544	−135.564	3.541

PREVIOUS: March 1962 CURRENT: June 1973

Enthalpy of Formation

$\Delta_f H°$(PbCl$_2$, l, 298.15 K) is calculated from that of the crystal by addition of $\Delta_{fus}H°$ and the difference in enthalpy, $H°(774\ \text{K})-H°(298.15\ \text{K})$, between the crystal and liquid. Independent values of $\Delta_f H°$(l) (or $\Delta_f H°$(cr)) can be obtained from a 2nd and 3rd analysis of nine sets of emf data[1-9] for the formation cell of molten PbCl$_2$ ((A) Pb(l) + Cl$_2$(g) = PbCl$_2$(l)) and three sets of equilibrium data[10,11] for (B) PbCl$_2$(l) + H$_2$(g) = Pb(l) + 2 HCl(g). Auxiliary enthalpies of formation used in the analysis are $\Delta_f H°$(Pb, l, 298.15 K) = 1.025 kcal·mol^{-1} [12] and $\Delta_f H°$(HCl, g, 298.15 K) = −22.063 ± 0.05 kcal·mol^{-1}.[12] Five of the nine sets of emf data yield values for $\Delta_f H°$(cr) which are in good agreement (±0.2 kcal·mol^{-1}) with the adopted value. Also, the results of the extensive emf measurements of Warner and Seifert[8] by the electronic commutator method are quite compatible with our adopted functions.

Source	Reaction	Data Points	T/K	$-\Delta_r H°$, kcal·mol^{-1} 2nd law	$-\Delta_r H°$, kcal·mol^{-1} 3rd law	Drift cal·K^{-1}·mol^{-1}	$-\Delta_f H°$(298.15 K) kcal·mol^{-1} (l)	$-\Delta_f H°$(298.15 K) kcal·mol^{-1} (cr)
Lorenz and Fox[1]	A	14	776–942	86.9	82.45 ± 0.58	5.1 ± 0.5	81.43	85.05
Hildenbrand and Ruhle[2]	A	7	774–880	88.9	82.95 ± 0.62	7.2 ± 0.3	81.93	85.55
Lorenz and Velde[3]	A	47[a]	826–1016	87.1	83.18 ± 0.52	4.4 ± 0.2	82.16	85.78
Wachter and Hildenbrand[4]	A	18	772–855	84.9	83.31 ± 0.11	2.0 ± 0.3	82.29	85.91
Holub *et al.*[5]	A	3	843–923	86.0	83.08 ± 0.27	3.3 ± 0.2	82.06	85.68
Lantratov and Alabyshev[6]	A	47[b]	814–954	82.5	83.69 ± 0.15	1.4 ± 0.1	82.67	86.29
Delimarskii and Roms[7]	A	2	8231, 873	83.5	83.56		82.54	86.16
Warner and Seifert[8]	A	Equation	775–1139	83.4	83.32 ± 0.03	0.1	82.30	85.92
Hagemark and Hengstenberg[9]	A	Equation	773–893	84.6	83.51 ± 0.15	1.3 ± 0.1	82.49	86.11
Bagdasarian[10] Set I	B	10	876–978	40.0	38.89 ± 0.36	−1.2 ± 1.4	81.99	85.61
Set II	B	21	871–1220	44.2	38.08 ± 1.26	−5.8 ± 0.3	81.18	84.80
Jellinek and Rudat[11]	B	5	833–1133	37.8	38.62 ± 0.51	0.8 ± 1.1	81.72	85.34

(3)[a] and (1)[b] points rejected due to failure of a statistical test.

Heat Capacity and Entropy

$C_p°$ is assumed constant at 26.65 cal·K^{-1}·mol^{-1} over the temperature range 500–2000 K and is based on the smoothed relative enthalpies (774–950 K) of Alim *et al.*[13] A glass transition is assumed at 500 K below which $C_p°$ is that of the crystal. The smoothed enthalpies of Kelley[14] (800–1000 K) deviate by +4.0% from our values, while those of Thompson and Flengas[15] (813–945 K) deviate by ±1%. The enthalpies of Bloom and Tricklebank[16] are consistently lower than our values by −3 1% at 823 K, and the deviation increases to −12.6% at 1073 K. Warner and Seifert[8] have determined $C_p°$ data for PbCl$_2$(l) from their emf measurements. They reported values of (all in cal·K^{-1}·mol^{-1}) 25.7 (800 K), 26.2 (900 K), 26.5 (1000 K) and 26.7 (1100 K). Bizouard and Pauty[17] measured $C_p°$ for the liquid as 24.7 cal·K^{-1}·mol^{-1}. $S°(298.15\ \text{K})$ is calculated in a manner analogous to that used for the enthalpy of formation.

Vaporization Data

T_{vap} is the temperature at which $\Delta_r G° = 0$ for the process PbCl$_2$(l) → PbCl$_2$(g). $\Delta_{vap}H°$ is calculated as the difference between the enthalpies of formation of the gas and liquid at T_{vap}.

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Lead Chloride ($PbCl_2$) CRYSTAL-LIQUID

0 to 774 K crystal
above 774 K liquid

Refer to the individual tables for details.

$M_r = 278.106$ Lead Chloride (PbCl) $Cl_2Pb_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	77.073	135.980	135.980	0.	−359.406	−314.121	55.033
300	77.170	136.457	135.981	0.143	−359.375	−313.840	54.644
400	80.094	159.059	139.043	8.006	−357.711	−298.911	39.034
500	82.985	177.242	144.922	16.160	−355.942	−284.413	29.712
600	85.881	192.628	151.622	24.603	−354.020	−270.285	23.530
700	88.772	206.083	158.460	33.336	−356.781	−255.694	19.080
774.000	90.915	215.110	163.451	39.984	CRYSTAL <−−> LIQUID TRANSITION		
774.000	111.504	243.382	163.451	61.867			
800	111.504	247.066	166.109	64.766	−332.068	−242.151	15.811
900	111.504	260.199	175.848	75.916	−327.623	−231.178	13.417
1000	111.504	271.947	184.881	87.067	−323.164	−220.701	11.528
1100	111.504	282.575	193.286	98.217	−318.689	−210.671	10.004
1200	111.504	292.277	201.137	109.367	−314.194	−201.050	8.751
1300	111.504	301.202	208.496	120.518	−309.687	−191.804	7.707
1400	111.504	309.465	215.416	131.668	−305.181	−182.905	6.824
1500	111.504	317 158	221.946	142.818	−300.686	−174.328	6.071
1600	111.504	324.354	228.124	153.969	−296.207	−166.050	5.421
1700	111.504	331.114	233.985	165.119	−291.751	−158.052	4.856
1800	111.504	337.488	239.560	176.269	−287.320	−150.315	4.362
1900	111.504	343.516	244.874	187.420	−282.917	−142.824	3.927
2000	111.504	349.236	249.951	198.570	−278.544	−135.564	3.541

PREVIOUS: CURRENT: June 1973

Lead Chloride ($PbCl_2$) IDEAL GAS $M_r = 278.106$ Lead Chloride ($PbCl_2$) $Cl_2Pb_1(g)$

$\Delta_f H°(0\ K) = -172.03 \pm 1.3\ kJ{\cdot}mol^{-1}$
$S°(298.15\ K) = 317.205 \pm 2.9\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = -174.05 \pm 1.3\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	[22000]	3
$^1B_1$	31000	1

Vibrational Frequencies and Degeneracies

ν_i, cm^{-1}
329 (1)
80 (1)
307 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Pb–Cl = 2.46 ± 0.02 Å
Bond Angle: Cl–Pb–Cl = 96 + 3°
Product of Moments of Inertia. $I_A I_B I_C = 5.90383 \times 10^{-113}\ g^3{\cdot}cm^6$

Enthalpy of Formation

$\Delta_f H°$ of $-41.6 \pm 0.3\ kcal{\cdot}mol^{-1}$ is obtained from $\Delta_f H°(cr) = -85.9 \pm 0.2\ kcal{\cdot}mol^{-1}$ by addition of $\Delta_{sub}H°(298.15\ K)$. The adopted value for $\Delta_{sub}H°(298.15\ K)$ is $44.3 \pm 0.1\ kcal{\cdot}mol^{-1}$ and is based on a 3rd law analysis of six sets of vapor pressure data[4,9,11,14,15] for both the crystal and liquid. Results of our analysis of a total of eighteen sets of Vp data are given below. Seven[1,2,3,7,8,10,12] of the remaining twelve sets yield $\Delta_f H°(g)$ values which are within $0.3\ kcal{\cdot}mol^{-1}$ of the adopted value. Mass spectrometric studies[16] of the equilibrium vapors over the condensed phases indicated that the predominant species is the monomer.

Source	Reaction*	T/K	Data Points	$\Delta_{sub}H°$(or v), $kcal{\cdot}mol^{-1}$ 2nd law	3rd law	Drift $cal{\cdot}K^{-1}{\cdot}mol^{-1}$	$\Delta_f H°(PbCl_2, g, 298.15\ K)$ $kcal{\cdot}mol^{-1}$
1	A	673–748	4	47.6	45.41 ± 0.21	−3.2 ± 0.1	40.5 ± 0.4
	B	773–1223	19	42.5	40.93 ± 0.49	−1.6 ± 0.2	41.3 ± 0.7
2	B	1043–1227	7	37.6	40.62 ± 0.42	2.6 ± 0.8	41.7 ± 0.6
3	B	955–1266	12[a]	39.8	40.75 ± 0.25	0.8 ± 0.3	41.5 ± 0.4
4	A	708–766	5	37.1	44.34 ± 0.53	9.8 ± 3.2	41.6 ± 0.7
	B	783–865	7	44.3	40.69 ± 0.30	−4.4 ± 0.7	41.6 ± 0.5
5	B	1033–1043	2	36.1	40.19 ± 0.06	3.9	42.1 ± 0.3
6	A	653–733	7	49.0	45.13 ± 0.31	−5.6 ± 0.2	40.8 ± 0.5
7	B	953–1215	9[a]	43.6	40.94 ± 0.69	−2.5 ± 0.9	41.3 ± 0.9
8	B	865–1272	18	38.9	40.60 ± 0.50	1.6 ± 0.5	41.7 ± 0.7
9	B	950–1250	Eqn	40.9	40.67 ± 0.04	−0.2	41.6 ± 0.3
10	B	931–1154	4	41.0	40.74 ± 0.24	−0.2 ± 0.8	41.5 ± 0.4
11	B	923	1		40.70		41.6 ± 0.3
12	B	821–1259	56[b]	39.9	40.73 ± 0.24	0.8 ± 0.1	41.5 ± 0.4
13	A	708–758	3	45.1	42.93 ± 0.37	−3.0 ± 6.8	43.0 ± 0.6
	B	793–893	3	31.3	40.24 ± 1.14	10.6 ± 3.8	41.6 ± 0.3
14	B	914–1249	Eqn	40.2	40.69 ± 0.12	0.5	41.6 ± 0.3
15	B	1071	1		40.63		41.6 ± 0.3

*A) $PbCl_2(cr) = PbCl_2(g)$ B) $PbCl_2(l) = PbCl_2(g)$. (1)[a] and (2)[b] points rejected due to failure of a statistical test

Heat Capacity and Entropy

The bond length is taken from the electron diffraction study of Lister and Sutton.[17] Electric deflection experiments by Buchler *et al.*[18] showed that $PbCl_2$ possessed a permanent dipole moment; thus, the molecule must have a bent structure. Infrared studies[19] of matrix isolated $PbCl_2$ have led to a value for the bond angle of 96 ± 3° which we adopt. This value is based on the observed Cl isotopic splitting of the antisymmetrical stretching frequency (ν_3). The principal moments of inertia are: $I_A = 23.7690 \times 10^{-39}$, $I_B = 39.3510 \times 10^{-39}$, and $I_C = 63.1200 \times 10^{-39}\ g{\cdot}cm^2$.

Continued on page 939

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
0	0.	0.	INFINITE	−14.038	−172.033	−172.033	INFINITE
100	44.386	262.096	363.997	−10.190	−172.863	−176.489	92.189
200	52.288	295.698	322.179	−5.296	−173.532	−179.824	46.965
250	54.098	307.577	318.109	−2.633	−173.793	−181.367	37.895
298.15	55.184	317.205	317.205	0.	−174.054	−182.802	32.026
300	55.218	317.547	317.207	0.102	−174.065	−182.857	31.838
350	55.946	326.117	317.882	2.882	−174.357	−184.299	27.505
400	56.442	333.622	319.390	5.693	−174.673	−185.698	24.250
450	56.793	340.291	321.349	8.524	−175.014	−187.056	21.713
500	57.050	346.289	323.548	11.371	−175.380	−188.375	19.679
600	57.392	356.724	328.233	17.094	−176.178	−190.900	16.619
700	57.602	365.587	332.952	22.845	−181.921	−192.487	14.364
800	57.740	373.289	337.524	28.612	−182.870	−193.932	12.662
900	57.836	380.095	341.883	34.391	−183.797	−195.259	11.333
1000	57.904	386.193	346.014	40.178	−184.701	−196.483	10.263
1100	57.955	391.714	349.922	45.972	−185.583	−197.619	9.384
1200	57.994	396.759	353.618	51.769	−186.441	−198.675	8.648
1300	58.025	401.402	357.117	57.570	−187.283	−199.660	8.022
1400	58.049	405.703	360.436	63.374	−188.124	−200.581	7.484
1500	58.068	409.709	363.589	69.180	−188.973	−201.441	7.015
1600	58.084	413.457	366.590	74.987	−189.838	−202.244	6.603
1700	58.098	416.978	369.451	80.797	−190.723	−202.992	6.237
1800	58.109	420.300	372.185	86.607	−191.631	−203.688	5.911
1900	58.119	423.442	374.800	92.418	−192.567	−204.333	5.617
2000	58.127	426.423	377.308	98.231	−193.532	−204.927	5.352
2100	58.135	429.259	379.715	104.044	−371.749	−198.357	4.934
2200	58.142	431.964	382.029	109.857	−372.389	−190.086	4.513
2300	58.149	434.548	384.256	115.672	−373.130	−181.783	4.128
2400	58.157	437.023	386.404	121.487	−373.975	−173.446	3.775
2500	58.166	439.398	388.476	127.303	−374.927	−165.071	3.449
2600	58.176	441.679	390.479	133.121	−375.985	−156.657	3.147
2700	58.188	443.875	392.416	138.939	−377.148	−148.199	2.867
2800	58.202	445.991	394.292	144.758	−378.414	−139.697	2.606
2900	58.220	448.034	396.110	150.579	−379.777	−131.147	2.362
3000	58.241	450.008	397.874	156.402	−381.232	−122.549	2.134
3100	58.266	451.918	399.587	162.228	−382.773	−113.901	1.919
3200	58.297	453.769	401.251	168.056	−384.392	−105.203	1.717
3300	58.332	455.563	402.870	173.887	−386.081	−96.452	1.527
3400	58.373	457.305	404.445	179.722	−387.830	−87.649	1.347
3500	58.421	458.998	405.980	185.562	−389.632	−78.794	1.176
3600	58.476	460.644	407.476	191.407	−391.476	−69.887	1.014
3700	58.537	462.247	408.934	197.257	−393.353	−60.928	0.860
3800	58 606	463.809	410.358	203.114	−395.254	−51.919	0.714
3900	58.683	465.333	411.748	208.979	−397.171	−42.858	0.574
4000	58.767	466.819	413.107	214.851	−399.094	−33.749	0.441
4100	58.859	468.272	414.434	220.732	−401.016	−24.591	0.313
4200	58.960	469.691	415.733	226.623	−402.928	−15.387	0.191
4300	59.068	471.080	417.004	232.525	−404.824	−6.138	0.075
4400	59.184	472.439	418.249	238.437	−406.697	3.156	−0.037
4500	59.308	473.770	419.468	244.362	−408.539	12.491	−0.145
4600	59.440	475.075	420.662	250.299	−410.347	21.868	−0.248
4700	59.579	476.355	421.834	256.250	−412.114	31.283	−0.348
4800	59.725	477.611	422.983	262.215	−413.836	40.735	−0.443
4900	59.878	478.844	424.110	268.195	−415.509	50.223	−0.535
5000	60.037	480.055	425.217	274.191	−417.130	59.744	−0.624
5100	60.203	481.246	426.304	280.203	−418.695	69.297	−0.710
5200	60.374	482.417	427.372	286.232	−420.201	78.880	−0.792
5300	60.551	483.568	428.421	292.278	−421.647	88.492	−0.872
5400	60.732	484.702	429.453	298.342	−423.031	98.130	−0.949
5500	60.918	485.818	430.468	304.424	−424.352	107.794	−1.024
5600	61.108	486.917	431.466	310.526	−425.608	117.480	−1.096
5700	61.301	488.000	432.448	316.646	−426.798	127.189	−1.166
5800	61.497	489.068	433.415	322.786	−427.924	136.918	−1.233
5900	61.696	490.121	434.368	328.946	−428.982	146.666	−1.298
6000	61.896	491.160	435.306	335.125	−429.976	156.431	−1.362

PREVIOUS: June 1973 (1 atm) CURRENT: June 1973 (1 bar)

Lead Chloride, Ion ($PbCl_2^+$) IDEAL GAS $M_r = 278.10545$ Lead Chloride, Ion ($PbCl_2^+$) $Cl_2Pb_1^+(g)$

$S°(298.15 K) = [318.57 \pm 8.4]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 812.26 \pm 50.2\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [816.298]\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2A_1$	0	[2]
$^2B_1$	[20000]	[2]

Vibrational Frequencies and Degeneracies

ν, cm^{-1}
[300](1)
[100](1)
[350](1)

Point Group: [C_{2v}] $\sigma = 2$

Bond Distance: Pb–Cl = [2.30] Å

Bond Angle: Cl–Pb–Cl = [116]°

Product of the Moments of Inertia: $I_A I_B I_C = [3.37567 \times 10^{-113}]\ g^3\cdot cm^6$

Enthalpy of Formation

The appearance potential for $PbCl_2^+$ from $PbCl_2(g)$ has been determined spectrometrically as (in eV) 11.2 ± 0.2,[1] 10.3 ± 0.2[2] and 10.3 ± 0.5.[3] Hastie *et al.*[2] preferred the lower AP for $PbCl_2^+$, since this value was obtained with more sensitive equipment. Subsequent measurements by Hastie and Swingler[4] confirm the lower result. They reported an ionization efficiency curve for $PbCl_2^+$ from which we obtain AP = 10.0 eV by the linear extrapolation method. Also, molecular orbital calculations by Hastie and Margrave[5] indicated IP($PbCl_2$,g) = 10.3 eV. We adopt a mean value from[2-4] of 10.2 ± 0.5 eV (235.2 kcal·mol^{-1}) for the process $PbCl_2(g) + e^- \rightarrow PbCl_{2+}(g) + 2\ e^-$ which gives $\Delta_f H°(PbCl_2^+,\ g,\ 0\ K) = 194.1 \pm 12.0\ kcal\cdot mol^{-1}$ when AP is combined with $\Delta_f H°(PbCl_2,\ g,\ 0\ K) = -41.1 \pm 0.3\ kcal\cdot mol^{-1}$.[6] $\Delta_f H°(298\ K) = 195.1\ kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

The correlation diagram of Walsh[7] predicts a bent configuration for $PbCl_2^+$, since the molecule has seventeen valence electrons. Also, Walsh[7] predicted that the apex angle for a non–hydride AB_2 molecule would decrease markedly in going from a 17– to an 18– electron molecule. We assume that the bond angle in $PbCl_2^+$ is 20° larger than that for $PbCl_2$.[6] The adopted value (116°) is consistent with JANAF bond angles for the isoelectronic molecules BCl_2(112°) and $AlCl_2$(120°).[6] The bond length is assumed to lie between that for PbCl and $PbCl_2$.[6] The principal moments of inertia are: $I_A = 13.0315 \times 10^{-39}$, $I_B = 44.7956 \times 10^{-39}$ and $I_C = 57.8271 \times 10^{-39}\ g\cdot cm^2$.

The vibrational frequencies are estimated by comparison with those for BCl_2, CCl_2, $SiCl_2$, and $PbCl_2$.[6] The ground state is assumed to be $^2A_1$ by analogy with that for the isoelectronic molecule NO_2.[8] MO calculations by Hastie and Margrave[5] for the Group III A dihalides predicted an upper $^2B_1$ state with the $^2A_1$–$^2B_1$ separation in the energy range 1–2 eV. We have included this state and estimated the $^2A_1$–$^2B_1$ separation (20,000 cm^{-1}) to be somewhat greater than that for AlO_2 (15,000 cm^{-1}),[6] BCl_2 (11,000 cm^{-1})[6] and NO_2(<15,000 cm^{-1}).[8]

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.896	812.264		
100	43.788	263.871	365.095	−10.122			
200	51.970	297.156	323.520	−5.273			
250	53.863	308.973	319.465	−2.623			
298.15	55.006	318.566	318.566	0.	816.298	800.890	−140.313
300	55.041	318.906	318.567	0.102	816.326	800.794	−139.431
350	55.809	327.452	319.240	2.874	817.066	798.147	−119.117
400	56.334	334.941	320.744	5.679	817.783	795.395	−103.868
450	56.705	341.599	322.698	8.505	818.476	792.555	−91.997
500	56.978	347.588	324.893	11.348	819.145	789.638	−82.493
600	57.340	358.011	329.569	17.065	820.420	783.616	−68.220
700	57.564	366.868	334.281	22.811	816.751	778.185	−58.069
800	57.711	374.565	338.846	28.575	817.877	772.599	−50.446
900	57.812	381.369	343.200	34.352	819.026	766.870	−44.508
1000	57.885	387.464	347.327	40.137	820.198	761.012	−39.751
1100	57.939	392.983	351.231	45.928	821.394	755.036	−35.854
1200	57.981	398.027	354.923	51.724	822.613	748.950	−32.601
1300	58.013	402.669	358.420	57.524	823.848	742.762	−29.845
1400	58.039	406.969	361.736	63.327	825.085	736.478	−27.478
1500	58.060	410.974	364.886	69.132	826.313	730.106	−25.425
1600	58.077	414.722	367.885	74.938	827.527	723.652	−23.625
1700	58.091	418.243	370.745	80.747	828.719	717.123	−22.035
1800	58.103	421.564	373.477	86.557	829.889	710.525	−20.619
1900	58.113	424.706	376.091	92.367	831.031	703.862	−19.351
2000	58.122	427.687	378.597	98.179	832.144	697.140	−18.207
2100	58.130	430.523	381.003	103.992	656.005	697.479	−17.349
2200	58.138	433.227	383.316	109.805	657.443	699.419	−16.606
2300	58.145	435.811	385.542	115.619	658.781	701.297	−15.927
2400	58.153	438.286	387.689	121.434	660.014	703.119	−15.303
2500	58.161	440.660	389.760	127.250	661.140	704.891	−14.728
2600	58.170	442.942	391.762	133.067	662.160	706.621	−14.196
2700	58.179	445.137	393.699	138.884	663.075	708.313	−13.703
2800	58.190	447.253	395.574	144.702	663.887	709.973	−13.245
2900	58.203	449.295	397.391	150.522	664.601	711.607	−12.817
3000	58.218	451.269	399.154	156.343	665.222	713.217	−12.418
3100	58.234	453.178	400.867	162.166	665.757	714.807	−12.044
3200	58.253	455.027	402.530	167.990	666.213	716.382	−11.694
3300	58.275	456.820	404.148	173.816	666.598	717.944	−11.364
3400	58.299	458.560	405.723	179.645	666.920	719.495	−11.054
3500	58.326	460.250	407.257	185.476	667.189	721.037	−10.761
3600	58.356	461.894	408.752	191.310	667.413	722.572	−10.484
3700	58.388	463.493	410.210	197.148	667.601	724.102	−10.222
3800	58.424	465.051	411.633	202.988	667.762	725.627	−9.974
3900	58.462	466.569	413.022	208.832	667.904	727.147	−9.739
4000	58.504	468.050	414.379	214.681	668.035	728.665	−9.515
4100	58.548	469.495	415.706	220.533	668.163	730.179	−9.303
4200	58.595	470.906	417.004	226.390	668.295	731.690	−9.100
4300	58.644	472.285	418.273	232.252	668.439	733.198	−8.907
4400	58.697	473.634	419.516	238.119	668.600	734.702	−8.722
4500	58.751	474.954	420.734	243.992	668.783	736.202	−8.546
4600	58.808	476.246	421.926	249.870	668.995	737.699	−8.377
4700	58.867	477.511	423.096	255.753	669.239	739.189	−8.215
4800	58.928	478.751	424.242	261.643	669.520	740.675	−8.060
4900	58.990	479.967	425.367	267.539	669.841	742.154	−7.911
5000	59.055	481.159	426.471	273.441	670.206	743.626	−7.769
5100	59.120	482.329	427.555	279.350	670.616	745.090	−7.631
5200	59.187	483.478	428.619	285.265	671.075	746.546	−7.499
5300	59.255	484.606	429.665	291.187	671.583	747.993	−7.372
5400	59.324	485.714	430.693	297.116	672.143	749.429	−7.249
5500	59.393	486.803	431.703	303.052	672.755	750.855	−7.131
5600	59.464	487.874	432.697	308.995	673.419	752.269	−7.017
5700	59.534	488.927	433.674	314.945	674.136	753.671	−6.907
5800	59.605	489.963	434.636	320.902	674.907	755.060	−6.800
5900	59.676	490.983	435.582	326.866	675.731	756.434	−6.697
6000	59.746	491.987	436.514	332.837	676.608	757.795	−6.597

PREVIOUS: June 1973 (1 atm)   CURRENT: June 1973 (1 bar)

Lead Chloride, Ion ($PbCl_2^+$) $Cl_2Pb_1^+(g)$

Sulfur Chloride (SCl_2) LIQUID $M_r = 102.966$ Sulfur Chloride (SCl_2) $Cl_2S_1(l)$

$S°(298.15\ K) = 183.678 \pm 4.2\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = -49.79 \pm 2.1\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Trautz and Hoffmann[1] have measured calorimetrically the enthalpy of solution of gaseous chlorine in dichlorodisulfane at 298.15 K. They reported $\Delta_{sln}H° = -9.8 \pm 0.4\ kcal{\cdot}mol^{-1}$ for a final state consisting of SCl_2 dissolved in an excess of S_2Cl_2. Combining their measured $\Delta_{sln}H$ value with $\Delta_fH°(S_2Cl_2,\ l,\ 298.15\ K) = -13.9 \pm 0.5\ kcal{\cdot}mol^{-1}$,[2] we obtain the adopted result of $\Delta_fH°(SCl_2,\ l,\ 298.15\ K) = -11.9 \pm 0.5\ kcal{\cdot}mol^{-1}$. In arriving at this value, no enthalpy corrections are applied for dissolution of the SCl_2 in the excess S_2Cl_2 and for the temperature difference since we expect both corrections to be small and they tend to cancel. Our adopted value agrees with the selected values of NBS ($-12\ kcal{\cdot}mol^{-1}$)[3] and Mills ($-11.8\ kcal{\cdot}mol^{-1}$).[4]

Heat Capacity and Entropy

The heat capacity of liquid SCl_2 is estimated as $21.75\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ using the value of $7.25\ cal{\cdot}K^{-1}{\cdot}g{\cdot}atom^{-1}$ recommended by Kubaschewski *et al.*[5] This estimated value of $C_p°$ corresponds to a specific heat of $0.21\ cal{\cdot}g^{-1}{\cdot}K^{-1}$ which agrees with the experimentally measured value for S_2Cl_2 of $0.22\ cal{\cdot}g^{-1}{\cdot}K^{-1}$.[2] We assume that $C_p°$ is constant in the temperature range 298–800 K. The value of $S°(298.15\ K)$ is selected as $43.9 \pm 1.0\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ which minimizes differences between the second and third law entropies of vaporization determined from vapor pressure data[6] on a pure stabilized sample of SCl_2. Further details on the results of these analyses can be found in the heat of formation section of the $SCl_2(g)$ table.[2]

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy of vaporization becomes zero. The value of $\Delta_{vap}H°$ is calculated as the difference between the $\Delta_fH°$ values for the gas and liquid at T_{vap}. The experimental value of T_{vap} determined from vapor pressure measurements is 332.7 K.[6]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	91.002	183.678	183.678	0.	−49.790	−28.485	4.990
300	91.002	184.241	183.679	0.168	−49.726	−28.353	4.937
400	91.002	210.420	187.249	9.269	−48.693	−21.639	2.826
500	91.002	230.727	193.989	18.369	−47.092	−15.075	1.575
600	91.002	247.318	201.537	27.469	−45.209	−8.843	0.770
700	91.002	261.346	209.105	36.569	−43.127	−2.945	0.220
800	91.002	273.498	216.411	45.669	−40.938	2.647	−0.173

PREVIOUS: CURRENT: June 1978

Sulfur Chloride (SCl_2) $Cl_2S_1(l)$

Sulfur Chloride (SCl_2) IDEAL GAS $M_r = 102.966$ Sulfur Chloride (SCl_2) $Cl_2S_1(g)$

$S°(298.15\ K) = 281.628 \pm 0.13\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -16.43 \pm 3.3\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -17.57 \pm 3.3\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^1A_2$	25810	1
$^1B_2$	29762	1

Vibrational Frequencies and Degeneracies

ν, cm^{-1}
528 (1)
205 (1)
525 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: S–Cl = 2.015 ± 0.001 Å
Bond Angle: Cl–S–Cl = 102.73 ± 0.05°
Product of the Moments of Inertia: $I_AI_BI_C = 5.91980 \times 10^{-114}\ g^3{\cdot}cm^6$

Enthalpy of Formation

Rosser and Whitt[1] have reported the results of a vapor pressure study of SCl_2. Measurements were conducted on a sample of SCl_2 stabilized with PCl_3 to suppress decomposition. Using JANAF free energy functions,[2] we analyze their vapor pressure points[1] lying above 298 K by the second and third law methods. In the analysis we select $S°(SCl_2, l, 298.15\ K) = 43.9\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ which minimizes the difference between the 2nd and 3rd law entropies of vaporization. Our results are $\Delta_{vap}H°$ (2nd law) = $\Delta_{vap}H°$ (3rd law) = $7.75 \pm 0.02\ kcal{\cdot}mol^{-1}$ which leads to the adopted heat of formation of $\Delta_fH°(SCl_2, g, 298.15\ K) = -4.2 \pm 0.8\ kcal{\cdot}mol^{-1}$ when combined with $\Delta_fH°(SCl_2, l, 298.15\ K) = -11.9 \pm 0.5\ kcal{\cdot}mol^{-1}$.[2] The adopted value of $\Delta_fH°$ is rounded to the nearest 0.1 kcal·mol^{-1}. The overall uncertainty is estimated as ±0.8 kcal·mol^{-1} based on contributions from the uncertainty in $\Delta_fH°$ of the liquid (±0.5 kcal·mol^{-1}) and from the uncertainty in the entropy (±1.0 cal·K^{-1}·mol^{-1}) of the liquid[2] which amounts to roughly 0.3 kcal·mol^{-1} in $\Delta_fH°$.

Barton and Yost[3] have studied the dissociation of $S_2Cl_2(g)$ at various temperatures. Their measured dissociation data above 760 K have been reanalyzed by Yost and Russell[4] who have determined equilibrium constants for the reactions (a) $S_2(g) + Cl_2(g) = S_2Cl_2(g)$ and (b) $0.5\ S_2(g) + Cl_2(g) = SCl_2(g)$ by combining the dissociation pressures with molecular data and an estimated value for the $\Delta_fH°$ of SCl_2. Second and third law analyses of the equilibrium data for reaction (b) give $\Delta_rH°(298.15\ K)$ (2nd law) = $\Delta_rH°(298.15\ K)$ (3rd law) = $-20.69 \pm 0.01\ kcal{\cdot}mol^{-1}$ which corresponds to $\Delta_fH°(SCl_2, g, 298.15\ K) = -5.3\ kcal{\cdot}mol^{-1}$ using the recent JANAF[2] value of $\Delta_fH°$ for $S_2(g)$. This $\Delta_fH°$ value for $SCl_2(g)$ is some 1.1 kcal·mol^{-1} more negative than that obtained from an analysis of vapor pressure data described above. We find a similar discrepancy in the equilibrium data for reaction (a) where the derived $\Delta_fH°$ value of $S_2Cl_2(g)$ is 3 kcal·mol^{-1} more negative than that obtained from an analysis of vapor pressure data. (See $S_2Cl_2(g)$ table for details). We conclude that the equilibrium constants reported by Yost and Russell[4] are biased, and we give no weight to the $\Delta_fH°$ values derived from their data.

Values of $\Delta_fH°$ previously selected by Colwell[5] and Mills[6] have been based primarily on the equilibrium data of Yost and Russell.[4] The value selected by NBS[7] is −4.7 kcal·mol^{-1}. Our adopted results give an enthalpy of atomization and mean S–Cl bond dissociation energy of 126.8 ± 0.9 kcal·mol^{-1} and 63.4 kcal·mol^{-1}, respectively.

Heat Capacity and Entropy

Early electron diffraction studies[8,9] and more recent microwave measurements[10,11] have shown that the SCl_2 molecule has C_{2v} symmetry. We adopt structural parameters from the microwave work of Davis and Gerry.[11] The bond length and angle refer to an average structure of $^{32}S^{35}Cl_2$ in the (000) vibrational state obtained from a quadratic potential function based solely on microwave data.[11] This average structure is only slightly different from the effective structure determined by Murray *et al.*[10] but quite different from the molecular structure derived from electron diffraction measurements[8,9] which are considered less accurate. The symmetrical stretch (ν_1) and bending (ν_2) frequencies are those observed by Frankiss and Harrison[12] in the Raman spectra of the vapor at 335 K. The asymmetrical stretching frequency (ν_3) was not detected in this recent Raman study[12] and still remains relatively uncertain (±10 cm^{-1}). We use $\nu_3 = 525\ cm^{-1}$ based on the infrared measurements of Savoie and Tremblay,[13] as suggested by Frankiss and Harrison.[12] The electronic levels and configurations are taken from the CNDO/2 MO calculations and electronic absorption spectral measurements of Colton and Rabalais.[14] The principal moments of inertia are: $I_A = 5.8026 \times 10^{-38}$, $I_B = 29.1706 \times 10^{-38}$, and $I_C = 34.9733 \times 10^{-39}\ g{\cdot}cm^{-2}$.

Our ideal gas thermal functions are essentially an extension of those previously published by Frankiss and Harrison[12] who also reviewed data published prior to their paper. All earlier functions require revision since they are based on liquid state vibrational frequencies and the molecular structure determined by electron diffraction.

Continued on page 940

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−12.445	−16.425	−16.425	INFINITE
100	37.966	233.457	323.231	−8.977	−16.559	−19.752	10.317
200	45.873	262.274	286.144	−4.774	−17.035	−22.770	5.947
250	48.815	272.842	282.455	−2.403	−17.303	−24.173	5.051
298.15	50.895	281.628	281.628	0.	−17.573	−25.472	4.463
300	50.962	281.943	281.629	0.094	−17.583	−25.521	4.444
350	52.512	289.922	282.255	2.683	−17.879	−26.820	4.003
400	53.643	297.011	283.665	5.338	−20.406	−27.989	3.655
450	54.482	303.380	285.508	8.043	−21.404	−28.885	3.353
500	55.117	309.155	287.588	10.783	−22.461	−29.658	3.098
600	55.992	319.288	292.051	16.342	−24.119	−30.935	2.693
700	56.547	327.964	296.576	21.971	−25.508	−31.958	2.385
800	56.919	335.540	300.983	27.646	−26.745	−32.794	2.141
900	57.179	342.260	305.203	33.351	−81.016	−32.400	1.880
1000	57.368	348.295	309.216	39.079	−80.881	−27.005	1.411
1100	57.509	353.770	313.021	44.823	−80.759	−21.624	1.027
1200	57.618	358.778	316.629	50.580	−80.651	−16.253	0.707
1300	57.703	363.394	320.051	56.346	−80.559	−10.890	0.438
1400	57.770	367.673	323.301	62.120	−80.486	−5.534	0.206
1500	57.825	371.660	326.394	67.900	−80.430	−0.182	0.006
1600	57.870	375.394	329.341	73.685	−80.393	5.166	−0.169
1700	57.908	378.903	332.154	79.473	−80.375	10.513	−0.323
1800	57.939	382.214	334.844	85.266	−80.377	15.860	−0.460
1900	57.966	385.347	337.421	91.061	−80.398	21.207	−0.583
2000	57.988	388.321	339.892	96.859	−80.440	26.555	−0.694
2100	58.008	391.151	342.266	102.659	−80.501	31.906	−0.794
2200	58.025	393.850	344.550	108.460	−80.582	37.261	−0.885
2300	58.040	396.430	346.750	114.264	−80.685	42.620	−0.968
2400	58.053	398.900	348.872	120.068	−80.810	47.983	−1.044
2500	58.065	401.270	350.920	125.874	−80.958	53.352	−1.115
2600	58.076	403.548	352.901	131.681	−81.128	58.728	−1.180
2700	58.086	405.740	354.818	137.490	−81.322	64.111	−1.240
2800	58.095	407.852	356.674	143.299	−81.540	69.501	−1.297
2900	58.104	409.891	358.474	149.109	−81.782	74.900	−1.349
3000	58.113	411.861	360.221	154.919	−82.047	80.307	−1.398
3100	58.121	413.767	361.918	160.731	−82.336	85.724	−1.444
3200	58.130	415.612	363.567	166.544	−82.647	91.150	−1.488
3300	58.139	417.401	365.172	172.357	−82.979	96.586	−1.529
3400	58.149	419.137	366.733	178.171	−83.332	102.033	−1.568
3500	58.160	420.823	368.255	183.987	−83.702	107 490	−1.604
3600	58.172	422.461	369.738	189.804	−84.089	112.958	−1.639
3700	58.186	424.055	371.185	195.621	−84.490	118.437	−1.672
3800	58.200	425.607	372.596	201.441	−84.902	123.927	−1.703
3900	58.217	427.119	373.975	207.262	−85.324	129.428	−1.733
4000	58.235	428.593	375.322	213.084	−85.752	134.940	−1.762
4100	58.256	430.032	376.639	218.909	−86.185	140.463	−1.790
4200	58.279	431.436	377.927	224.735	−86.619	145.996	−1.816
4300	58.304	432.807	379.188	230.565	−87.052	151.539	−1.841
4400	58.331	434.148	380.421	236.396	−87.481	157.093	−1.865
4500	58.362	435.459	381.630	242.231	−87.904	162.656	−1.888
4600	58.395	436.742	382.814	248.069	−88.318	168.229	−1.910
4700	58.430	437.998	383.975	253.910	−88.721	173.810	−1.932
4800	58.469	439.229	385.113	259.755	−89.111	179.400	−1.952
4900	58.511	440.435	386.230	265.604	−89.485	184.998	−1.972
5000	58.555	441.618	387.326	271.457	−89.843	190.603	−1.991
5100	58.603	442.778	388.402	277.315	−90.181	196.216	−2.010
5200	58.653	443.916	389.459	283.178	−90.499	201.834	−2.027
5300	58.707	445.034	390.497	289.046	−90.794	207.459	−2.045
5400	58.764	446.132	391.517	294.919	−91.066	213.089	−2.061
5500	58.823	447.210	392.520	300.799	−91.313	218.724	−2.077
5600	58.885	448.271	393.506	306.684	−91.535	224.363	−2.093
5700	58.950	449.314	394.476	312.576	−91.729	230.006	−2.108
5800	59.018	450.340	395.430	318.474	−91.896	235.652	−2.122
5900	59.089	451.349	396.369	324.380	−92.034	241.300	−2.136
6000	59.162	452.343	397.294	330.292	−92.143	246.951	−2.150

PREVIOUS June 1978 (1 atm) CURRENT: June 1978 (1 bar)

Sulfur Chloride, Ion (SCl_2^+) IDEAL GAS M_r = 102.96545 Sulfur Chloride, Ion (SCl_2^+) $Cl_2S_1^+(g)$

$\Delta_fH°(0 K) = 896.43 \pm 5.4 kJ·mol^{-1}$

$S°(298.15 K) = [287.32 \pm 4.2] J·K^{-1}·mol^{-1}$ $\Delta_fH°(298.15 K) = [901.485] kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2B_1$	0	2
$^2A_1$	20325	2
$^2A_1$	[21000]	2
$^2A_2$	22422	2
$^2A_2$	34198	2

Vibrational Frequencies and Degeneracies ν, cm^{-1}
530 ± 30 (1)
[200] (1)
[530] (1)

Point Group: [C_{2v}] σ = 2
Bond Distance: S–Cl = [2.00] Å
Bond Angle: Cl–S–Cl = [105]°
Product of the Moments of Inertia: $I_AI_BI_C = [5.65102 \times 10^{-114}] g^3·cm^6$

Enthalpy of Formation

$\Delta_fH°(0 K)$ is calculated from IP = 9.46 ± 0.02 eV by addition of the JANAF $\Delta_fH°(0 K)$ value for SCl_2.[1] The selected value of IP is calculated as the adiabatic IP from the first band system observed in the HeI photoelectron spectrum of SCl_2 by Solouki *et al.*[2] The adiabatic IP is 0.21 eV less than the vertical value determined by photoelectron spectroscopy[2] and 0.24–0.74 eV less than the vertical IP's measured by electron impact.[3,4]

$\Delta_fH°(298.15 K)$ is obtained from the adopted $\Delta_fH°(0 K)$ value by using JANAF enthalpies[1] for S(α, cr), $Cl_2(g)$, and $e^-(g)$. $\Delta_rH°(298.15 K)$ determined for the direct ionization $SCl_2 = SCl_2^+ + e^-$ from our tables differs from a room–temperature threshold energy due to inclusion of the enthalpies of all the species in this ionization process and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_fH°(298.15 K)$ should be changed by $-1.481 kcal·mol^{-1}$ if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

We perform bond energy calculations which show that the S–Cl primary bond dissociation energy for SCl_2^+ ($66.6 kcal·mol^{-1}$) is quite similar to that for the neutral dichloride ($69.7 kcal·mol^{-1}$), indicating that the removal of the electron during ionization should produce minimal structural changes. According to the Walsh diagram[6] for AB_2 molecules, the most loosely bound electron in SCl_2 occupies a $4b_1$ orbital which is S–Cl antibonding and Cl–Cl bonding. Thus, we would expect a slight increase in the bond angle and a decrease in the S–Cl bond distance upon removing this electron to form SCl_2^+. We estimate the Cl–S–Cl bond angle as 105° (102.7° for SCl_2) and the S–Cl bond distance as 2.00 Å (2.015 Å for SCl_2). Based on this estimated structure, the principal moments of inertia are: $I_A = 5.4345 \times 10^{-39}$, $I_B = 29.6437 \times 10^{-39}$, and $I_C = 35.0782 \times 10^{-39} g·cm^2$.

The photoelectron spectrum of SCl_2 has been measured by Solouki *et al.*[2] who reported observing a vibrational spacing of $530 \pm 30 cm^{-1}$ in the first band system. They assigned this progression to the S–Cl symmetric stretching frequency ν_1. By analogy with the observed vibrational frequencies for SCl_2,[1] the difference between ν_1 and ν_3 is expected to be small. We adopt $\nu_1 = \nu_3 = 530 cm^{-1}$, and we estimate the bending frequency to be $5 cm^{-1}$ lower than that for SCl_2 ($205 cm^{-1}$).[1]

The electronic configurations of the ground and excited states are predicted from Walsh's empirical diagram[6] which correlates well with the observed photoelectron spectra and calculated orbital energies for the related dihalide molecules SCl_2,[2] OCl_2, and OF_2.[7] We use relative term values for three of the four predicted states calculated from the vertical ionization energies reported by Solouki *et al.*[2] We include a second $^2A_1$ state at $21000 cm^{-1}$ based on the fact that this state has been observed in the PE spectrum of OCl_2,[7] lying $2258 cm^{-1}$ above the first $^2A_1$ state. Inclusion of this state is also supported by the results of orbital energy calculations[2] on SCl_2. The enthalpy between 0 K and 298.15 K is $-2.9764 kcal·mol^{-1}$.

References

[1] JANAF Thermochemical Tables: $SCl_2(g)$, 6–30–78; S(α, cr), 9–30–77; e–(g),3–31–77; $Cl_2(g)$, 9–30–65.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−12.453	896.427	896.427	INFINITE
100	38.080	239.130	328.914	−8.978	898.379	894.791	−467.391
200	45.858	267.979	291.835	−4.771	899.985	890.573	−232.594
250	48.783	278.542	288.148	−2.402	900.755	888.131	−185.565
298.15	50.860	287.322	287.322	0.	901.485	885.633	−155.159
300	50.928	287.636	287.323	0.094	901.512	885.535	−154.185
350	52.479	295.610	287.949	2.681	902.254	882.813	−131.753
400	53.613	302.695	289.357	5.335	900.765	880.074	−114.926
450	54.456	309.061	291.199	8.038	900.806	877.476	−101.855
500	55.095	314.833	293.278	10.777	900.787	874.888	−91.399
600	55.975	324.962	297.738	16.334	901.205	869.675	−75.712
700	56.533	333.636	302.262	21.962	901.892	864.369	−64.500
800	56.908	341.211	306.667	27.635	902.733	858.952	−56.084
900	57.170	347.930	310.886	33.340	850.540	854.505	−49.594
1000	57.361	353.964	314.897	39.067	852.753	854.827	−44.652
1100	57.503	359.438	318.701	44.810	854.953	854.928	−40.597
1200	57.613	364.446	322.307	50.566	857.139	854.829	−37.210
1300	57.698	369.061	325.729	56.332	859.308	854.548	−34.336
1400	57.767	373.340	328.979	62.105	861.461	854.101	−31.867
1500	57.822	377.327	332.070	67.885	863.594	853.501	−29.722
1600	57.867	381.060	335.017	73.669	865.709	852.759	−27.840
1700	57.905	384.570	337.829	79.458	867.805	851.885	−26.175
1800	57.937	387.880	340.519	85.250	869.882	850.889	−24.692
1900	57.964	391.013	343.095	91.045	871.939	849.777	−23.362
2000	57.988	393.987	345.566	96.843	873.977	848.558	−22.162
2100	58.009	396.817	347.939	102.643	875.994	847.237	−21.074
2200	58.028	399.516	350.223	108.445	877.991	845.821	−20.082
2300	58.047	402.096	352.423	114.249	879.968	844.314	−19.175
2400	58.065	404.567	354.544	120.054	881.922	842.722	−18.341
2500	58.083	406.937	356.593	125.862	883.855	841.049	−17.573
2600	58.103	409.216	358.573	131.671	885.765	839.299	−16.862
2700	58.124	411.409	360.490	137.482	887.653	837.476	−16.202
2800	58.148	413.523	362.346	143.296	889.518	835.583	−15.588
2900	58.176	415.564	364.146	149.112	891.361	833.625	−15.015
3000	58.208	417.537	365.893	154.931	893.183	831.603	−14.479
3100	58.244	419.446	367.590	160.754	894.983	829.520	−13.977
3200	58.286	421.296	369.240	166.580	896.765	827.380	−13.506
3300	58.334	423.090	370.845	172.411	898.528	825.184	−13.062
3400	58.388	424.833	372.407	178.247	900.276	822.935	−12.643
3500	58.449	426.526	373.929	184.089	902.011	820 635	−12.247
3600	58.517	428.174	375.413	189.937	903.734	818.286	−11.873
3700	58.592	429.778	376.861	195.792	905.450	815.889	−11.518
3800	58.676	431.341	378.274	201.656	907.160	813.445	−11.182
3900	58.767	432.867	379.655	207.528	908.868	810.957	−10.862
4000	58.866	434.356	381.003	213.409	910.577	808.425	−10.557
4100	58.973	435.811	382.323	219.301	912.291	805.850	−10.267
4200	59.088	437.233	383.613	225.204	914.011	803.233	−9.990
4300	59.211	438.625	384.876	231.119	915.743	800.575	−9.725
4400	59.342	439.988	386.113	237.047	917.488	797.876	−9.472
4500	59.479	441.323	387.326	242.988	919.250	795.138	−9.230
4600	59.624	442.632	388.514	248.943	921.032	792.361	−8.998
4700	59.776	443.916	389.679	254.913	922.836	789.544	−8.775
4800	59.934	445.176	390.822	260.898	924.666	786.688	−8.561
4900	60.098	446.413	391.944	266.900	926.522	783.795	−8.355
5000	60.267	447.629	393.045	272.918	928.408	780.863	−8.158
5100	60.442	448.824	394.127	278.953	930.326	777.893	−7.967
5200	60.622	450.000	395.191	285.007	932.277	774.885	−7.784
5300	60.805	451.156	396.236	291.078	934.264	771.839	−7.607
5400	60.993	452.294	397.263	297.168	936.287	768.756	−7.436
5500	61.183	453.415	398.274	303.277	938.348	765.635	−7.271
5600	61.377	454.519	399.269	309.404	940.448	762.475	−7.112
5700	61.573	455.607	400.248	315.552	942.588	759.278	−6.958
5800	61.770	456.680	401.211	321.719	944.768	756.044	−6.809
5900	61.969	457.738	402.160	327.906	946.990	752.771	−6.665
6000	62.169	458.781	403.095	334.113	949.254	749.460	−6.525

PREVIOUS: June 1978 (1 atm) CURRENT: June 1978 (1 bar)

Sulfur Chloride (ClSSCl) LIQUID $M_r = 135.026$ Sulfur Chloride (ClSSCl) $Cl_2S_2(l)$

$S°(298.15\ K) = 223.844 \pm 4.2\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(298.15\ K) = -58.158 \pm 2.1\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Feher and Strater[1] have measured calorimetrically the heats of chlorination of sulfur and liquid at 298.15 K. Recalculation of their calorimetric data using 1975 atomic weights[2] and a $\Delta C_p°$ of 10.80 cal·K⁻¹·mol⁻¹ for the formation reactions $2S(rh) + Cl_2(g) \rightarrow S_2Cl_2(l)$ leads to the adopted $\Delta_f H°$ of −13.9 ± 0.5 kcal·mol⁻¹. (−58.158 ± 2.1 kJ·mol⁻¹).

Other calorimetric values for $\Delta_f H°$ which were published prior to 1930 have been recently summarized by Mills.[3] Two of these four values, which range from −14.3 to −17.6 kcal·mol⁻¹, agree with the adopted $\Delta_f H°$ value within the combined experimental error. Our selected value agrees with that from Mills[3] but is some 0.3 kcal·mol⁻¹ less negative than the value (−14.2 kcal·mol⁻¹) recommended by NBS.[4]

Heat Capacity and Entropy

$C_p°$ has been measured calorimetrically as 29.706 cal·K⁻¹·mol⁻¹ by Trautz and Rick[5] at 295.15 K and by Ogier[6] as the mean $C_p°$ value over the temperature range 285–343 K. We adopt this value and assume $C_p°$ is constant from 298.15 K to 1000 K. The value of $S°(298.15\ K)$ is selected as 53.5 ± 1.0 cal·K⁻¹·mol⁻¹ which minimizes differences between the second and third law entropies of vaporization determined from two independent sets[7,8] of vapor pressure data. Further details on the results of these analyses can be found in the heat of formation section of the S_2Cl_2 gas phase table.[9]

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy of vaporization becomes zero. The value of $\Delta_{vap}H°$ is calculated as the difference between the $\Delta_f H°$ values for the gas and liquid at T_{vap}. Experimental values of T_{vap} determined from vapor pressure measurements include 411 K[7] and 408.9 K.[8]

References

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[4] U.S. Nat. Bur. Stand. Tech. Note 270-3, (1968).
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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	124.290	223.844	223.844	0.	−58.158	−39.271	6.880
300	124.290	224.613	223.846	0.230	−58.075	−39.154	6.817
400	124.290	260.369	228.721	12.659	−58.310	−33.318	4.351
500	124.290	288.103	237.927	25.088	−57.308	−27.213	2.843
600	124.290	310.764	248.236	37.517	−55.681	−21.336	1.857
700	124.290	329.923	258.572	49.946	−53.617	−15.771	1.177
800	124.290	346.520	268.551	62.375	−51.310	−10.519	0.687
900	124.290	361.159	278.044	74.804	−155.115	−3.405	0.198
1000	124.290	374.254	287.022	87.233	−150.135	13.185	−0.689

PREVIOUS: March 1978   CURRENT: June 1978

Sulfur Chloride (ClSSCl) IDEAL GAS $M_r = 135.026$ Sulfur Chloride (ClSSCl) $Cl_2S_2(g)$

$S°(298.15\ K) = 327.21 \pm 0.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -15.2 \pm 4\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -16.7 \pm 4\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
546 (1)	Internal Rotation
466 (1)	461 (1)
202 (1)	244 (1)

Ground State Quantum Weight: 1 σ(overall) = 2
Point Group: C_2
Bond Distances: S–Cl = 2.057 ± 0.002 Å; S–S = 1.931 ± 0.005 Å
Bond Angles: S–S–Cl = 108.2 ± 0.3°; Dihedral Angle = 84.8 ± 1.3°
Product of Moments of Inertia: $I_AI_BI_C = 6.36049 \times 10^{-113}\ g^3\ cm^6$
Reduced Moment of Inertia: $I_{red} = 5.487 \times 10^{-39}\ g{\cdot}cm^2$
Potential Function for Internal Rotation: $V = 11.99 - 5.60(1-\cos 2\phi) - 0.70(1-\cos 3\phi)\ kcal{\cdot}mol^{-1}$

Enthalpy Reference Temperature = T_r = 298.15 K						Standard State Pressure = $p°$ = 0.1 MPa	
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−16.479	−15.210	−15.210	INFINITE
100	49.149	260.367	385.447	−12.508	−15.531	−20.162	10.532
200	64.455	299.547	333.379	−6.766	−16.111	−24.572	6.418
298.15	72.768	327.215	327.215	0.	−16.736	−28.669	5.023
300	72.881	327.665	327.216	0.135	−16.748	−28.743	5.005
400	77.032	349.244	330.130	7.646	−21.901	−32.460	4.239
500	79.350	366.698	335.754	15.472	−25.503	−34.705	3.626
600	80.818	381.301	342.162	23.484	−28.292	−36.269	3.158
700	81.839	393.840	348.670	31.619	−30.523	−37.417	2.792
800	82.588	404.819	355.016	39.842	−32.422	−38.270	2.499
900	83.140	414.580	361.102	48.130	−140.368	−36.736	2.132
1000	83.529	423.361	366.897	56.464	−139.482	−25.269	1.320
1100	83.780	431.335	372.398	64.831	−138.609	−13.890	0.660
1200	83.931	438.632	377.618	73.217	−137.758	−2.589	0.113
1300	83.990	445.353	382.573	81.614	−136.939	8.641	−0.347
1400	83.969	451.576	387.282	90.012	−136.158	19.810	−0.739
1500	83.902	457.368	391.764	98.406	−135.422	30.925	−1.077

PREVIOUS: June 1978 (1 atm) CURRENT: June 1978 (1 bar)

Enthalpy of Formation

Harvey and Schuette[1] and Trautz *et al.*[2] have used a static method to measure vapor pressures for liquid S_2Cl_2 at various temperatures below the normal boiling point. Barton and Yost[3] measured the extent of dissociation for gaseous S_2Cl_2 above 760 K. These dissociation data have been reanalyzed by Yost and Russell[4] who reported equilibrium constants for the reaction $S_2(g) + Cl_2(g) = S_2Cl_2(g)$. We analyze these data by the 2nd and 3rd law methods with the results presented below:

Source	Reaction	Data Points	T/K	$\Delta_fH°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_fH°$(298.15 K) kcal·mol^{-1}
1	A	12[a]	304–411	9.46	9.89 ± 0.07	1.1 ± 0.2	4.01
2	A	Set 1 20[b]	374–410	10.0	9.93 ± 0.01	−0.1 ± 0.2	3.97
		Set 2 39[c]	329–374	10.15	9.95 ± 0.02	−0.6 ± 0.1	3.95
2	A	22	336–405	10.23	9.98 ± 0.04	−0.8 ± 0.1	3.92
4	B	Equation	760–1100	−35.4	−38.1 ± 0.9	−3.1 ± 7	7.4

Reaction: (A) $S_2Cl_2(l) = S_2Cl_2(g)$ (B) $S_2(g) + Cl_2(g) = S_2Cl_2(g)$.
[a] Points below 298.15 K not analyzed; 2 points rejected due to failure of a statistical test.
[b] Two points rejected due to failure of a statistical test.
[c] Three points rejected.

We adopt $\Delta_fH°(S_2Cl_2, g, 298.15\ K) = -4.0\ kcal{\cdot}mol^{-1}$ which is the rounded mean value determined from the four 3rd law enthalpies of vaporization. We estimate the uncertainty in the $\Delta_fH°$ value as ± 1.0 kcal·mol^{-1} which includes contributions from the uncertainties in the values of $\Delta_fH°$(298.15 K) and $S°$(298.15 K) for the liquid.[5] $\Delta_fH°$(0 K) is − 3.6 kcal·mol^{-1} and the enthalpy of atomization is 192.1 ± 1.0 kcal·mol^{-1}.

Bodewig and Plambeck[6] determined $\Delta_rG = -12.4\ kcal{\cdot}mol^{-1}$ for $2\ S(l) + 2\ Cl^- = S_2Cl_2(g) + 2\ e^-$ in fused LiCl–KCL eutectic at 693 K. This datum has been analyzed by Mills[7] who reported $\Delta_fH°$(298.15 K) value of −5.8 ± 2 kcal·mol^{-1}. Our selected $\Delta_fH°$ value is some 0.4 kcal·mol^{-1} less negative than that recommended by NBS[8] and is only 0.1 kcal·mol^{-1} less negative than the value adopted by Mills.[7]

Heat Capacity and Entropy

The heat capacity and entropy values from 298.15 K to 1500 K are those calculated by Frankiss and Harrison[9] who used gas–phase infrared ($\nu_1 = 546\ cm^{-1}$)[10] and Raman[9] frequencies and the most recent structural data determined in an electron diffraction study by Beagley *et al.*[11] Contributions to the thermal functions for internal rotation were determined by integration of the potential function from $\phi = 0°$ to 2π. Terms in the potential function were established from the torsional vibration ($\nu_4 = 92\ cm^{-1}$) and the dihedral angle (84.8°)[11] of the two rotamers. Thermal functions are calculated below 298.15 K by treating the torsion as a harmonic oscillator and including its contribution in the vibrational partition function. Justification for this treatment lies in the fact that values of the ratio V_0/RT become extremely large (>20) at these lower temperatures. We add $R\ln 2$ to the calculated entropies below 298.15 K to account for the optical activity of the skew rotamer. The absorption spectra[12] reported for S_2Cl_2 vapor indicate no low–lying electronic states which would contribute to the thermal functions below 1500 K. The principal moments of inertia are: $I_A = 15.2331 \times 10^{-39}$, $I_B = 60.6645 \times 10^{-39}$, and $I_C = 68.8282 \times 10^{-9} g{\cdot}cm^2$.

Thermodynamic functions previously published for S_2Cl_2 have been reviewed by Frankiss and Harrison[9] who concluded that all previous calculations had treated incorrectly the internal rotation of the SCl top. Noble and Mei[13] have discussed the vibrational spectral data on S_2Cl_2 published prior to 1974.

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Dichlorosilylene (SiCl$_2$) IDEAL GAS $M_r = 98.9915$ Dichlorosilylene (SiCl$_2$) Cl$_2$Si$_1$(g)

$S°(298.15 \text{ K}) = [281.333 \pm 0.8] \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = -168.74 \pm 3.3 \text{ kJ·mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = -168.62 \pm 3.3 \text{ kJ·mol}^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
[$^1A_1$]	0	[1]
[$^3B_1$]	[23000]	[3]
	[28300]	[1]
	[29950]	[1]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
514.0 (1)
202.2 (1)
502.7 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Si–Cl = [2.03] Å
Bond Angle. Cl–Si–Cl = 105° ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = [5.55300 \times 10^{-114}] \text{ g}^3\text{·cm}^6$

Enthalpy of Formation

The adopted $\Delta_f H°(\text{SiCl}_2, \text{g}, 298.15 \text{ K}) = -40.3 \text{ kcal·mol}^{-1}$ is the mean value derived from four studies.[2,3,7,8] JANAF analyses of all the equilibrium data are summarized below. The $\Delta_f H°(298.15 \text{ K})$ values are calculated from the third law $\Delta_r H°(298.15 \text{ K})$ values using auxiliary JANAF data.[1] Four sets of data[2,3,7,8] yield average values of $\Delta_f H°$ (from third law) which agree within 0.4 kcal·mol^{-1} and values of $\Delta_r S°$(second law) which are in reasonable agreement with the JANAF functions. Two of these equilibrium studies used flow techniques, one used mass spectrometry, while the fourth used a static technique. The adopted $\Delta_f H°(298.15 \text{ K})$ value corresponds to $\Delta_a H°(0 \text{ K}) = 204.2 \text{ kcal·mol}^{-1}$ and an average bond energy of 102.1 kcal·mol^{-1}. This latter value compares with 94.7 kcal·mol^{-1} for SiCl$_4$(g), implying that the average bond energy in SiCl$_2$(g) is 7% larger.

Two other flow studies[4,5] yield large entropy errors, suggesting that there are temperature–dependent errors in $K_p°$. The reported equilibrium constants are reasonable at the lower temperatures but deviate progressively at the higher temperatures. In contrast, the static study of Ishino[6] gave $K_p°$ values which differ by a factor of five from the adopted ones. These data yield a consistent entropy but $\Delta_r H°$ (third law) is lower by 5 kcal·mol^{-1}.

Source	Method	Points	T/K	Reaction*	$\Delta_r H°$(298.15 K), kcal mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Schafer *et al.*[2]	flow	Equation	1273–1473	A	80.56	77.93	−1.9	−40.2
Teichmann and Wolf[3]	flow	Equation	1223–1573	A	80.83	78.06	−2.0	−40.2
Chechentsev *et al.*[4]	flow	3	1473–1573	A	131.78	75.96	−37 ± 6	−41.2
Antipin and Sergeev[5]	flow	5	1273–1673	A	113.99	75.00	−26 ± 3	−41.7
Ishino *et al.*[6]	static	27	1448–1573	A	70.24	72.97	1.8 ± 4	−42.7
Schafer and Nickl[7]	static	Equation	1400–1593	A	79.78	78.38	−0.9	−40.0
Farber and Srivastava[8]	mass spec	10	1593–1792	B	−31.62	−30.95	0.4 ± 2.0	−40.8

*Reactions (A) $\text{Si(cr)} + \text{SiCl}_4\text{(g)} = 2\ \text{SiCl}_2\text{(g)}$ (B) $\text{Si(g)} + \text{SiCl}_4\text{(g)} = 2\ \text{SiCl}_2\text{(g)}$

Heat Capacity and Entropy

Maass *et al.*[9] observed the infrared spectra of SiCl$_2$ in argon, neon, and nitrogen matrices. They observed and assigned all three fundamental frequencies. The bond angle was calculated to be 105 ± 3° from the isotopic splitting. The bond length is assumed to be the same as in SiH$_2$Cl$_2$.[1] The earlier work of Milligan and Jacox[10] is consistent with these results. The principal moments of inertia are: $I_A = 5.1016 \times 10^{-39}$, $I_B = 30.5397 \times 10^{-39}$, $I_C = 35.6413 \times 10^{-39} \text{ g·cm}^2$.

The ground state is assumed to be $^1A_1$ as suggested by Huckel-molecular-orbital calculation.[12] Singlet excited states[11,12] are included near 28000 and 30000 cm^{-1}, but the values are placed in brackets to emphasize the uncertainty in the analysis. Also tentatively adopted is the suggestion by Hastie *et al.*[13] that the continuous spectrum near 23000 cm^{-1} is due to a triplet excited state.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.524	−168.740	−168.740	INFINITE
100	38.144	232.778	323.282	−9.050	−168.445	−172.439	90.073
200	46.298	261.819	285.885	−4.813	−168.424	−176.462	46.087
250	49.217	272.481	282.167	−2.421	−168.501	−178.464	37.288
298.15	51.248	281.333	281.333	0.	−168.615	−180.373	31.601
300	51.313	281.651	281.334	0.095	−168.620	−180.446	31.418
350	52.810	289.679	281.965	2.700	−168.769	−182.405	27.222
400	53.893	296.806	283.383	5.369	−168.938	−184.342	24.073
450	54.693	303.202	285.236	8.085	−169.122	−186.256	21.620
500	55.297	308.997	287.327	10.835	−169.321	−188.150	19.656
600	56.125	319.158	291.809	16.410	−169.754	−191.875	16.704
700	56.648	327.852	296.352	22.050	−170.234	−195.525	14.590
800	56.998	335.441	300.774	27.733	−170.759	−199.103	13.000
900	57.243	342.169	305.006	33.446	−171.328	−202.612	11.759
1000	57.421	348.210	309.030	39.180	−171.942	−206.056	10.763
1100	57.553	353.689	312.845	44.929	−172.599	−209.435	9.945
1200	57.655	358.701	316.460	50.689	−173.299	−212.754	9.261
1300	57.734	363.320	319.889	56.459	−174.042	−216.012	8.679
1400	57.798	367.600	323.146	62.236	−174.830	−219.211	8.179
1500	57.849	371.590	326.244	68.018	−175.663	−222.352	7.743
1600	57.891	375.325	329.196	73.805	−176.541	−225.436	7.360
1700	57.926	378.836	332.014	79.596	−227.644	−228.017	7.006
1800	57.956	382.147	334.708	85.390	−228.387	−228.018	6.617
1900	57.981	385.282	337.288	91.187	−229.137	−227.977	6.268
2000	58.003	388.256	339.763	96.987	−229.895	−227.896	5.952
2100	58.021	391.087	342.140	102.788	−230.662	−227.778	5.666
2200	58.038	393.786	344.427	108.591	−231.439	−227.622	5.404
2300	58.053	396.366	346.629	114.395	−232.228	−227.431	5.165
2400	58.068	398.837	348.754	120.201	−233.031	−227.205	4.945
2500	58.081	401.208	350.805	126.009	−233.847	−226.946	4.742
2600	58.095	403.486	352.787	131.818	−234.680	−226.653	4.554
2700	58.110	405.679	354.706	137.628	−235.529	−226.329	4.379
2800	58.126	407.793	356.564	143.440	−236.396	−225.972	4.216
2900	58.144	409.833	358.366	149.253	−237.281	−225.584	4.063
3000	58.164	411.804	360.115	155.069	−238.183	−225.166	3.920
3100	58.188	413.712	361.813	160.886	−239.102	−224.717	3.786
3200	58.215	415.560	363.464	166.706	−240.037	−224.238	3.660
3300	58.247	417.352	365.070	172.529	−240.987	−223.729	3.541
3400	58.284	419.091	366.633	178.356	−241.951	−223.192	3.429
3500	58.326	420.781	368.156	184.186	−242.926	−222.626	3.323
3600	58.374	422.425	369.641	190.021	−628.061	−211.571	3.070
3700	58.429	424.025	371.089	195.861	−628.637	−199.994	2.823
3800	58.492	425.584	372.503	201.707	−629.217	−188.402	2.590
3900	58.561	427.104	373.884	207.560	−629.799	−176.794	2.368
4000	58.639	428.588	375.233	213.420	−630.378	−165.171	2.157
4100	58.725	430.037	376.552	219.288	−630.951	−153.533	1.956
4200	58.819	431.453	377.842	225.165	−631.514	−141.882	1.765
4300	58.922	432.838	379.105	231.052	−632.064	−130.218	1.582
4400	59.033	434.194	380.342	236.950	−632.597	−118.541	1.407
4500	59.154	435.522	381.553	242.859	−633.109	−106.852	1.240
4600	59.283	436.824	382.741	248.781	−633.598	−95.152	1.080
4700	59.421	438.100	383.905	254.716	−634.059	−83.441	0.927
4800	59.567	439.353	385.047	260.665	−634.490	−71.721	0.780
4900	59.722	440.582	386.168	266.630	−634.887	−59.993	0.640
5000	59.885	441.791	387.269	272.610	−635.250	−48.257	0.504
5100	60.055	442.978	388.349	278.607	−635.573	−36.514	0.374
5200	60.234	444.146	389.411	284.621	−635.857	−24.765	0.249
5300	60.420	445.295	390.455	290.654	−636.098	−13.010	0.128
5400	60.612	446.426	391.481	296.705	−636.295	−1.252	0.012
5500	60.811	447.540	392.490	302.776	−636.446	10.510	−0.100
5600	61.016	448.638	393.483	308.868	−636.550	22.273	−0.208
5700	61.227	449.720	394.460	314.980	−636.606	34.039	−0.312
5800	61.442	450.786	395.422	321.113	−636.613	45.805	−0.413
5900	61.663	451.838	396.369	327.268	−636.571	57.570	−0.510
6000	61.887	452.877	397.302	333.446	−636.477	69.334	−0.604

PREVIOUS December 1977 (1 atm) CURRENT. December 1977 (1 bar)

Strontium Chloride ($SrCl_2$) CRYSTAL (α–β) $M_r = 158.526$ Strontium Chloride ($SrCl_2$) $Cl_2Sr_1(cr)$

$S°(298.15\ K) = 114.809 \pm 0.17\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs} = 1000 \pm 10\ K$
$T_{fus} = 1147 \pm 1\ K$

$\Delta_f H°(0\ K) = -829.34 \pm 2.5\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -828.85 \pm 2.5\ kJ{\cdot}mol^{-1}$
$\Delta_{trs} H° = [6.008 \pm 1.3]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus} H° = 16.221 \pm 0.63\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is from[1] and was selected by Parker in a manner analogous to that described[2] for $\Delta_f H°(BaCl_2, cr)$. The adopted value is essentially that derived by Ehrlich *et al.*[3] from their measurements of $\Delta_{sol} H°$ of Sr(cr) and $SrCl_2(cr)$ in HCl(aq, 550 H_2O). Earlier solution data for Sr[4] and $SrCl_2$[5] are in good agreement.

Parker[2] rejected $\Delta_f H° = -210\ kcal{\cdot}mol^{-1}$ obtained by Siemonsen[6] from direct chlorination and $\Delta_f H° = -201.0\ kcal{\cdot}mol^{-1}$ which would result from SrO(cr) based on Mah's direction combustion.[7] Parker noted that these more negative values are inconsistent with data for $SrCl_2$(cr, aq) and related compounds. They are also less consistent with equilibrium data discussed on the tables for $SrCl_2$(l, g). Impurity effects are of concern in all these studies involving Sr(cr), but the evidence favors the solution calorimetry.

Heat Capacity and Entropy

$C_p°$ is based on adiabatic calorimetry (7.4–300 K) of Smith *et al.*[8] with omission of the point at 11.22 K which appears to be about 30% low. $S°$ is calculated from $C_p°$ using $S°(7\ K) = 0.012\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. $C_p°$ above 300 K is from constrained fitting of enthalpy data (418–936 K for α–phase and 1034–1134 K for β–phase) from Dworkin and Bredig.[9]

The transition near 1000 K is gradual and may be second order rather than first order as we have treated it. Gradual transitions also are observed for BaF_2, SrF_2 and perhaps CaF_2, all of which have α–phases of the fluorite structure. Reasonable $C_p°$ curves are obtained by omitting from the curve fits those enthalpy data from about 50 below to 30 above T_{trs}. The resulting Gibbs–energy functions agree well with those obtained[9] by second–order analysis.

Deviations of the fitted data[9] from the adopted functions for α–phase are −0.5 to +0.3% except for +2.0% at 417.6 K. Data of Efremova and Matizen[10] deviate by +0.6 to +2.2% (805–959 K), while the equation of Janz *et al.*[11] agrees almost exactly near 850 K but deviates by −4.8% at 600 K. The β–phase deviations are −0.4 to +0.3%[9], 0.0 to −1.0%, (1047–1142 K)[10] and −2 to 0%, (1050–1147 K).[11]

Transition Data

$T_{trs} = 1000$ K is arbitrarily selected as the peak of the gradual transition. Reported values include 1003,[9] 1002[11] and 990 K.[10] $\Delta_{trs} H°$ is calculated as the difference in the enthalpy curve fits (cf. above) at T_{trs}. $\Delta_{trs} H°$ is assigned an uncertainty of 0.3 $kcal{\cdot}mol^{-1}$ as a first–order transition, but the result is placed in brackets to emphasize that the transition may be a second order. Reported values of $\Delta_{trs} H°$ include 1.65[9] and 0.65[11] $kcal{\cdot}mol^{-1}$.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.242	−829.344	−829.344	INFINITE
100	54.296	41.459	178.054	−13.659	−831.172	−813.612	424.988
200	70.735	85.571	121.583	−7.202	−830.241	−796.320	207.978
298.15	75.588	114.809	114.809	0.	−828.850	−779.965	136.647
300	75.659	115.277	114.810	0.140	−828.823	−779.661	135.751
400	78.889	137.512	117.820	7.877	−827.285	−763.503	99.703
500	81.321	155.385	123.603	15.891	−825.670	−747.743	78.116
600	83.659	170.415	130.185	24.138	−823.985	−732.315	63.754
700	86.580	183.518	136.887	32.642	−822.187	−717.177	53.516
800	90.793	195.336	143.465	41.497	−820.171	−702.309	45.856
900	96.977	206.364	149.846	50.866	−818.397	−687.644	39.910
1000	105.826	217.013	156.032	60.981	−815.052	−673.287	35.169
1000.010	105.827	217.014	156.033	60.982	ALPHA <--> BETA		
1000 010	123.010	223.022	156.033	66.990	TRANSITION		
1100	123.010	234.745	162.663	79.290	−811.429	−659.613	31.322
1147.000	123.010	239.892	165.723	85.071	---- BETA <--> LIQUID ----		
1200	123.010	245.448	169.123	91.591	−806.836	−646.014	28.120
1300	123.010	255.294	175.378	103.892	−802.254	−632.798	25.426
1400	123.010	264.410	181.415	116.193	−797.681	−619.935	23.130
1500	123.010	272.897	187.235	128.494	−793.117	−607.398	21.151
1600	123.010	280.836	192.839	140.795	−788.562	−595.166	19.430
1700	123.010	288.293	198.237	153.096	−920.931	−582.038	17.884
1800	123.010	295.324	203.437	165.397	−914.533	−562.288	16.317
1900	123.010	301.975	208.450	177.698	−908.151	−542.893	14.925
2000	123.010	308.285	213.285	189.999	−901.787	−523.833	13.681

PREVIOUS: CURRENT: December 1972

Strontium Chloride ($SrCl_2$) LIQUID M_r = 158.526 Strontium Chloride ($SrCl_2$) $Cl_2Sr_1(l)$

$S°(298.15 \text{ K}) = [135.820] \text{ J·K}^{-1}\text{·mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = [-805.352] \text{ kJ·mol}^{-1}$
$T_{fus} = 1147 \pm 1 \text{ K}$
$\Delta_{fus} H° = 16.221 \pm 0.63 \text{ kJ·mol}^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of the crystal by addition of $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1147 \text{ K})–H°(298.15 \text{ K})$, between the crystal and liquid. An independent value of $\Delta_f H°$ for liquid (and crystal) may be derived from equilibrium data[1] for $Ca(l) + SrCl_2(l) \rightarrow Sr(l) + CaCl_2(l)$ at 1273 K. Our third–law analysis yields $\Delta_r H°(298.15 \text{ K}) = 6.5 \pm 1.3 \text{ kcal·mol}^{-1}$ or $\Delta_f H°(l) = -191.5 \pm 1.5 \text{ kcal·mol}^{-1}$ and $\Delta_f H°(cr) = -197.2 \pm 1.5 \text{ kcal·mol}^{-1}$. This confirms the adopted values as opposed to the more negative values (cf. $SrCl_2$, cr).

Heat Capacity and Entropy

The constant $C_p°$ of 25.0 cal·K^{-1}·mol^{-1} is a compromise chosen by comparison with $BaCl_2$ and $CaCl_2$. Our fits of the enthalpy data yield 26.8[2] and 23.5[3] cal·K^{-1}·mol^{-1}; the adopted value is roughly their mean. The value 26.7 cal·K^{-1}·mol^{-1} was also reported.[4] Deviations from our adopted functions are ±0.3% (1154–1204 K),[2] +1.1 to −1.7% (1152–1797 K),[3] and −1.1 to −0.2% (equation, 1148–1287 K).[4] $C_p°$ is taken equal to that of the crystal from 298.15 to 800 K, the assumed glass transition. $S°(298.15 \text{ K})$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} is selected from 1146,[2] 1147 ± 2[3] and 1148 K[4] reported in the enthalpy studies. $\Delta_{fus} H°$ is obtained from the difference in the adopted enthalpy fits for liquid and β–phases. Published values include 3.85,[2,3] 3.88,[2] 3.65 ± 0.17[4] and 3.73 kcal·mol^{-1},[5] the last value obtained by dynamic differential calorimetry.

Vaporization Data

T_{vap} is calculated as the temperature at which $\Delta_r G° = 0$ for $SrCl_2(l) \rightarrow SrCl_2(g)$. $\Delta_{vap} H°$ is calculated as the corresponding $\Delta_r H°$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	75.588	135.820	135.820	0.	−805.351	−762.730	133.627
300	75.659	136.288	135.822	0.140	−805.323	−762.465	132.757
400	78.889	158.524	138.832	7.877	−803.786	−748.408	97.732
500	81.321	176.397	144.615	15.891	−802.170	−734.749	76.759
600	83.659	191.426	151.196	24.138	−800.486	−721.422	62.805
700	86.580	204.529	157.898	32.642	−798.687	−708.385	52.860
800	90.793	216.348	164.476	41.497	−796.671	−695.619	45.419
800.010	90.793	216.349	164.477	41.498	GLASS <--> LIQUID TRANSITION		
800.010	104.600	216.349	164.477	41.498			
900	104 600	228.668	170.938	51.957	−793.806	−683.126	39.648
1000	104.600	239.688	177.271	62.417	−790.116	−671.027	35.051
1100	104.600	249.658	183.406	72.877	−794.343	−658.930	31.290
1147.000	104.600	254.034	186.211	77.793	---- BETA <--> LIQUID ----		
1200	104.600	258.759	189.312	83.337	−791.591	−646.742	28.152
1300	104.600	267.132	194.980	93.797	−788.849	−634.782	25.506
1400	104.600	274.883	200.414	104.257	−786.117	−623.033	23.246
1500	104.600	282.100	205.622	114.717	−783.394	−611.480	21.294
1600	104.600	288.851	210.615	125.177	−780.680	−600.107	19.591
1700	104.600	295.192	215.406	135.637	−914.890	−587.725	18.059
1800	104.600	301.171	220.006	146.097	−910.333	−568.611	16.501
1900	104.600	306.826	224.428	156.557	−905.792	−549.751	15.114
2000	104.600	312.191	228.683	167.017	−901.269	−531.129	13.872
2100	104.600	317.295	232.782	177.477	−896.769	−512.732	12.754
2200	104.600	322.161	236.735	187.937	−892.298	−494.550	11.742
2300	104.600	326.811	240.551	198.397	−887.862	−476.570	10.823
2400	104.600	331.262	244.239	208.857	−883.470	−458.782	9.985
2500	104.600	335.532	247.805	219.317	−879.131	−441.176	9.218
2600	104.600	339.635	251.259	229.777	−874.852	−423.742	8.513
2700	104.600	343.582	254.606	240.237	−870.645	−406.472	7.864
2800	104.600	347.386	257.852	250.697	−866.521	−389.356	7.264
2900	104.600	351.057	261.003	261.157	−862.488	−372.386	6.707
3000	104.600	354.603	264.064	271.617	−858.558	−355.553	6.191

PREVIOUS: CURRENT: December 1972

Strontium Chloride ($SrCl_2$)

CRYSTAL(α–β)–LIQUID

0 to 1000 K crystal, alpha
1000 to 1147 K crystal, beta
above 1147 K liquid

Refer to the individual tables for details.

M_r = 158.526 Strontium Chloride ($SrCl_2$)

$Cl_2Sr_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K

Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	0.	0.	INFINITE	0.	−813.101	−813.101	INFINITE
100	65.775	38.171	178.944	−14.077	−831.590	−813.701	425.034
200	71.271	85.512	121.591	−7.216	−830.254	−796.322	207.978
298.15	75.588	114.809	114.809	0.	−828.850	−779.965	136.647
300	75.659	115.277	114.810	0.140	−828.823	−779.661	135.751
400	78.889	137.512	117.820	7.877	−827.285	−763.503	99.703
500	81.321	155.385	123.603	15.891	−825.670	−747.743	78.116
600	83.659	170.415	130.185	24.138	−823.985	−732.315	63.754
700	86.580	183.518	136.887	32.642	−822.187	−717.177	53.516
800	90.793	195.336	143.465	41.497	−820.171	−702.309	45.856
900	96.977	206.364	149.846	50.866	−818.397	−687.644	39.910
1000	105.826	217.013	156.032	60.981	−815.052	−673.287	35.169
1000.010	105.827	217.014	156.033	60.982	ALPHA <--> BETA		
1000.010	123.010	223.022	156.033	66.990		TRANSITION	
1100	123.010	234.745	162.663	79.290	−811.429	−659.613	31.322
1147.000	123.010	239.892	165.723	85.071	BETA <--> LIQUID		
1147.000	104.600	254.034	165.723	101.293		TRANSITION	
1200	104.600	258.759	169.729	106.836	−791.591	−646.742	28.152
1300	104.600	267.132	176.903	117.296	−788.849	−634.782	25.506
1400	104.600	274.883	183.629	127.756	−786.117	−623.033	23.246
1500	104.600	282.100	189.956	138.216	−783.394	−611.480	21.294
1600	104.600	288.851	195.928	148.676	−780.680	−600.107	19.591
1700	104.600	295.192	201.582	159.136	−914.890	−587.725	18.059
1800	104.600	301.171	206.950	169.596	−910.333	−568.611	16.501
1900	104.600	306.826	212.060	180.056	−905.792	−549.751	15.114
2000	104.600	312.191	216.933	190.516	−901.269	−531.129	13.872
2100	104.600	317.295	221.592	200.976	−896.769	−512.732	12.754
2200	104.600	322.161	226.053	211.436	−892.298	−494.550	11.742
2300	104.600	326.811	230.334	221.896	−887.862	−476.570	10.823
2400	104.600	331.262	234.447	232.356	−883.470	−458.782	9.985
2500	104.600	335.532	238.406	242.816	−879.131	−441.176	9.218
2600	104.600	339.635	242.221	253.276	−874.852	−423.742	8.513
2700	104.600	343.582	245.902	263.736	−870.645	−406.472	7.864
2800	104.600	347.386	249.459	274.196	−866.521	−389.356	7.264
2900	104.600	351.057	252.900	284.656	−862.488	−372.386	6.707
3000	104.600	354.603	256.231	295.116	−858.558	−355.553	6.191

PREVIOUS.

CURRENT: December 1972

Strontium Chloride ($SrCl_2$) IDEAL GAS $M_r = 158.526$ Strontium Chloride ($SrCl_2$) $Cl_2Sr_1(g)$

$S°(298.15\ K) = 316.340 \pm 5.0\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -471.91 \pm 6.3\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -473.21 \pm 6.3\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
270 (1)	44 (1)	300 (1)

Ground State Quantum Weight: 1
Point Group: C_{2v}
Bond Distance: Sr–Cl = 2.67 ± 0.03 Å
Bond Angle: Cl–Sr–Cl = 120° ± 20°
Product of the Moments of Inertia: $I_AI_BI_C = 5.44364 \times 10^{-113}\ g^3{\cdot}cm^6$

$\sigma = 2$

Enthalpy of Formation

$\Delta_fH°(298.15\ K)$ is calculated from $\Delta_fH°(cr)$ by addition of $\Delta_{sub}H° = 85.0 \pm 1.5\ kcal{\cdot}mol^{-1}$ derived by third law analysis of the vapor–pressure equation of Hildenbrand *et al.*[1,2] The equation[1] summarized five torsion–effusion runs (102 total points) and is reasonably consistent with three boiling pressures in the mmHg range measured by Novikov and Gavryuchenkov.[3] Effusion studies[4-7] yield lower values of $\Delta_{sub}H°$, but that of Loehman *et al.*[6] is consistent with the adopted value. Langmuir data[6] suggest that the sublimation coefficient is 0.3 ± 0.2. Equilibria derived from flame studies[8,9] and mass–spectrometric effusion[10] confirm the adopted $\Delta_fH°$ via independent paths (cf. below). Mass spectra[11] at 1220 K showed that the saturated vapor consists predominantly of $SrCl_2$ with considerably less than 1% of dimer.

Source	Method	T/K	$\Delta_{sub}H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_fH°$(298.15 K) kcal·mol^{-1}
[1,2]Hildenbrand *et al.* (1965)	Torsion effusion[a]	1220–1425	84.0	85.00	−0.8	−113.1
[3]Novik and Gavryuchenkov	Boiling Point	1620–1710	75.8 ± 9.4	85.52 ± 0.7	−5.8 ± 5.6	−112.6
[4]Novikov *et al.*	Total effusion[a]	1137–1422	75.2	82.3	−5.1	
[5]Naryshkin *et al.*	Effusion[a]	893–1141	75.6	78.0	−2.3	
[6]Loehman *et al.*	Effusion	1195–1307	82.9 ± 3.9	84.2 ± 0.7	−1.0 ± 3.1	−113.9
[6]Loehman *et al.*	Langmuir[b]	968–1119	78.7 ± 3.6	86.3 ± 1.5	−7.4 ± 3.5	−111.8
[7]Van Westenburg	Effusion	1175–1287	80.3 ± 0.5	82.8 ± 0.2	−2.0 ± 0.4	
[8]Schofield and Sugden	Flame K_p[c]	~2134–2350	−9.1 ± 3.7[c]	−1.6 ± 0.8[c]	−3.3 ± 1.6	−110.7 ± 2
[9]Ryabova *et al.*	Flame K_p	1813–2209	9.0 ± 25[c]	−2.0 ± 7.2[c]	5.5 ± 12	−111.1 ± 7
[10]Hildenbrand	Mass spec. K_p[d]	1661		3.7[d]		−112.7 ± 2

[a] Pressures obtained from an equation.
[b] Assuming a sublimation coefficient of 1.0; agreement with[1] requires α = 0.5.
[c] $\Delta_rH°$ for $Sr(g) + 2\ HCl(g) = SrCl_2(g) + 2\ H(g)$.
[d] $\Delta_rH°$ for $Sr(g) + CaCl_2(g) = SrCl_2(g) + Ca(g)$.

Heat Capacity and Entropy

Vibrations ν_2 and ν_3 are the values quoted by Hildenbrand[10] and derived from IR spectra of molecules in matrix isolation.[12] The bending mode was observed.[13] Hastie *et al.*[14] failed to observe ν_2 but estimated a higher value of 60 ± 15 cm^{-1}. Agreement is better for $\nu_1 = 269$[10,13] or 274 cm^{-1} [14] and for $\nu_3 = 300 \pm 7$,[15](gas) 300[10,13] or 307 cm^{-1}.[14] We adopt a rounded value of 270 cm^{-1} for ν_1.

Bond length is from gas–phase electron diffraction[16] which also gave the bond angle 180° ± 30°. Later studies[17] of electric deflection of molecular beams revealed a permanent electric dipole moment, leading to the conclusion that $SrCl_2$ is bent. The matrix spectra[10,12] were first interpreted to give an angle of 155° but reanalysis[13] gave the angle 112°, calculated from the three observed fundamentals. An angle of 130° ± 8° was derived by Hastie *et al.*[14] from the Cl–isotope splitting of ν_3. We adopt an intermediate value of 120° ± 20°. $S°$ would change by +0.1 cal·K^{-1}·mol^{-1} for 112° and −1.3 cal·K^{-1}·mol^{-1} for 155°. The singlet ground state is taken by analogy with $BaCl_2(g)$. Principal moments of inertia are $I_A = 11.5986 \times 10^{-39}$, $I_B = 62.9539 \times 10^{-39}$, and $I_C = 74.5525 \times 10^{-39}\ g{\cdot}cm^2$.

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Continued on page 940

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$ (kJ·mol^{-1})	$\Delta_fG°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−14.449	−471.910	−471.910	INFINITE
100	46.112	259.888	363.999	−10.411	−472.284	−476.567	248.933
200	53.351	294.507	321.380	−5.375	−472.773	−480.640	125.530
250	54.877	306.591	317.253	−2.666	−472.985	−482.588	100.831
298.15	55.775	316.339	316.339	0.	−473.210	−484.411	84.867
300	55.802	316.685	316.341	0.103	−473.220	−484.480	84.356
350	56.397	325.334	317.022	2.909	−473.485	−486.337	72.582
400	56.798	332.893	318.544	5.740	−473.782	−488.153	63.746
450	57.080	339.600	320.518	8.587	−474.112	−489.930	56.870
500	57.286	345.625	322.732	11.446	−474.475	−491.668	51.364
600	57.559	356.096	327.446	17.190	−475.293	−495.032	43.096
700	57.727	364.982	332.190	22.955	−476.234	−498.249	37.180
800	57.836	372.698	336.782	28.733	−477.295	−501.323	32.733
900	57.912	379.515	341.158	34.521	−479.102	−504.185	29.262
1000	57.966	385.620	345.305	40.315	−480.078	−506.920	26.479
1100	58.007	391.146	349.225	46.114	−488.965	−509.191	24.179
1200	58.038	396.195	352.932	51.916	−490.871	−510.945	22.241
1300	58.062	400.842	356.441	57.721	−492.785	−512.541	20.594
1400	58.081	405.145	359.768	63.528	−494.706	−513.988	19.177
1500	58.096	409.153	362.928	69.337	−496.634	−515.298	17.944
1600	58.109	412.903	365.936	75.147	−498.570	−516.480	16.861
1700	58.119	416.426	368.803	80.959	−637.427	−516.360	15.866
1800	58.128	419.748	371.542	86.771	−637.519	−509.236	14.778
1900	58.136	422.891	374.162	92.584	−637.624	−502.106	13.804
2000	58.142	425.873	376.674	98.398	−637.747	−494.970	12.927
2100	58.147	428.710	379.085	104.213	−637.893	−487.828	12.134
2200	58.152	431.415	381.403	110.028	−638.067	−480.678	11.413
2300	58.156	434.000	383.634	115.843	−638.276	−473.520	10.754
2400	58.160	436.475	385.784	121.659	−638.528	−466.351	10.150
2500	58.163	438.850	387.860	127.475	−638.832	−459.171	9.594
2600	58.166	441.131	389.865	133.292	−639.197	−451.978	9.080
2700	58.168	443.326	391.805	139.108	−639.634	−444.769	8.605
2800	58.171	445.442	393.683	144.925	−640.152	−437.542	8.162
2900	58.173	447.483	395.503	150.742	−640.762	−430.296	7.750
3000	58.175	449.455	397.269	156.560	−641.474	−423.026	7.366
3100	58.176	451.363	398.983	162.377	−642.299	−415.732	7.005
3200	58.178	453.210	400.649	168.195	−643.246	−408.408	6.667
3300	58.179	455.000	402.269	174.013	−644.323	−401.053	6.348
3400	58.180	456.737	403.845	179.831	−645.539	−393.664	6.048
3500	58.182	458.423	405.381	185.649	−646.900	−386.236	5.764
3600	58.183	460.062	406.877	191.467	−648.411	−378.767	5.496
3700	58.184	461.657	408.336	197.285	−650.078	−371.255	5.241
3800	58.185	463.208	409.760	203.104	−651.904	−363.695	4.999
3900	58.185	464.720	411.150	208.922	−653.889	−356.085	4.769
4000	58.186	466.193	412.508	214.741	−656.035	−348.422	4.550
4100	58.187	467.630	413.835	220.560	−658.341	−340.703	4.341
4200	58.187	469.032	415.132	226.378	−660.800	−332.927	4.141
4300	58.188	470.401	416.402	232.197	−663.416	−325.090	3.949
4400	58.189	471.739	417.644	238.016	−666.182	−317.190	3.766
4500	58.189	473.046	418.861	243.835	−669.091	−309.226	3.589
4600	58.190	474.325	420.053	249.654	−672.072	−301.201	3.420
4700	58.190	475.577	421.221	255.473	−675.229	−293.105	3.257
4800	58.191	476.802	422.366	261.292	−678.503	−284.940	3.101
4900	58.191	478.002	423.489	267.111	−681.886	−276.706	2.950
5000	58.191	479.177	424.591	272.930	−685.364	−268.402	2.804
5100	58.192	480.330	425.673	278.749	−688.913	−260.030	2.663
5200	58.192	481.460	426.735	284.568	−692.560	−251.585	2.527
5300	58.192	482.568	427.778	290.388	−696.276	−243.069	2.396
5400	58.193	483.656	428.803	296.207	−700.052	−234.483	2.268
5500	58.193	484.724	429.810	302.026	−703.877	−225.826	2.145
5600	58.193	485.772	430.800	307.845	−707.743	−217.099	2.025
5700	58.194	486.802	431.773	313.665	−711.641	−208.303	1.909
5800	58.194	487.814	432.731	319.484	−715.560	−199.438	1.796
5900	58.194	488.809	433.673	325.304	−719.284	−190.530	1.687
6000	58.194	489.787	434.600	331.123	−723.193	−181.536	1.580

PREVIOUS: December 1972 (1 atm) — CURRENT: December 1972 (1 bar)

Strontium Chloride ($SrCl_2$) $Cl_2Sr_1(g)$

$\Delta_fH°(0\ K) = -514.76 \pm 16.7\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = 87.345 \pm 4.2\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -515.47 \pm 16.7\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of $TiCl_2(cr)$ has been measured calorimetrically. The chosen value of $\Delta_fH°(298.15\ K)$ is the average of two such determinations. Values of $\Delta_fH°(298.15\ K)$ are also calculated from the heats of reaction for the processes (A) $2TiCl_3(cr) = TiCl_2(cr) + TiCl_4(g)$, (B) $3TiCl_2(cr) = 2TiCl_3(g) + Ti(cr)$, and (C) $2TiCl_2(cr) = TiCl_4(g) + Ti(cr)$. These enthalpies of reaction are combined with auxiliary JANAF values for the heats of formation of $TiCl_3(cr)$, $TiCl_4(g)$, $TiCl_3(cr)$ and $Ti(cr)$. The following table summarizes the data used to calculate $\Delta_fH°(298.15\ K)$.

Source	Reaction	Method	Data Points	T/K	$\Delta_rH°(298.15\ K)$ 2nd law	$\Delta_rH°(298.15\ K)$ 3rd law	Drift $cal\cdot K^{-1}\cdot mol^{-1}$	$\Delta_fH°(298.15\ K)$ $kcal\cdot mol^{-1}$
Clifton and MacWood[1]	Calorimetric							−123.4, −123.8
Krieve *et al.*[2]	Calorimetric							−122.4
Farber and Darnell[3]	A	Effusion	11	615–732	36.0 ± 1.4	38.9	4.2 ± 2.1	−123.7
Sanderson and MacWood[4]	A	Knudsen	22*	593–720	35.6 ± 0.8	39.6	6.1 ± 1.3	−123.0
Sanderson and MacWood[4]	A	Static	15**	679–821	38.5 ± 0.5	35.9	−3.4 ± 0.7	−126.7
Farber and Darnell[5]	B	Effusion	13	798–893	94.4 ± 1.9	112.6	21.4 ± 2.2	−123.1
Farber and Darnell[5]	C	Effusion	11	794–894	51.5 ± 1.4	63.0	13.6 ± 1.7	−122.7
Hartman and Rinds[6]	A	Effusion	20	815–974	38.6 ± 0.5	35.7	−3.3 ± 0.5	−126.9
Skinner and Ruehrwein[7]	A	Manometric	5	802–928	37.6 ± 0.5	36.0	−1.9 ± 0.6	−126.9

*Four points rejected due to failure of a statistical test.

**Two points rejected due to failure of a statistical test.

Heat Capacity and Entropy

The heat capacity for $TiCl_2(cr)$ has been measured by Kim and Stout[8] over the range 6 to 300 K. They calculated the adopted value of $S°(298.15\ K)$ from their measurements based on $S°(6\ K) = 0.017\ cal\cdot K^{-1}\cdot mol^{-1}$. The heat capacity above 300 K is estimated by graphical extrapolation. The large uncertainty on $S°(298.15\ K)$ is due to the possibility of sizeable electronic contributions to the heat capacity below 6 K which would account for the rather low value of $S°(298.15\ K)$ reported by Kim and Stout.[8]

Sublimation Data

The enthalpy of sublimation is calculated from the enthalpies of formation of $TiCl_2(cr)$ and $TiCl_2(g)$. The temperature of sublimation is taken as the point at which $\Delta_rG° = 0$ for the process $TiCl_2(cr) = TiCl_2(g)$. These values are hypothetical since $TiCl_2$ would be decomposed to $TiCl_3(g)$ and $TiCl_4(g)$ below this temperature.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ $J\cdot K^{-1}mol^{-1}$	$S°$ $J\cdot K^{-1}mol^{-1}$	$-[G°-H°(T_r)]/T$ $J\cdot K^{-1}mol^{-1}$	$H°-H°(T_r)$ $kJ\cdot mol^{-1}$	$\Delta_fH°$ $kJ\cdot mol^{-1}$	$\Delta_fG°$ $kJ\cdot mol^{-1}$	log K_f
0	0.	0.	INFINITE	−13.301	−514.759	−514.759	INFINITE
100	37.777	25.966	142.867	−11.690	−516.621	−499.490	260.907
200	61.505	61.095	93.500	−6.481	−516.366	−482.347	125.976
298.15	69.831	87.345	87.345	0.	−515.469	−465.829	81.611
300	69.899	87.777	87.347	0.129	−515.449	−465.521	81.054
400	73.392	108.374	90.131	7.297	−514.365	−449.040	58.639
500	76.484	125.090	95.502	14.794	−513.179	−432.843	45.219
600	78.375	139.202	101.640	22.537	−511.894	−416.896	36.294
700	80.266	151.426	107.898	30.469	−510.522	−401.170	29.936
800	82.157	162.267	114.029	38.590	−509.025	−385.649	25.180
900	84.048	172.053	119.941	46.901	−507.426	−370.322	21.493
1000	85.939	181.006	125.606	55.400	−505.785	−355.176	18.552
1100	87.831	189.286	131.024	64.088	−504.161	−340.194	16.154
1200	89.722	197.009	136.204	72.966	−506.540	−325.239	14.157
1300	91.613	204.265	141.163	82.033	−504.226	−310.223	12.465
1400	93.504	211.124	145.918	91.289	−501.811	−295.390	11.021
1500	95.395	217.640	150.484	100.734	−499.307	−280.732	9.776
1600	97.286	223.857	154.877	110.368	−496.728	−266.245	8.692
1700	99.178	229.811	159.111	120.191	−494.086	−251.920	7.741
1800	101.069	235.534	163.199	130.203	−491.395	−237.752	6.899
1900	102.960	241.049	167.152	140.405	−488.668	−223.735	6.151
2000	104.851	246.378	170.980	150.795	−500.607	−209.409	5.469

PREVIOUS: June 1968 CURRENT: December 1968

Titanium Chloride ($TiCl_2$) IDEAL GAS M_r = 118.786 Titanium Chloride ($TiCl_2$) $Cl_2Ti_1(g)$

$S°(298.15 K) = [278.338 \pm 12.6] J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0 K) = -236.77 \pm 12.6 kJ{\cdot}mol^{-1}$

$\Delta_fH°(298.15 K) = -237.23 \pm 12.6 kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[279](1)
[196](2)
[439](1)

Ground State Quantum Weight: 3 $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distance: Ti–Cl = [2.3] Å
Bond Angle: Cl–Ti–Cl = [180]°
Rotational Constant: $B_0 = [0.044943] cm^{-1}$

Enthalpy of Formation

Gross and Levi[1] have measured the equilibrium $2TiCl_3(g) + Ti(cr) \rightarrow 3TiCl_2(g)$ at 1723 K and obtain $\Delta_rG°(1723) = 21.7 kcal{\cdot}mol^{-1}$ from four measurements. This yields $\Delta_fH°(TiCl_2, g, 298.15 K) = -56.7 \pm 3 kcal{\cdot}mol^{-1}$. They discuss the measurements of Farber and Darnell,[2] on the vapor pressure of $TiCl_2(cr)$, and show that the results are probably in error due to disproportionation of $TiCl_3(g)$ on condensation. In the work of Skinner and Ruehrwein[3] on the reaction $2NaCl(g) + Ti(cr) = 2Na(g) + TiCl_2(g)$, Gross and Levi indicate that the basic assumption, of conversion to $TiCl_2$ only, is erroneous. In the 3rd law analysis of both these data sets significant drifts are obtained which tends to confirm the above arguments.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiCl_2(cr)$ reported by Benzinger and Rundle.[4] The vibrational frequencies are estimated from a valence force field model.

The electronic levels are assumed to correspond to the inverted states of $NiCl_2(g)$.[5] The linear configuration is adopted, since experimental evidence indicates that other transition metal dihalides are linear.[6-9]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−13.545	−236.767	−236.767	INFINITE
100	41.124	223.342	326.011	−10.267	−236.961	−239.569	125.138
200	53.079	256.188	283.484	−5.459	−237.108	−242.108	63.232
250	55.821	268.352	279.276	−2.731	−237.163	−243.351	50.846
298.15	57.503	278.338	278.338	0.	−237.233	−244.537	42.842
300	57.555	278.694	278.339	0.106	−237.236	−244.583	42.586
350	58.701	287.658	279.044	3.015	−237.333	−245.800	36.684
400	59.490	295.551	280.624	5.971	−237.455	−247.001	32.255
450	60.054	302.592	282.681	8.960	−237.600	−248.186	28.809
500	60.469	308.942	284.995	11.974	−237.764	−249.354	26.050
600	61.025	320.020	289.936	18.051	−238.144	−251.637	21.907
700	61.371	329.455	294.924	24.172	−238.583	−253.852	18.943
800	61.605	337.666	299.765	30.321	−239.058	−256.001	16.715
900	61.782	344.933	304.387	36.491	−239.600	−258.087	14.979
1000	61.938	351.450	308.773	42.677	−240.272	−260.107	13.587
1100	62.098	357.361	312.926	48.878	−241.135	−262.050	12.444
1200	62.280	362.772	316.858	55.097	−246.173	−263.787	11.482
1300	62.496	367.765	320.584	61.336	−246.687	−265.234	10.657
1400	62.750	372.406	324.122	67.598	−247.266	−266.639	9.948
1500	63.044	376.745	327.487	73.887	−247.918	−268.001	9.333
1600	63.373	380.824	330.694	80.208	−248.652	−269.316	8.792
1700	63.732	384.677	333.757	86.563	−249.478	−270.583	8.314
1800	64.115	388.330	336.689	92.955	−250.407	−271.798	7.887
1900	64.513	391.807	339.499	99.386	−251.451	−272.959	7.504
2000	64.919	395.127	342.198	105.858	−267.309	−273.608	7.146
2100	65.326	398.304	344.794	112.370	−269.369	−273.872	6.812
2200	65.728	401.352	347.296	118.923	−271.400	−274.038	6.506
2300	66.120	404.282	349.711	125.515	−273.406	−274.113	6.225
2400	66.499	407.105	352.044	132.146	−275.387	−274.102	5.966
2500	66.861	409.827	354.301	138.814	−277.348	−274.008	5.725
2600	67.206	412.456	356.487	145.518	−279.290	−273.836	5.501
2700	67.531	414.998	358.608	152.255	−281.217	−273.589	5.293
2800	67.837	417.460	360.666	159.023	−283.131	−273.272	5.098
2900	68.125	419.845	362.665	165.822	−285.034	−272.886	4.915
3000	68.394	422.159	364.610	172.648	−286.930	−272.435	4.744
3100	68.647	424.406	366.503	179.500	−288.819	−271.920	4.582
3200	68.884	426.590	368.347	186.377	−290.701	−271.345	4 429
3300	69.107	428.713	370.144	193.276	−292.579	−270.711	4.285
3400	69.317	430.779	371.897	200.198	−294.452	−270.020	4.148
3500	69.516	432.791	373.608	207.139	−296.320	−269.275	4.019
3600	69.705	434.752	375.280	214.101	−298.181	−268.475	3.895
3700	69.884	436.664	376.913	221.080	−709.134	−259.836	3.668
3800	70.056	438.530	378.510	228.077	−709.745	−247.685	3.405
3900	70.220	440.352	380.073	235.091	−710.402	−235.517	3.154
4000	70.378	442.132	381.602	242.121	−711.100	−223.332	2.916
4100	70.531	443.872	383.100	249.167	−711.837	−211.129	2.690
4200	70.679	445.573	384.567	256.227	−712.608	−198.907	2.474
4300	70.822	447.238	386.005	263.302	−713.410	−186.667	2.268
4400	70.960	448.868	387.415	270.391	−714.240	−174.407	2.070
4500	71.094	450.464	388.799	277.494	−715.092	−162.129	1.882
4600	71.224	452.028	390.156	284.610	−715.964	−149.831	1.701
4700	71.350	453.561	391.489	291.739	−716.851	−137.514	1.528
4800	71.472	455.065	392.798	298.880	−717.750	−125.179	1.362
4900	71.590	456.539	394.084	306.033	−718.657	−112.824	1.203
5000	71.703	457.987	395.347	313.198	−719.568	−100.451	1.049
5100	71.812	459.408	396.590	320.373	−720.482	−88.059	0.902
5200	71.916	460.803	397.811	327.560	−721.393	−75.650	0.760
5300	72.016	462.174	399.013	334.757	−722.300	−63.223	0.623
5400	72.111	463.521	400.195	341.963	−723.200	−50.779	0.491
5500	72.201	464.845	401.358	349.179	−724.091	−38.319	0.364
5600	72.286	466.147	402.504	356.403	−724.969	−25.842	0.241
5700	72.365	467.427	403.631	363.635	−725.834	−13.350	0.122
5800	72.439	468.686	404.742	370.876	−726.683	−0.843	0.008
5900	72.508	469.925	405.837	378.123	−727.515	11.679	−0.103
6000	72.571	471.144	406.915	385.377	−728.327	24.214	−0.211

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

Tungsten Chloride (WCl$_2$) CRYSTAL $M_r = 254.756$ Tungsten Chloride (WCl$_2$) Cl$_2$W$_1$(cr)

$S°(298.15\ K) = [130.54]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = $ Unknown

$\Delta_f H°(298.15\ K) = -257.32 \pm 12.6\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(WCl_2, cr, 298.15\ K) = -61.5 \pm 3\ kcal{\cdot}mol^{-1}$, is derived from the heat of combustion, $\Delta_c H° = -140 \pm 3\ kcal{\cdot}mol^{-1}$ for $WCl_2(cr) + 3/2\ O_2(g) \rightarrow WO_3(cr) + Cl_2(g)$, reported by Shchukarev *et al.*[1] The value of $\Delta_c H°$ was determined calorimetrically, but no further information about the combustion process was given in the paper.

Heat Capacity and Entropy

$C_p°(298.15\ K) = 6.2\ cal{\cdot}K^{-1}\ g{\cdot}atom^{-1}$ and $C_p°(900\ K) = 7.25\ cal{\cdot}K^{-1}\ g{\cdot}atom^{-1}$ are estimated using the method described by Kubaschewski and Evans.[2] Between 298 and 900, which is near the decomposition temperature, the heat capacity is obtained by linear interpolation.

The entropy, $S°(298.15\ K) = 31.2\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, *is estimated by the method of Latimer.*[3] *Shchukarev et al.,*[1] *have estimated* $\Delta_r S° = -30\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ for $W(cr) + Cl_2(g) = WCl_2(cr)$ which leads to $S°(WCl_2, cr, 298.15\ K) = 31.1\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, using JANAF auxiliary data.

Decomposition Data

The decomposition temperature, $T_{dcm} = 862\ K$, is obtained by extrapolation to one atmosphere total pressure of a log P versus 1/T fit of the decomposition pressure data reported by Shchukarev *et al.*[4] Decomposition pressure data for Cl:W ratios less than two suggest that the decomposition reaction is not simple.

References

[1] S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, Zhur. Neorg. Khim. 5, 1650 (1960).
[2] O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).
[3] W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice–Hall, Inc., New York, (1952).
[4] S. A. Shchukarev, G. I. Novikov, and N. V. Andreeva, *Vestnik Leningrad. Univ. 14, No. 10, Ser. Fiz. i Khim., No. 2,* 78 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	77.822	130.541	130.541	0.	−257.316	−219.988	38.541
300	77.864	131.022	130.542	0.144	−257.280	−219.757	38.263
400	80.052	153.721	133.622	8.040	−255.318	−207.544	27.102
500	82.241	171.817	139.511	16.153	−253.290	−195.833	20.459
600	84.429	187.006	146.194	24.487	−251.145	−184.541	16.066
700	86.617	200.185	152.986	33.039	−248.866	−173.619	12.956
800	88.805	211.893	159.631	41.810	−246.440	−163.033	10.645
900	91.002	222.480	166.035	50.801	−243.859	−152.760	8.866
1000	93.190	232.181	172.171	60.010	−241.119	−142.784	7.458
1100	95.378	241.166	178.040	69.439	−238.220	−133.089	6.320
1200	97.567	249.559	183.654	79.086	−235.159	−123.666	5.383
1300	99.755	257.455	189.030	88.952	−231.935	−114.504	4.601
1400	101.943	264.927	194.187	99.037	−228.548	−105.597	3.940
1500	104.131	272.035	199.142	109.341	−224.998	−96.938	3.376
1600	106.320	278.826	203.911	119.863	−221.285	−88.521	2.890
1700	108.508	285.337	208.511	130.605	−217.409	−80.341	2.469
1800	110.696	291.601	212.954	141.565	−213.371	−72.393	2.101
1900	112.884	297.645	217.253	152.744	−209.172	−64.675	1.778
2000	115.073	303.491	221.420	164.142	−204.812	−57.182	1.493

PREVIOUS: September 1962 CURRENT: December 1966

Tungsten Chloride (WCl_2) IDEAL GAS $M_r = 254.756$ Tungsten Chloride (WCl_2) $Cl_2W_1(g)$

$S°(298.15\ K) = [309.416]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [-13.0 \pm 105]\ kJ{\cdot}mol^{-1}$

$\Delta_f H°(298.15\ K) = [-12.6 \pm 105]\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i
0	[5]
[5600]	[10]
[8900]	[10]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[360](1)
[60](2)
[423](1)

Ground State Quantum Weight: [5] $\sigma = [2]$

Point Group: $[D_{\infty h}]$

Bond Distance: W–Cl = [2.26] Å

Bond Angle: Cl–W–Cl = [180]°

Rotational Constant: $B_o = [0.046548]\ cm^{-1}$

Enthalpy of Formation

The value of $\Delta_f H°(WCl_2, g, 298.15\ K) = -3 \pm 25\ kcal{\cdot}mol^{-1}$ is calculated from the heat of formation of the crystal plus the heat of sublimation, $\Delta_{sub} H°(298.15\ K) = 58.5 \pm 25\ kcal{\cdot}mol^{-1}$. The latter is estimated from the heats of sublimation of $TiCl_2$, $CrCl_2$, $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$ given by Brewer *et al.*[1] among the above compounds and also the possible error in transference from the first row transition metal dichlorides to tungsten dichloride.

Heat Capacity and Entropy

The molecular configuration of $WCl_2(g)$ is assumed to be linear. The bond distance is estimated to be the same as that in $WCl_6(g)$. The ground state configuration ($^5\Sigma$), the low lying electronic levels and their quantum weights are assumed to be the same as those for $CrCl_2(g)$, observed by DeKock and Gruen.[3]

The vibrational frequencies are calculated from a valence force field model. The stretching force constant, K_1, is estimated to be the same as that of $HgCl_2(g)$, 2.7 millidyne/Å. The bending force constant is assumed to be one hundredth of the stretching force constant.

References

[1] L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963).

[2] S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, Zh. Neorg. Khim. 5, 1650 (1960).

[3] C. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.626	−13.024	−13.024	INFINITE
100	46.708	251.950	358.279	−10.633	−12.595	−17.928	9.365
200	54.413	286.912	314.630	−5.544	−12.551	−23.286	6.082
250	56.638	299.310	310.364	−2.764	−12.547	−25.971	5.426
298.15	58.060	309.416	309.416	0.	−12.552	−28.556	5.003
300	58.105	309.775	309.417	0.107	−12.552	−28.655	4.989
350	59.097	318.811	310.128	3.039	−12.564	−31.338	4.677
400	59.789	326.750	311.720	6.012	−12.581	−34.019	4.442
450	60.288	333.823	313.790	9.015	−12.607	−36.697	4.260
500	60.657	340.195	316.117	12.039	−12.640	−39.372	4.113
600	61.159	351.302	321.082	18.132	−12.737	−44.710	3.892
700	61.485	360.756	326.092	24.265	−12.877	−50.029	3.733
800	61.740	368.983	330.950	30.426	−13.060	−55.324	3.612
900	61.984	376.269	335.588	36.612	−13.283	−60.594	3.517
1000	62.261	382.813	339.989	42.824	−13.541	−65.838	3.439
1100	62.595	388.763	344.157	49.067	−13.828	−71.054	3.374
1200	62.996	394.226	348.104	55.346	−14.136	−76.242	3.319
1300	63.465	399.286	351.849	61.668	−14.455	−81.405	3.271
1400	63.997	404.009	355.408	68.041	−14.781	−86.543	3.229
1500	64.579	408.443	358.797	74.469	−15.106	−91.657	3.192
1600	65.198	412.631	362.032	80.958	−15.427	−96.750	3.159
1700	65.838	416.603	365.126	87.509	−15.741	−101.823	3.129
1800	66.486	420.384	368.092	94.126	−16.047	−106.878	3.102
1900	67.126	423.996	370.940	100.806	−16.346	−111.916	3.077
2000	67.748	427.455	373.680	107.550	−16.640	−116.939	3.054
2100	68.339	430.775	376.320	114.355	−16.934	−121.946	3.033
2200	68.892	433.967	378.869	121.217	−17.232	−126.940	3.014
2300	69.401	437.041	381.331	128.132	−17.539	−131.920	2.996
2400	69.860	440.004	383.715	135.095	−17.863	−136.886	2.979
2500	70.268	442.865	386.024	142.102	−18.209	−141.838	2.964
2600	70.622	445.628	388.263	149.147	−18.582	−146.776	2.949
2700	70.924	448.299	390.438	156.225	−19.013	−151 699	2.935
2800	71.174	450.883	392.551	163.330	−19.545	−156.604	2.921
2900	71.374	453.384	394.605	170.458	−20.223	−161.487	2.909
3000	71.527	455.806	396.605	177.603	−21.077	−166.344	2.896
3100	71.637	458.154	398.553	184.762	−22.155	−171.170	2.884
3200	71.707	460.429	400.451	191.930	−23.494	−175.956	2.872
3300	71.740	462.636	402.302	199.102	−25.120	−180.696	2.860
3400	71.740	464.778	404.109	206.276	−27.072	−185.382	2.848
3500	71.711	466.857	405.872	213.449	−29.415	−190.005	2.836
3600	71.656	468.877	407.594	220.618	−32.247	−194.555	2.823
3700	71.578	470.839	409.277	227.780	−70.433	−198.827	2.807
3800	71.481	472.747	410.922	234.933	−70.955	−202.290	2.781
3900	71.367	474.602	412.531	242.075	−71.495	−205.739	2.756
4000	71.238	476.407	414.106	249.206	−72.050	−209.174	2.732
4100	71.098	478.165	415.647	256.323	−72.620	−212.595	2.708
4200	70.948	479.876	417.156	263.425	−73.204	−216.002	2.686
4300	70.791	481.544	418.634	270.512	−73.799	−219.395	2.665
4400	70.627	483.169	420.082	277.583	−74.404	−222.774	2.645
4500	70.459	484.755	421.502	284.637	−75.016	−226.140	2.625
4600	70.288	486.301	422.894	291.675	−75.634	−229.491	2.606
4700	70.114	487.811	424.259	298.695	−76.256	−232.829	2.588
4800	69.940	489.286	425.599	305.697	−76.880	−236.154	2.570
4900	69.765	490.726	426.913	312.683	−77.503	−239.465	2.553
5000	69.591	492.134	428.203	319.651	−78.125	−242.765	2.536
5100	69.419	493.510	429.471	326.601	−78.742	−246.051	2.520
5200	69.248	494.856	430.715	333.534	−79.355	−249.326	2.505
5300	69.079	496.174	431.938	340.451	−79.960	−252.589	2.489
5400	68.912	497.463	433.139	347.350	−80.557	−255.840	2.475
5500	68.749	498.726	434.320	354.233	−81.144	−259.081	2.461
5600	68.589	499.964	435.482	361.100	−81.720	−262.311	2.447
5700	68.432	501.176	436.623	367.951	−82.285	−265.531	2.433
5800	68.278	502.365	437.747	374.787	−82.836	−268.741	2.420
5900	68.128	503.531	438.852	381.607	−83.373	−271.941	2.408
6000	67.982	504.675	439.939	388.412	−83.896	−275.133	2.395

PREVIOUS. December 1966 (1 atm) CURRENT: December 1966 (1 bar)

Tungsten Chloride (WCl_2) $Cl_2W_1(g)$

Zirconium Chloride ($ZrCl_2$) CRYSTAL M_r = 162.126 Zirconium Chloride (ZrCl) $Cl_2Zr_1(cr)$

$S°(298.15\ K) = [110.039 \pm 12.6]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = [1000]\ K$

$\Delta_fH°(0\ K)$ = Unknown
$\Delta_fH°(298.15\ K) = [-430.95 \pm 41.8]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = [26.778 \pm 12.6]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The value of $\Delta_fH°(ZrCl_2, cr, 298.15\ K) = -103.0\ kcal{\cdot}mol^{-1}$ is calculated from the estimated $\Delta_{sub}H°(298.15\ K) = 58.5\ kcal{\cdot}mol^{-1}$ for $ZrCl_2(cr) \rightarrow ZrCl_2(g)$, using $\Delta_fH°(ZrCl_2, g, 298.15\ K) = -44.5\ kcal{\cdot}mol^{-1}$.[1] The estimated $\Delta_{sub}H°(298.15\ K)$ is obtained as an average of the heats of sublimation at 298.15 K for $TiCl_2$, VCl_2, $CrCl_2$, $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$ given by Brewer *et al.*[2]

Heat Capacity and Entropy

The heat capacities of $ZrCl_2(cr)$ are estimated based on the assumption that $C_p°(ZrCl_2, cr) = 1/2[C_p°(ZrCl_4, cr) + C_p°(Zr, cr)]$. The entropy, $S°(298.15\ K)$, is also estimated in a manner similar to that of the heat capacity.

Fusion Data

The melting point was estimated to be 1000 K by Brewer[3] and the heat of melting was also estimated by Glassner.[4]

References

[1] JANAF Thermochemical Tables: $ZrCl_2(g)$, 12–31–69.
[2] L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963).
[3] L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, Ed., McGraw-Hill New York, (1949).
[4] A. Glassner, "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500 K," ANL Report 5750, Argonne National Laboratory, (1957).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	72.592	110.039	110.039	0.	−430.952	−385.660	67.566
300	72.710	110.489	110.041	0.134	−430.927	−385.379	67.101
400	76.015	131.884	112.935	7.580	−429.511	−370.407	48.370
500	78.241	149.094	118.502	15.296	−427.991	−355.805	37.171
600	80.040	163.520	124.834	23.211	−426.399	−341.516	29.732
700	81.714	175.987	131.271	31.301	−424.748	−327.498	24.438
800	83.128	186.990	137.562	39.543	−423.055	−313.721	20.484
900	84.542	196.863	143.611	47.927	−421.339	−300.157	17.421
1000	85.923	205.843	149.392	56.450	−419.608	−286.785	14.980
1000.000	85.923	205.843	149.392	56.450	--- CRYSTAL <--> LIQUID ---		
1100	86.692	214.073	154.904	65.086	−417.894	−273.586	12.992
1200	87.446	221.649	160.155	73.793	−419.951	−260.319	11.331
1300	88.199	228.680	165.159	82.578	−417.807	−247.103	9.929
1400	88.617	235.232	169.933	91.420	−415.657	−234.053	8.733
1500	88.910	241.357	174.492	100.297	−413.534	−221.155	7.701

PREVIOUS June 1962 CURRENT: December 1969

Zirconium Chloride ($ZrCl_2$) LIQUID $M_r = 162.126$

S°(298 15 K) = [122.493] J·K^{-1}·mol^{-1} $\Delta_f H^\circ$(298.15 K) = [−411.594] kJ·mol^{-1}

T_{fus} = [1000] K $\Delta_{fus}H^\circ$ = [26.778 ± 12.6] kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H^\circ$($ZrCl_2$, l, 298.15 K) is calculated from $\Delta_f H^\circ$($ZrCl_2$, cr, 298.15 K) by adding $\Delta_{fus}H^\circ$ and the difference in enthalpy, H°(1000 K)–H°(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The heat capacities are assumed to be constant at 7.25 cal·K^{-1} g·atom^{-1}. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting point was estimated to be 1000 K by Brewer,[1] and the heat of melting was also estimated by Glassner.[2]

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change approaches zero for the process $ZrCl_2(l) \rightarrow ZrCl_2(g)$. The difference between $\Delta_f H^\circ$ for $ZrCl_2$(l) and $ZrCl_2$(g) at T_{vap} is $\Delta_{vap}H^\circ$.

References

[1] L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L L. Quill, E Ed, McGraw–Hill Book Company, New York, (1949).

[2] A. Glassner, "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500 K," ANL Report 5750, Argonne National Laboratory, (1957).

Zirconium Chloride ($ZrCl_2$) $Cl_2Zr_1(l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0							
100							
200							
298.15	91.002	122.493	122.493	0.	−411.594	−370.015	64.825
300	91.002	123.056	122.495	0.168	−411.535	−369.758	64.381
400	91.002	149.236	126.064	9.269	−408.464	−356.300	46.528
500	91.002	169.542	132.805	18.369	−405.560	−343.598	35.895
600	91.002	186.134	140.352	27.469	−402.783	−331.468	28.857
700	91.002	200.162	147.920	36.569	−400.121	−319.794	23.863
800	91.002	212.314	155.227	45.669	−397.571	−308.495	20.143
900	91.002	223.032	162.177	54.770	−395.138	−297.507	17.267
1000	91.002	232.620	168.750	63.870	−392.831	−286.785	14.980
1000.000	91.002	232.620	168.750	63.870	--- CRYSTAL <--> LIQUID ---		
1100	91.002	241.294	174.957	72.970	−390.652	−276.286	13.120
1200	91.002	249.212	180.820	82.070	−392.315	−265.759	11.568
1300	91.002	256.496	186.365	91.170	−389.856	−255.313	10.259
1400	91.002	263.240	191.618	100.271	−387.448	−245.054	9.143
1500	91.002	269.518	196.604	109.371	−385.103	−234.966	8.182
1600	91.002	275.391	201.347	118.471	−382.829	−225.031	7.347
1700	91.002	280.908	205.866	127.571	−380.638	−215.236	6.613
1800	91.002	286.110	210.181	136.671	−378.541	−205.568	5.965
1900	91.002	291.030	214.308	145.772	−376.549	−196.013	5.389
2000	91.002	295.698	218.262	154.872	−374.673	−186.560	4.872

EVIOUS: June 1962 CURRENT: December 1969

Zirconium Chloride ($ZrCl_2$) CRYSTAL-LIQUID

0 to 1000 K crystal
above 1000 K liquid

Refer to the individual tables for details.

$M_r = 162.126$ Zirconium Chloride ($ZrCl_2$) $Cl_2Zr_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	72.592	110.039	110.039	0.	−430.952	−385.660	67.566
300	72.710	110.489	110.041	0.134	−430.927	−385.379	67.101
400	76.015	131.884	112.935	7.580	−429.511	−370.407	48.370
500	78.241	149.094	118.502	15.296	−427.991	−355.805	37.171
600	80.040	163.520	124.834	23.211	−426.399	−341.516	29.732
700	81.714	175.987	131.271	31.301	−424.748	−327.498	24.438
800	83.128	186.990	137.562	39.543	−423.055	−313.721	20.484
900	84.542	196.863	143.611	47.927	−421.339	−300.157	17.421
1000	85.923	205.843	149.392	56.450	−419.608	−286.785	14.980
1000.000	85.923	205.843	149.392	56.450	CRYSTAL <--> LIQUID		
1000.000	91.002	232.620	149.392	83.228	TRANSITION		
1100	91.002	241.294	157.359	92.328	−390.652	−276.286	13.120
1200	91.002	249.212	164.688	101.428	−392.315	−265.759	11.568
1300	91.002	256.496	171.474	110.528	−389.856	−255.313	10.259
1400	91.002	263.240	177.791	119.629	−387.448	−245.054	9.143
1500	91.002	269.518	183.699	128.729	−385.103	−234.966	8.182
1600	91.002	275.391	189.248	137.829	−382.829	−225.031	7.347
1700	91.002	280.908	194.479	146.929	−380.638	−215.236	6.613
1800	91.002	286.110	199.427	156.029	−378.541	−205.568	5.965
1900	91.002	291.030	204.120	165.130	−376.549	−196.013	5.389
2000	91.002	295.698	208.583	174.230	−374.673	−186.560	4.872

PREVIOUS: CURRENT: December 1969

Zirconium Chloride ($ZrCl_2$) $Cl_2Zr_1(cr,l)$

Zirconium Chloride ($ZrCl_2$) **IDEAL GAS** **M_r = 162.126** **Zirconium Chloride ($ZrCl_2$)** **$Cl_2Zr_1(g)$**

$S°(298.15\ K) = [292.558 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -185.75 \pm 20.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -186.19 \pm 20.9\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[346] (1)
[92] (2)
[461] (1)

Ground State Quantum Weight = [3]
Point Group = [$D_{\infty h}$]
Bond Distance: Zr–Cl = [2.3] Å
Bond Angle: Cl–Zr–Cl = [180]°
Rotational Constant: B_0 = [0.044943] cm^{-1}

σ = [2]

Enthalpy of formation

Potter[1] investigated mass spectrometrically the gaseous equilibria among ZrCl, $ZrCl_2$, $ZrCl_3$ and $ZrCl_4$. Ion intensities were measured 2.5 cal·K^{-1}·mol^{-1} above the ionization threshold. Using the reported equilibrium constants for the reaction $ZrCl_4(g) + ZrCl_2(g) \rightarrow 2\ ZrCl_3(g)$ in the temperature range 1673–2110 K, second and third law analyses give the heat of reaction at 298 K as −15.8 and +1.7 kcal·mol^{-1}, respectively. The third law drift is 8.9 ± 3.7 cal·K^{-1}·mol^{-1}. Based on the third law heat of reaction and $\Delta_f H°(ZrCl_4, g, 298.15\ K) = -207.77$ kcal·mol^{-1} [2] and $\Delta_f H°(ZrCl_3, g, 298.15\ K) = -125.3$ kcal·mol^{-1},[2] we obtain $\Delta_f H°(ZrCl_2, g, 298.15\ K) = -44.5$ kcal·mol^{-1} (−186.188 ± 20.9 kJ·mol^{-1}) which is adopted in the tabulation.

Farber *et al.*[3] also studied mass spectrometrically the reaction (a) $Zr(cr) + ZrCl_4(g) \rightarrow 2\ ZrCl_2(g)$ and the reaction (b) $Zr(cr) + 2\ Cl(g) \rightarrow ZrCl_2(g)$. They reported second law heats of reaction as $\Delta_r H°(298.15\ K) = 28.8 \pm 1.8$ kcal·mol^{-1} for reaction (a); and −141.1 ± 2.2 kcal·mol^{-1} for reaction (b). Third law analysis of the equilibrium constants which were calculated from their ion intensities of run 3 (the only available values) gives $\Delta_f H°(ZrCl_2, g, 298.15\ K) = -43.4$ kcal·mol^{-1}. Refer to JANAF $ZrCl_3(g)$ table[2] for details.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that other transition metal dichlorides are linear[4-9] even though some fluorides are bent.[10] The bond distance is assumed to be the same as that of $ZrCl_4(g)$. The electronic levels and quantum weights are estimated to be the same as those of $TiCl_2(g)$.[2]

The vibrational frequencies are calculated from a valence force field model. The stretching force constant is estimated to be 2.5 millidyne/Å and the bending force constant 0.05 millidyne/Å.

References

[1] N. D. Potter, Aeronutronic Div., Philco-Ford Corp., Newport Beach, Calif., personal communication, (December 4, 1969).
[2] JANAF Thermochemical Tables: $ZrCl_4(g)$ and $ZrCl_3(g)$, 12–31–69; $TiCl_2(g)$, 12–31–68.
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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.243	−185.753	−185.753	INFINITE
100	45.422	235.909	340.900	−10.499	−185.807	−189.092	98.771
200	53.791	270.254	297.731	−5.495	−186.034	−192.282	50.219
250	56.153	282.529	293.500	−2.743	−186.116	−193.834	40.499
298.15	57.676	292.558	292.558	0.	−186.188	−195.314	34.218
300	57.724	292.915	292.559	0.107	−186.191	−195.371	34.017
350	58.793	301.898	293.266	3.021	−186.266	−196.895	29.385
400	59.543	309.801	294.849	5.981	−186.346	−198.408	25.909
450	60.085	316.847	296.909	8.972	−186.436	−199.911	23.205
500	60.488	323.199	299.226	11.987	−186.536	−201.402	21.040
600	61.033	334.280	304.171	18.065	−186.781	−204.354	17.791
700	61.374	343.716	309.163	24.187	−187.098	−207.259	15.466
800	61.606	351.927	314.007	30.336	−187.498	−210.112	13.719
900	61.782	359.194	318.631	36.506	−187.996	−212.910	12.357
1000	61.937	365.711	323.019	42.692	−188.603	−215.647	11.264
1100	62.097	371.622	327.173	48.894	−189.322	−218.318	10.367
1200	62.280	377.033	331.106	55.112	−193.867	−220.696	9.607
1300	62.495	382.026	334.833	61.351	−194.270	−222.916	8.957
1400	62.749	386.666	338.372	67.613	−194.700	−225.103	8.399
1500	63.043	391.005	341.737	73.902	−195.166	−227.259	7.914
1600	63.372	395.084	344.945	80.222	−195.672	−229.382	7.489
1700	63.732	398.937	348.009	86.577	−196.226	−231.473	7.112
1800	64.114	402.590	350.941	92.970	−196.837	−233.529	6.777
1900	64.512	406.068	353.751	99.401	−197.514	−235.549	6.476
2000	64.918	409.387	356.451	105.872	−198.267	−237.532	6.204
2100	65.325	412.564	359.048	112.384	−199.106	−239.475	5.957
2200	65.727	415.612	361.550	118.937	−221.368	−240.630	5.713
2300	66.120	418.543	363.965	125.530	−222.833	−241.472	5.484
2400	66.498	421.365	366.298	132.161	−224.275	−242.252	5.272
2500	66.861	424.087	368.555	138.829	−225.696	−242.972	5.077
2600	67.205	426.716	370.742	145.532	−227.098	−243.635	4.895
2700	67.531	429.258	372.863	152.269	−228.485	−244.244	4.725
2800	67.837	431.720	374.921	159.038	−229.860	−244.803	4.567
2900	68.125	434.106	376.921	165.836	−231.224	−245.312	4.419
3000	68.394	436.420	378.866	172.662	−232.579	−245.775	4.279
3100	68.647	438.666	380.759	179.514	−233.928	−246.193	4.148
3200	68.884	440.850	382.603	186.391	−235.272	−246.567	4.025
3300	69.107	442.973	384.400	193.291	−236.610	−246.899	3.908
3400	69.317	445.039	386.153	200.212	−237.943	−247.191	3.798
3500	69.516	447.051	387.865	207.154	−239.271	−247.444	3.693
3600	69.704	449.012	389.536	214.115	−240.593	−247.658	3.593
3700	69.884	450.925	391.169	221.094	−241.907	−247.837	3.499
3800	70.056	452.791	392.767	228.091	−243.213	−247.979	3.409
3900	70.220	454.612	394.329	235.105	−244.509	−248.088	3.323
4000	70.378	456.392	395.858	242.135	−245.792	−248.163	3.241
4100	70.531	458.132	397.356	249.181	−247.061	−248.207	3.162
4200	70.679	459.833	398.824	256.241	−248.314	−248.220	3.087
4300	70.821	461.498	400.262	263.316	−249.549	−248.203	3.015
4400	70.960	463.128	401.672	270.405	−250.763	−248.157	2.946
4500	71.094	464.724	403.056	277.508	−251.955	−248.085	2.880
4600	71.224	466.288	404.413	284.624	−253.122	−247.986	2.816
4700	71.350	467.821	405.746	291.753	−254.263	−247.862	2.755
4800	71.472	469.325	407.055	298.894	−816.312	−236.096	2.569
4900	71.590	470.800	408.341	306.047	−817.047	−224.001	2.388
5000	71.703	472.247	409.605	313.212	−817.768	−211.891	2.214
5100	71.812	473.668	410.847	320.387	−818.473	−199.766	2.046
5200	71.916	475.063	412.069	327.574	−819.158	−187.628	1.885
5300	72.016	476.434	413.270	334.770	−819.822	−175.477	1.729
5400	72.111	477.781	414.452	341.977	−820.463	−163.313	1.580
5500	72.201	479.105	415.616	349.192	−821.079	−151.138	1.435
5600	72.285	480.407	416.761	356.417	−821.668	−138.952	1.296
5700	72.365	481.687	417.889	363.649	−822.228	−126.756	1.162
5800	72.439	482.946	419.000	370.890	−822.759	−114.549	1.032
5900	72.508	484.185	420.094	378.137	−823.259	−102.335	0.906
6000	72.571	485.404	421.173	385.391	−823.728	−90.112	0.784

PREVIOUS: December 1969 (1 atm)   CURRENT: December 1969 (1 bar)

Cobalt Chloride ($CoCl_3$) IDEAL GAS M_r = 165.2922 Cobalt Chloride ($CoCl_3$) $Cl_3Co_1(g)$

$S°(298.15\ K) = [334.209 \pm 8.4]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -161.78 \pm 10.5\ kJ{\cdot}mol^{-1}$

$\Delta_fH°(298.15\ K) = -163.59 \pm 10.5\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights ϵ_i,cm^{-1}	g_i
0	[5]
[500]	[5]
[1000]	[5]
[5000]	[5]
[10000]	[5]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[500] (1)
[250] (1)
[550] (2)
[150] (2)

Ground State Quantum Weight = [5] $\sigma = 3$
Point Group: [C_{3v}]
Bond Distance: Co–Cl = [2.09] Å
Bond Angle: Cl–Co–Cl = [100]°
Product of the Moments of Inertia: $I_AI_BI_C = [7.9528 \times 10^{-113}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

Schafer and Krehl[1] studied the reaction of chlorine with $CoCl_2$ by a transpiration method. They ascribed the enhanced volatility of $CoCl_2(cr,l)$ in the presence of Cl_2 to the formation of gaseous $CoCl_3$ according to the reaction $Cl_2(g) + 2\ CoCl_2(g) = 2\ CoCl_3(g)$. Partial pressures for the three species involved in the reaction were reported for the temperature range 918–1073 K. No consideration was given to possible dimerization of either the di– or trichloride. Subsequent measurements by Schafer and Breil[2] have confirmed the increased volatility of $CoCl_2(l)$ in the presence of Cl_2. However, the latter study was conducted at only one temperature (1056 K). JANAF data[3] for $CoCl_2(g)$ and $Co_2Cl_4(g)$ are used to correct their pressures[1 2] for dimerization of the dichloride. Our corrected $CoCl_2$ pressures are 5% less than those reported by Schafer and Krehl[1] at 918 K and 11.4% less at 1073 K. We tentatively assume that dimerization of the trichloride is negligible over the temperature range investigated and treat the equilibrium pressures by the second and third law methods. Results of the analysis are: $\Delta_rH°(298.15\ K)$ (2nd Law) = −32.9 and $\Delta_rH°(298.15\ K)$ (3rd Law) = $-33.36 \pm 2.0\ kcal{\cdot}mol^{-1}$. The third law drift is $-0.5 \pm 2.9\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. The measurements of Schafer and Breil[2] at 1056 K give $\Delta_rH°(298.15\ K)$ (3rd Law) = $-33.31\ kcal{\cdot}mol^{-1}$. Combining the average value for the third law heats of reaction with $\Delta_fH°(CoCl_2, g, 298.15\ K) = -22.4 \pm 2.0\ kcal{\cdot}mol^{-1}$,[3] we obtain $\Delta_fH°(CoCl_3, g, 298.15\ K) = -39.1 \pm 2.5\ kcal{\cdot}mol^{-1}$. This value is adopted and corresponds to a bond dissociation energy of $D_0°(CoCl_2–Cl, 298.15\ K) = 45.7\ kcal{\cdot}mol^{-1}$. A comparison of this value with that for the monochloride ($D_0°(Co–Cl, 0\ K) = 84.4\ kcal{\cdot}mol^{-1}$) and dichloride ($D_0°(CoCl–Cl) = 97.5\ kcal{\cdot}mol^{-1}$) clearly reveals the instability of the trichloride molecule.

Heat Capacity and Entropy

The structure of CoCl is not known; however, it can be limited to two possibilities. The molecule has either a pyramidal structure of C_{3v} symmetry, or a planar structure of D_{3h} symmetry. By analogy with the geometries for PCl_3,[3] $SiCl_3$[3] and TiF_3,[3 4] we adopt the pyramidal structure. The bond length is taken equal to that for CoCl [3]. The Cl–Co–Cl bond angle is estimated as 100°. The principal moments of inertia are: $I_A = I_B = 36.1659 \times 10^{-39}$, and $I_C = 60.3628 \times 10^{-39}\ g{\cdot}cm^2$.

The vibrational frequencies are estimated by comparison with those for PCl_3,[3] $SiCl_3$[3] and TiF_3.[4] The ground state quantum weight is taken equal to that for Co^{+3}.[5] The electronic levels are estimated from those for Fe^{+2},[5] since few levels have been observed in the spectrum of Co^{+3}. The Fe^{+2} ion is isoelectronic with Co^{+3}. The adopted upper levels and quantum weights contribute $0.65\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ at 298.15 K and $2.4\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ at 3000 K to the entropy of $CoCl_3$.

References

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[3] JANAF Thermochemical Tables: $CoCl_2(g)$, $CoCl(g)$, and $Co_2Cl_4(g)$, 12–31–73; $PCl_3(g)$, 6–30–70; $SiCl_3(g)$, 12–31–69; $TiF_3(g)$, 6–30–68.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$ (kJ·mol^{-1})	$\Delta_fG°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−16.731	−161.783	−161.783	INFINITE
100	48.842	266.224	394.607	−12.838	−162.780	−160.283	83.723
200	66.145	305.685	340.909	−7.045	−163.452	−157.483	41.130
250	72.162	321.128	335.443	−3.579	−163.570	−155.974	32.589
298.15	76.238	334.209	334.209	0.	−163.594	−154.508	27.069
300	76.366	334.681	334.210	0.141	−163.593	−154.451	26.892
350	79.198	346.680	335.152	4.035	−163.540	−152.931	22.824
400	81.067	357.387	337.274	8.045	−163.463	−151.421	19.774
450	82.281	367.010	340.053	12.131	−163.389	−149.920	17.402
500	83.059	375.723	343.191	16.266	−163.337	−148.427	15.506
600	83.853	390.948	349.918	24.618	−163.327	−145.448	12.662
700	84.136	403.899	356.728	33.020	−163.469	−142.459	10.630
800	84.213	415.140	363.342	41.438	−164.200	−139.376	9.100
900	84.219	425.060	369.660	49.860	−164.703	−136.246	7.907
1000	84.212	433.933	375.651	58.282	−165.459	−133.046	6.950
1100	84.214	441.959	381.320	66.703	−166.499	−129.757	6.162
1200	84.233	449.287	386.683	75.125	−167.855	−126.359	5.500
1300	84.268	456.031	391.762	83.550	−169.671	−122.831	4.935
1400	84.317	462.277	396.578	91.979	−172.073	−119.141	4.445
1500	84.375	468.097	401.154	100.414	−173.472	−115.309	4.015
1600	84.440	473.544	405.510	108.854	−174.624	−111.393	3.637
1700	84.509	478.665	409.664	117.302	−175.685	−107.409	3.300
1800	84.580	483.498	413.633	125.756	−193.019	−103.068	2.991
1900	84.651	488.073	417.432	134.218	−194.348	−98.035	2.695
2000	84.721	492.416	421.073	142.686	−195.686	−92.931	2.427
2100	84.789	496.552	424.570	151.162	−197.033	−87.760	2.183
2200	84.854	500.498	427.932	159.644	−198.392	−82.525	1.959
2300	84.917	504.271	431.170	168.133	−199.765	−77.228	1.754
2400	84.975	507.886	434.291	176.627	−201.154	−71.870	1.564
2500	85.031	511.356	437.305	185.128	−202.561	−66.455	1.388
2600	85.082	514.692	440.218	193.633	−203.988	−60.982	1.225
2700	85.129	517.904	443.036	202.144	−205.438	−55.454	1.073
2800	85.173	521.001	445.765	210.659	−206.911	−49.873	0.930
2900	85.212	523.990	448.412	219.178	−208.409	−44.238	0.797
3000	85.248	526.880	450.979	227.701	−209.933	−38.551	0.671
3100	85.280	529.676	453.473	236.228	−211.482	−32.813	0.553
3200	85.308	532.384	455.897	244.757	−587.870	−25.251	0.412
3300	85.333	535.009	458.255	253.289	−588.043	−7.667	0.121
3400	85.354	537.557	460.550	261.824	−588.240	9.923	−0.152
3500	85.372	540.031	462.786	270.360	−588.460	27.519	−0.411
3600	85.387	542.436	464.965	278.898	−588.704	45.122	−0.655
3700	85.399	544.776	467.090	287.437	−588.968	62.732	−0.886
3800	85.408	547.054	469.165	295.978	−589.251	80.349	−1.104
3900	85.415	549.272	471.191	304.519	−589.551	97.974	−1.312
4000	85.419	551.435	473.170	313.060	−589.866	115.607	−1.510
4100	85.420	553.544	475.104	321.602	−590.194	133.248	−1.698
4200	85.420	555.603	476.997	330.144	−590.532	150.897	−1.877
4300	85.417	557.612	478.848	338.686	−590.877	168.554	−2.048
4400	85.413	559.576	480.661	347.228	−591.228	186.220	−2.211
4500	85.406	561.496	482.436	355.769	−591.581	203.893	−2.367
4600	85.399	563.373	484.175	364.309	−591.936	221.574	−2.516
4700	85.389	565.209	485.880	372.848	−592.288	239.263	−2.659
4800	85.379	567.007	487.551	381.387	−592.638	256.959	−2.796
4900	85.367	568.767	489.191	389.924	−592.983	274.663	−2.928
5000	85.353	570.492	490.799	398.460	−593.321	292.373	−3.054
5100	85.339	572.182	492.379	406.995	−593.651	310.090	−3.176
5200	85.324	573.839	493.929	415.528	−593.973	327.814	−3.293
5300	85.308	575.464	495.452	424.060	−594.284	345.543	−3.406
5400	85.292	577.058	496.949	432.590	−594.585	363.279	−3.514
5500	85.274	578.623	498.420	441.118	−594.876	381.020	−3.619
5600	85.256	580.159	499.866	449.644	−595.154	398.766	−3.720
5700	85.238	581.668	501.288	458.169	−595.422	416.517	−3.817
5800	85.219	583.150	502.686	466.692	−595.679	434.273	−3.911
5900	85.199	584.607	504.063	475.213	−595.880	452.029	−4.002
6000	85.179	586.039	505.417	483.732	−596.104	469.792	−4.090

PREVIOUS: December 1973 (1 atm) CURRENT. December 1973 (1 bar)

Copper Chloride ((CuCl)$_3$) IDEAL GAS $M_r = 296.997$ Copper Chloride ((CuCl)$_3$) $Cl_3Cu_3(g)$

$S°(298.15\ K) = [429.526]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -258.50 \pm 2.1\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -258.57 \pm 2.1\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
[100](1)	350 (2)
[150](1)	[300](2)
[250](1)	[60](2)
[200](1)	[80](2)

Ground State Quantum Weight: [1]
Point Group: D_{3h} $\sigma = 6$
Bond Distance: Cu–Cl = 2.16 Å
Bond Angles: Cl–Cu–Cl = 150°; Cu–Cl–Cu = 90°
Product of the Moments of Inertia: $I_A I_B I_C = 2.02938 \times 10^{-111}\ g^3{\cdot}cm^6$

Enthalpy of Formation

The heat of sublimation was determined by second and third law analysis of the following vapor pressure data. Magee[1] measured both vapor pressure by torsion effusion and vapor density in the range 533–644 K and found only trimer present. The second and third law analyses gave $\Delta_{sub}H°(298.15\ K) = 37.37 \pm 0.04$ and $37.24 \pm 0.02\ kcal{\cdot}mol^{-1}$ with a drift of $-0.25 \pm 0.07\ cal{\cdot}K^{-1}mol^{-1}$. Shelton,[2] using Knudsen effusion in the range 547–657 K, obtained $\Delta_{sub}H°(298.15\ K) = 40.35 \pm 1.4$ and $37.42 \pm 0.4\ kcal{\cdot}mol^{-1}$ with a drift of $-4.9\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. Fedorov and Shakhova,[3] using transport methods, obtained vapor pressure over the liquid from 751–1057 K. Using second and third law analysis these gave $\Delta_{sub}H°(298.15\ K) = 38.6 \pm 1.0$ and $39.27 \pm 0.5\ kcal{\cdot}mol^{-1}$.

Brewer and Lofgren[4] obtained equilibrium constants for the reaction $3\ Cu(cr) + 3\ HCl(g) \rightarrow Cu_3Cl_3(g) + 1.5\ H_2(g)$. Second and third law analysis of these constants gave $\Delta_r H°(298.15\ K) = 3.9 \pm 0.6$ and $4.39 \pm 0.3\ kcal{\cdot}mol^{-1}$ which leads to $\Delta_f H° = -61.8 \pm 0.5\ kcal{\cdot}mol^{-1}$ ($-258.571 \pm 2.1\ kJ{\cdot}mol^{-1}$). This was the value adopted since it is dependent only on HCl(g) and does not involve three times the uncertainty of CuCl(cr) as do the sublimation experiments, which yield values in good agreement but of larger uncertainty.

Heat Capacity and Entropy

The structure of the trimer has been investigated by Wong and Schomaker.[5] They conclude that the molecule is planar with D_{3h} symmetry and a Cu–Cl bond length of 2.16 Å. They also state that a very large amplitude of the symetric in–plane bending appears plausible from the diffraction pattern. The infra–red spectrum has been investigated by Klemperer *et al.*[6] They observed one strong absorption with a maximumm at 350 cm^{-1}; they attribute this to bond stretching motion of type E′. They also suggest that the broad absorption may involve another mode of approximately equal frequency.

In order to estimate the remaining frequencies we assumed that the other infra–red active E′ mode would be close to the observed 350 cm^{-1} and this was estimated as 300 cm^{-1}. The in–plane bending is the third E′ model and since this has a very large amplitude it was estimated as 60 cm^{-1}. By analogy with other D_{3h} rings the A_2' mode was assumed to be in the same region as the E′ stretches and was taken to be 250 cm^{-1}. The $2A_1'$ stretches were estimated as 100 and 150 cm^{-1}, while the out of plane A_2'' was taken as 200 cm^{-1} and the E″ as 80 cm^{-1}. These values gave calculated entropies in excellent agreement with the equilibrium data and thus support the estimates.

The principal moments of inertia are: $I_A = I_B = 100.4872 \times 10^{-39}$, $I_C = 200.9745 \times 10^{-39}\ g{\cdot}cm^2$.

References

[1] D. W. Magee, Ph. D. Thesis, Ohio State University (1955).
[2] R. A. J. Shelton, Trans. Faraday Soc. 57, 2113 (1961).
[3] P. I. Fedorov and M. N. Shakhova, Izv. Vyssahikh Uchebn. Zavendenii, Khim. i Khim. Tekhnol. 4, 550 (1961).
[4] L. Brewer and N. L. Lofgren, J. Amer. Chem. Soc. 72, 3038 (1950).
[5] C. H. Wong and V. Schomaker, J. Phys. Chem. 61, 358 (1957).
[6] W. Klemperer, S. A. Rice and R. S. Berry, J. Amer. Chem. Soc. 79, 1810 (1957).

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0	INFINITE	−28.723	−258.503	−258.503	INFINITE
100	91.029	308.854	533.649	−22.480	−258.633	−258.157	134.848
200	116.232	381.296	440.710	−11.883	−258.633	−257.665	67.295
250	121.471	407.846	431.562	−5.929	−258.595	−257.427	53.786
298.15	124.570	429.526	429.526	0.	−258.571	−257.204	45.061
300	124.664	430.297	429.529	0.231	−258.571	−257.196	44.782
350	126.724	449.680	431.055	6.519	−258.570	−256.967	38.350
400	128.120	466.698	434.468	12.892	−258.596	−256.737	33.526
450	129 105	481.849	438.907	19.324	−258.655	−256.501	29.774
500	129.823	495.490	443.894	25.798	−258.743	−256.257	26.771
600	130.778	519.252	454.531	38.832	−259.017	−255.737	22.264
700	131.365	539.459	465.257	51.942	−259.438	−255.159	19.040
800	131.749	557.027	475.654	65.099	−260.002	−254.511	16.618
900	132.015	572.561	485.575	78.288	−260.724	−253.783	14.729
1000	132.206	586.481	494.982	91.499	−261.619	−252.965	13.214
1100	132.348	599.088	503.882	104.727	−262.731	−252.048	11.969
1200	132.457	610.609	512.303	117.968	−264.119	−251.018	10.927
1300	132.541	621.215	520.278	131.218	−265.912	−249.857	10.039
1400	132.608	631.040	527.843	144.475	−307.574	−247.320	9.228
1500	132.662	640.190	535.031	157.739	−309.850	−242.937	8.460
1600	132.707	648.754	541.874	171.008	−312.135	−238.402	7.783
1700	132.744	656.800	548.400	184.280	−314.428	−233.723	7.181
1800	132.775	664.389	554.635	197.556	−316.732	−228.909	6.643
1900	132.801	671.568	560.602	210.835	−319.047	−223.967	6.157
2000	132.823	678.380	566.322	224.116	−321.376	−218.903	5.717
2100	132.842	684.861	571.814	237.399	−323.718	−213.722	5.316
2200	132.859	691.042	577.094	250.684	−326.078	−208.428	4.949
2300	132.874	696.948	582.178	263.971	−328.456	−203.028	4.611
2400	132.886	702.603	587.078	277.259	−330.854	−197.523	4.299
2500	132.898	708.028	591.809	290.548	−333.275	−191.918	4.010
2600	132.908	713.240	596.379	303.839	−335.721	−186.215	3.741
2700	132.917	718.257	600.801	317.130	−338.193	−180.418	3.490
2800	132.925	723.091	605.083	330.422	−340.693	−174.529	3.256
2900	132.932	727.755	609.233	343.715	−1243.833	−150.563	2.712
3000	132.938	732.262	613.259	357.008	−1244.005	−112.861	1.965
3100	132.944	736.621	617.169	370.302	−1244.357	−75.151	1.266
3200	132.949	740.842	620.968	383.597	−1244.888	−37.427	0.611
3300	132.954	744.933	624.663	396.892	−1245.599	0.317	−0.005
3400	132.959	748.902	628.259	410.188	−1246.487	38.085	−0.585
3500	132.963	752.756	631.761	423.484	−1247.548	75.881	−1.132
3600	132.966	756.502	635.174	436.780	−1248.778	113.711	−1.650
3700	132.970	760.145	638.503	450.077	−1250.168	151.576	−2.140
3800	132.973	763.691	641.751	463.374	−1251.710	189.481	−2.605
3900	132.976	767.146	644.922	476.672	−1253.396	227.429	−3.046
4000	132.979	770.512	648.020	489.969	−1255.215	265.422	−3.466
4100	132.981	773.796	651.048	503.267	−1257.157	303.462	−3.866
4200	132.983	777.000	654.009	516.566	−1259.211	341.550	−4.248
4300	132.986	780.130	656.905	529.864	−1261.365	379.689	−4.612
4400	132.988	783.187	659.741	543.163	−1263.609	417.879	−4.961
4500	132.989	786.176	662.517	556.462	−1265.931	456.120	−5.295
4600	132.991	789.098	665.237	569.761	−1268.322	494.415	−5.614
4700	132.993	791.959	667.903	583.060	−1270.770	532.761	−5.921
4800	132.994	794.759	670.517	596.359	−1273.265	571.160	−6.215
4900	132.996	797.501	673.081	609.659	−1275.800	609.612	−6.499
5000	132.997	800.188	675.596	622.958	−1278.365	648.115	−6.771
5100	132.999	802.821	678.065	636.258	−1280.952	686.671	−7.033
5200	133.000	805.404	680.489	649.558	−1283.554	725.277	−7.285
5300	133.001	807.937	682.870	662.858	−1286.164	763.933	−7.529
5400	133.002	810.424	685.209	676.158	−1288.777	802.639	−7.764
5500	133.003	812.864	687.508	689.459	−1291.389	841.393	−7.991
5600	133.004	815.261	689.768	702.759	−1293.994	880.194	−8.210
5700	133.005	817.615	691.990	716.059	−1296.590	919.042	−8.422
5800	133.006	819.928	694.176	729.360	−1299.173	957.936	−8.627
5900	133.007	822.202	696.327	742.661	−1301.743	996.873	−8.826
6000	133.007	824.437	698.443	755.961	−1304.296	1035.854	−9.018

PREVIOUS: March 1966 (1 atm)   CURRENT: March 1966 (1 bar)

Trichlorofluorosilane ($SiCl_3F$) IDEAL GAS $M_r = 153.442903$ Trichlorofluorosilane ($SiCl_3F$) $Cl_3F_1Si_1(g)$

$S°(298.15\ K) = [336.055 \pm 16.7]\ J{\cdot}K^{-1}mol^{-1}$

$\Delta_fH°(0\ K) = -838.80 \pm 62.8\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -840.98 \pm 62.8\ kJ{\cdot}mol^{-1}$

Vibrational Levels and Quantum Weights ν, cm^{-1}
[925](1)
[350](1)
[500](2)
[270](2)
[200](2)

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: C_{3v}
Product of the Moments of Inertia: $I_AI_BI_C = [142{,}900 \times 10^{-117}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

All data are from Henderson and Scheffee.[1]

Heat Capacity and Entropy

All data are from Henderson and Scheffee.[1]

Reference

[1] C. B. Henderson and R. S. Scheffee, "Survey of Thermochemical Data," Atlantic Research Corp., Alexandria, Va., (January 1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	$\log K_f$
0	0.	0.	INFINITE	−19.214	−838.796	−838.796	INFINITE
100	55.092	255.734	407.697	−15.196	−840.866	−829.187	433.123
200	78.839	302.234	343.986	−8.350	−841.220	−817.279	213.451
250	85.487	320.584	337.514	−4.233	−841.131	−811.303	169.513
298.15	90.081	336.055	336.055	0.	−840.984	−805.570	141.133
300	90.231	336.613	336.057	0.167	−840.977	−805.351	140.224
350	93.713	350.797	337.169	4.770	−840.782	−799.428	119.308
400	96.325	363.489	339.680	9.524	−840.557	−793.535	103.625
450	98.321	374.955	342.973	14.392	−840.310	−787.672	91.431
500	99.873	385.398	346.701	19.348	−840.050	−781.837	81.678
600	102.076	403.816	354.726	29.454	−839.505	−770.246	67.056
700	103.521	419.667	362.898	39.739	−838.952	−758.746	56.618
800	104.511	433.559	370.880	50.143	−838.410	−747.325	48.795
900	105.217	445.912	378.543	60.631	−837.892	−735.971	42.715
1000	105.735	457.026	385.845	71.180	−837.404	−724.673	37.853
1100	106.126	467.122	392.782	81.774	−836.951	−713.423	33.878
1200	106.429	476.370	399.368	92.403	−836.537	−702.211	30.566
1300	106.667	484.899	405.623	103.058	−836.165	−691.033	27.766
1400	106.857	492.811	411.572	113.734	−835.839	−679.881	25.367
1500	107.012	500.189	417.237	124.428	−835.561	−668.751	23.288
1600	107.140	507.099	422.639	135.136	−835.333	−657.638	21.470
1700	107.246	513.598	427.801	145.855	−885.335	−646.091	19.852
1800	107.335	519.730	432.739	156.585	−884.981	−632.028	18.341
1900	107.411	525.536	437.472	167.322	−884.640	−617.985	16.990
2000	107.476	531.047	442.014	178.066	−884.312	−603.959	15.774
2100	107.532	536.292	446.379	188.817	−883.997	−589.949	14.674
2200	107.581	541.296	450.581	199.573	−883.697	−575.954	13.675
2300	107.624	546.079	454.630	210.333	−883.412	−561.972	12.763
2400	107.661	550.660	458.536	221.097	−883.142	−548.002	11.927
2500	107.694	555.056	462.310	231.865	−882.888	−534.043	11.158
2600	107.724	559.280	465.959	242.636	−882.651	−520.094	10.449
2700	107.750	563.346	469.491	253.410	−882.430	−506.154	9.792
2800	107.774	567.265	472.913	264.186	−882.225	−492.222	9.183
2900	107.795	571.048	476.232	274.964	−882.037	−478.296	8.615
3000	107.814	574.702	479.454	285.745	−881.863	−464.377	8.086
3100	107.831	578.238	482.584	296.527	−881.704	−450.464	7.590
3200	107.847	581.662	485.627	307.311	−881.556	−436.555	7.126
3300	107.861	584.980	488.588	318.096	−881.419	−422.651	6.690
3400	107.874	588.201	491.470	328.883	−881.290	−408.751	6.280
3500	107.886	591.328	494.279	339.671	−881.166	−394.855	5.893
3600	107.897	594.367	497.017	350.460	−1265.195	−370.501	5.376
3700	107.907	597.324	499.688	361.251	−1264.658	−345.656	4.880
3800	107.916	600.201	502.296	372.042	−1264.118	−320.825	4.410
3900	107.925	603.005	504.842	382.834	−1263.571	−296.009	3.965
4000	107.933	605.737	507.331	393.627	−1263.013	−271.206	3.542
4100	107.940	608.403	509.763	404.420	−1262.440	−246.418	3.139
4200	107.947	611.004	512.143	415.215	−1261.849	−221.644	2.757
4300	107.954	613.544	514.472	426.010	−1261.234	−196.885	2.392
4400	107.960	616.026	516.752	436.806	−1260.593	−172.140	2.044
4500	107.965	618.452	518.985	447.602	−1259.922	−147.410	1.711
4600	107.971	620.825	521.173	458.399	−1259.217	−122.695	1.393
4700	107.975	623.147	523.318	469.196	−1258.476	−97.996	1.089
4800	107.980	625.420	525.422	479.994	−1257.695	−73.313	0.798
4900	107.984	627.647	527.485	490.792	−1256.873	−48.647	0.519
5000	107.988	629.828	529.510	501.591	−1256.006	−23.998	0.251
5100	107.992	631.967	531.498	512.390	−1255.093	0.633	−0.006
5200	107.996	634.064	533.451	523.189	−1254.131	25.246	−0.254
5300	107.999	636.121	535.369	533.989	−1253.120	49.840	−0.491
5400	108.003	638.140	537.253	544.789	−1252.059	74.414	−0.720
5500	108.006	640.122	539.105	555.589	−1250.944	98.968	−0.940
5600	108.008	642.068	540.927	566.390	−1249.778	123.502	−1.152
5700	108.011	643.980	542.718	577.191	−1248.558	148.014	−1.356
5800	108.014	645.858	544.480	587.992	−1247.284	172.504	−1.554
5900	108.016	647.705	546.214	598.794	−1245.957	196.972	−1.744
6000	108.019	649.520	547.921	609.596	−1244.576	221.416	−1.928

PREVIOUS: December 1960 (1 atm) CURRENT: December 1960 (1 bar)

Iron Chloride ($FeCl_3$) CRYSTAL $M_r = 162.206$ Iron Chloride ($FeCl_3$) $Cl_3Fe_1(cr)$

$S°(298.15 K) = 142.336 J·K^{-1}·mol^{-1}$
$T_{fus} = 577 K$

$\Delta_f H°(0 K) = -400.833 \pm 0.84 kJ·mol^{-1}$
$\Delta_f H°(298.15 K) = -399.405 \pm 0.84 kJ·mol^{-1}$
$\Delta_{fus} H° = 43.095 kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy change, $\Delta_r H°(298.15 K) = -24.49 \pm 0.07 kcal·mol^{-1}$, for the reaction $Fe(cr) + 3(HCl·12.731 H_2O)(l) + 1/2(H_2O_2·12.580 H_2O)(l) = FeCl_3(cr) + H_2(g) + 45.483 H_2O(l)$ was determined by Koehler and Coughlin.[1] This leads to $\Delta_f H°(298.15 K) = -95.46 \pm 0.20 kcal·mol^{-1}$ for $FeCl_3(cr)$, using $\Delta_f H°(298.15 K) = -38.9 \pm 0.05$ and $-68.32 \pm 0.01 kcal·mol^{-1}$ for hydrochloric acid and hydrogen peroxide solution, respectively, obtained from Rossini *et al.*[2] From $\Delta_r H°(298.15 K) = -38.0 \pm 0.2 kcal·mol^{-1}$ for the reaction $FeCl_3(cr) = Fe^{+++}(aq)$ reported by Li and Gregory,[3] the value of $\Delta_f H°(FeCl_3, cr, 298.15 K)$ was calculated as $-93.26 \pm 0.2 kcal·mol^{-1}$. The former $\Delta_f H°(298.15 K)$ value is adopted.

The equilibrium pressures of the reaction $2 FeCl_2(cr) + Cl_2(g) = 2FeCl_3(cr)$, in the temperature range of 435.7–482.2 K, were measured by Schafer and Oehler.[4] Using the reported partial pressures for $Cl_2(g)$, the enthalpy change $\Delta_r H°(298.15 K)$ of the reaction was evaluated as -27.49 ± 0.44 and $-27.21 kcal·mol^{-1}$ by the 2nd and 3rd law methods, respectively. Based on the 3rd law value for $\Delta_r H°(298.15 K)$, the value of $\Delta_f H°(FeCl_3, cr, 298.15 K)$ was derived to be $-95.36 \pm 0.12 kcal·mol^{-1}$ which is in good agreement with the adopted value.

Heat Capacity and Entropy

The low temperature (51–298.16 K) heat capacities and high temperature (339.6–560.9 K) heat content of $FeCl_3(cr)$ were determined by Todd and Coughlin.[5] The low temperature $C_p°$ and the derived high temperature $C_p°$ were plotted. The two $C_p°$ curves were joined smoothly at 298.15 K). The $C_p°$ values above 560.9 K were obtained by graphical extrapolation. The value of $S°(298.15 K)$ was derived from the low temperature data reported by Todd and Coughlin,[5] using $S°(51 K) = 6.29 cal·K^{-1}·mol^{-1}$. The value of $S°(51 K)$ was selected to make the second and third law values of $\Delta_r H°$, derived from the equilibrium data reported by Schafer and Oehler,[4] in good agreement. The difference in $S°(51 K)$ between the selected value, 6.29, and the reported value, $4.50 cal·K^{-1}·mol^{-1}$, by Todd and Coughlin,[5] is assumed to be the magnetic entropy remaining at 51 K which was unaccounted for in the report.

Fusion Data

T_{fus} and $\Delta_{fus}H°$ were obtained from Todd and Coughlin.[5]

Sublimation Data

The difference between $\Delta_f H°(298.15 K)$ for $Fe_2Cl_6(g)$ and $2FeCl_3(cr)$ is the enthalpy of sublimation at 298.15 K. The former is obtained by the 2nd and 3rd law analyses of related equilibrium data. See $Fe_2Cl_6(g)$ table for details.

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[4] H. Schafer and E. Oehler, Z. Anorg. Alleg. Chem. 271, 206 (1953).
[5] S. S. Todd and J. P. Coughlin, J. Amer. Chem. Soc. 73, 4184 (1951).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.706	−400.833	−400.833	INFINITE
100	58.254	54.924	220.004	−16.508	−402.425	−378.960	197.948
200	86.219	105.867	150.854	−8.997	−401.240	−355.834	92.934
298.15	96.650	142.336	142.336	0.	−399.405	−333.930	58.503
300	96.860	142.935	142.338	0.179	−399.366	−333.524	58.072
400	106.692	172.135	146.251	10.354	−397.025	−311.913	40.732
500	119.872	197.194	153.973	21.611	−393.977	−290.964	30.397
577.000	121.754	214.368	160.911	30.845	--- CRYSTAL <--> LIQUID ---		
600	123.428	219.165	163.053	33.667	−390.455	−270.691	23.566
700	128.658	238.611	172.484	46.289	−386.667	−251.027	18.732
800	131.796	256.012	181.857	59.324	−382.796	−231.914	15.142
900	133.470	271.644	190.980	72.598	−379.131	−213.278	12.378
1000	133.888	285.731	199.763	85.968	−376.113	−195.021	10.187
1100	133.888	298.491	208.167	99.357	−373.992	−177.000	8.405
1200	133.888	310.141	216.187	112.745	−371.336	−159.229	6.931
1300	133.888	320.858	223.832	126.134	−367.049	−141.727	5.695
1400	133.888	330.780	231.121	139.523	−362.860	−124.553	4.647
1500	133.888	340.017	238.076	152.912	−358.769	−107.674	3.750

PREVIOUS: CURRENT: June 1965

Iron Chloride ($FeCl_3$) $Cl_3Fe_1(cr)$

Iron Chloride ($FeCl_3$) LIQUID $M_r = 162.206$ Iron Chloride ($FeCl_3$) $Cl_3Fe_1(l)$

$S°(298.15 K) = [200.657] J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15 K) = [-362.815] kJ·mol^{-1}$
$T_{fus} = 577 K$ $\Delta_{fus}H° = 43.095 kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(FeCl_3, l, 298.15 K)$ is calculated from $\Delta_f H°(FeCl_3, cr, 298.15 K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(577 K)-H°(298.15 K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity for $FeCl_3(l)$ was taken from Todd and Coughlin[1] and assumed as constant between 298.15 and 1500 K. $S°(298.15 K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} and $\Delta_{fus}H°$ were reported by Todd and Coughlin.[1]

Vaporization Data

The boiling point (T_{vap}) is determined as the temperature at which the Gibbs energy change ($\Delta_r G°$) of the reaction $2FeCl_3(l) = Fe_2Cl_6(g)$ is zero. The corresponding enthalpy change at T_{vap} is the enthalpy vaporization.

References

[1] S. S. Todd and J. P. Coughlin, J. Amer. Chem. Soc. 73, 4184 (1951).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
0							
100							
200							
298.15	133.888	200.657	200.657	0.	−362.815	−314.728	55.139
300	133.888	201.485	200.660	0.248	−362.708	−314.430	54.747
400	133.888	240.002	205.911	13.636	−357.152	−299.187	39.070
500	133.888	269.879	215.828	27.025	−351.973	−285.302	29.805
577.000	133.888	289.056	224.351	37.335	--- CRYSTAL <--> LIQUID ---		
600	133.888	294.289	226.932	40.414	−347.118	−272.429	23.717
700	133.888	314.928	238.067	53.803	−342.563	−260.345	19.427
800	133.888	332.806	248.817	67.192	−338.338	−248.892	16.251
900	133.888	348.576	259.042	80.580	−334.558	−237.944	13.810
1000	133.888	362.683	268.713	93.969	−331.522	−227.382	11.877
1100	133.888	375.444	277.845	107.358	−329.401	−217.057	10.307
1200	133.888	387.093	286.471	120.747	−326.745	−206.980	9.010
1300	133.888	397.810	294.629	134.136	−322.458	−197.174	7.923
1400	133.888	407.732	302.358	147.524	−318.269	−187.695	7.003
1500	133.888	416.970	309.694	160.913	−314.177	−178.511	6.216

PREVIOUS: CURRENT: June 1965

Iron Chloride ($FeCl_3$)

CRYSTAL-LIQUID

0 to 577 K crystal
above 577 K liquid

Refer to the individual tables for details.

M_r = 162.206 Iron Chloride ($FeCl_3$) $Cl_3Fe_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	0.	0.	INFINITE	−19.706	−400.833	−400.833	INFINITE
100	58.254	54.924	220.004	−16.508	−402.425	−378.960	197.948
200	86.219	105.867	150.854	−8.997	−401.240	−355.834	92.934
298.15	96.650	142.336	142.336	0.	−399.405	−333.930	58.503
300	96.860	142.935	142.338	0.179	−399.366	−333.524	58.072
400	106.692	172.135	146.251	10.354	−397.025	−311.913	40.732
500	119.872	197.194	153.973	21.611	−393.977	−290.964	30.397
577.000	121.754	214.368	160.911	30.845	CRYSTAL <--> LIQUID TRANSITION		
577.000	133.888	289.056	160.911	73.940			
600	133.888	294.289	165.924	77.019	−347.103	−272.414	23.716
700	133.888	314.928	185.774	90.408	−342.548	−260.330	19.426
800	133.888	332.806	203.060	103.797	−338.323	−248.877	16.250
900	133.888	348.576	218.370	117.186	−334.543	−237.929	13.809
1000	133.888	362.683	232.108	130.574	−331.507	−227.367	11.876
1100	133.888	375.444	244.568	143.963	−329.386	−217.041	10.306
1200	133.888	387.093	255.967	157.352	−326.730	−206.965	9.009
1300	133.888	397.810	266.471	170.741	−322.443	−197.159	7.922
1400	133.888	407.732	276.211	184.130	−318.254	−187.679	7.002
1500	133.888	416.970	285.291	197.518	−314.162	−178.496	6.216

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = [344.206]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -253.07 \pm 5.0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -253.13 \pm 5.0\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[350](1)
[160](1)
[310](2)
[130](2)

Ground State Quantum Weight: [6]
Point Group: D_{3h}
Bond Distance: Fe–Cl = [2.17] Å
Bond Angle: Cl–Fe–Cl = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.43810 \times 10^{-112}]\ g^3 \cdot cm^6$

$\sigma = [6]$

Enthalpy of Formation

The equilibrium pressures for the reaction $Fe_2Cl_6(g) = 2FeCl_3(g)$ were determined by Kangro and Bernstorff[1] and Schafer,[2] respectively. Using their vapor pressure data the corresponding values of $\Delta_r H°(298.15\ K)$ for that reaction were evaluated by both the 2nd and 3rd law methods. Based on the 3rd law values for $\Delta_r H°(298.15\ K)$, the heats of formation $\Delta_f H°(298.15\ K)$ for $FeCl_3(g)$ were derived. The results obtained are presented as follows.

Source	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Kangro and Bernstorff[1]	760.2–1014.2	34.99 ± 0.44	35.73	−60.34 ± 0.30
Schafer[2]	673.2–1073.2	34.81 ± 0.02	34.93	−60.74 ± 0.20

The adopted value of $\Delta_f H°(FeCl_3, g, 298.15\ K)$ is −60.5 ± 1.2 kcal·mol^{-1}.

Heat Capacity and Entropy

The molecular structure was assumed to be the same as that of $AlCl_3(g)$ due to the similarities in structure between $Fe_2Cl_6(g)$ and $Al_2Cl_6(g)$. The Fe–Cl bond distance was estimated by comparison with those for $Fe_2Cl_6(g)$ reported by Zasorin *et al.*[3] and Hassel and Viervoll.[4] Both the ground state quantum weight and vibrational frequencies were estimated so that the second and third law values of $\Delta_r H°(298.15\ K)$, derived from the vapor pressure data, for the reaction $Fe_2Cl_6(g) = 2FeCl_3(g)$ are in reasonable agreement. The principal moments of inertia are: $I_A = I_B = 41.5834 \times 10^{-39}$ and $I_C = 83.1667 \times 10^{-39}\ g \cdot cm^2$.

References

[1] W. Kangro and H. Bernstorff, Z. anorg. allg. Chem. 263, 316 (1950).
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[3] E. Z. Zasorin, N. G. Rambidi and P. A. Akishin, Zh. Strukt. Khim., 4, 910 (1963).
[4] O. Hassel and H. Viervoll, Acta Chem. Scand. 1, 149 (1947).

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−18.214	−253.068	−253.068	INFINITE
100	56.528	269.115	409.062	−13.995	−253.639	−251.593	131.419
200	72.371	314.146	351.179	−7.406	−253.377	−249.627	65.196
250	75.716	330.687	345.475	−3.697	−253.233	−248.707	51.964
298.15	77.702	344.206	344.206	0.	−253.132	−247.845	43.421
300	77.762	344.687	344.208	0.144	−253.129	−247.812	43.148
350	79.085	356.780	345.160	4.067	−253.070	−246.931	36.852
400	79.981	367.403	347.290	8.045	−253.060	−246.055	32.132
450	80.615	376.862	350.060	12.061	−253.106	−245.178	28.459
500	81.077	385.381	353.173	16.104	−253.211	−244.292	25.521
600	81.692	400.222	359.814	24.245	−253.604	−242.475	21.109
700	82.070	412.846	366.510	32.435	−254.248	−240.573	17.952
800	82.318	423.822	373.003	40.655	−255.192	−238.559	15.576
900	82.489	433.528	379.199	48.896	−256.560	−236.403	13.720
1000	82.613	442.226	385.075	57.151	−258.657	−234.060	12.226
1100	82.704	450.104	390.634	65.417	−261.659	−231.441	10.990
1200	82.774	457.303	395.894	73.691	−264.118	−228.605	9.951
1300	82.828	463.931	400.876	81.971	−264.939	−225.613	9.065
1400	82.872	470.071	405.602	90.257	−265.854	−222.554	8.304
1500	82.907	475.790	410.093	98.546	−266.862	−219.426	7.641
1600	82.935	481.141	414.368	106.838	−267.964	−216.228	7.059
1700	82.959	486 170	418.445	115.132	−270.111	−212.940	6.543
1800	82.979	490.912	422.341	123.429	−271.737	−209.531	6.080
1900	82.996	495.399	426.069	131.728	−287.557	−205.326	5.645
2000	83.010	499.657	429.643	140.028	−289.615	−200.945	5.248
2100	83.023	503.707	433.074	148.330	−291.689	−196.461	4.887
2200	83.033	507.570	436.373	156.633	−293.779	−191.877	4.556
2300	83.043	511.261	439.549	164.937	−295.889	−187.198	4.251
2400	83.051	514.795	442.611	173.241	−298.020	−182.427	3.970
2500	83.058	518.186	445.567	181.547	−300.174	−177.566	3.710
2600	83.065	521.444	448.423	189.853	−302.353	−172.619	3.468
2700	83.071	524.579	451.186	198.160	−304.559	−167.587	3.242
2800	83.076	527.600	453.861	206.467	−306.792	−162.474	3.031
2900	83.080	530.515	456 455	214.775	−309.054	−157.280	2.833
3000	83.085	533.332	458.971	223.083	−311.345	−152.007	2.647
3100	83.088	536.056	461.414	231.392	−313.664	−146.658	2.471
3200	83.092	538.694	463.788	239.701	−664.312	−133.809	2.184
3300	83.095	541.251	466.096	248.010	−664.785	−117.224	1.855
3400	83.098	543.732	468.343	256.320	−665.316	−100.623	1.546
3500	83.100	546.140	470.532	264.630	−665.902	−84.006	1.254
3600	83.103	548.482	472.665	272.940	−666.542	−67.372	0.978
3700	83.105	550.758	474.745	281.250	−667.233	−50.718	0.716
3800	83.107	552.975	476.775	289.561	−667.974	−34.046	0.468
3900	83.109	555.134	478.756	297.872	−668.760	−17.354	0.232
4000	83.111	557.238	480.692	306.183	−669.589	−0.640	0.008
4100	83.112	559.290	482.584	314.494	−670.459	16.094	−0.205
4200	83.114	561.293	484.434	322.805	−671.366	32.850	−0.409
4300	83.115	563.248	486.245	331.117	−672.308	49.628	−0.603
4400	83.116	565.159	488.017	339.428	−673.281	66.429	−0 789
4500	83.118	567.027	489.752	347.740	−674.283	83.251	−0.966
4600	83.119	568.854	491.451	356.052	−675.312	100.097	−1.137
4700	83.120	570.642	493 117	364.364	−676.365	116.964	−1.300
4800	83.121	572.392	494.751	372.676	−677.441	133.855	−1.457
4900	83.122	574.105	496.353	380.988	−678.537	150.769	−1.607
5000	83.123	575.785	497.925	389.300	−679.651	167.704	−1.752
5100	83.123	577.431	499.468	397.612	−680.784	184.663	−1.891
5200	83.124	579.045	500.982	405.925	−681.933	201.643	−2.026
5300	83.125	580.628	502.470	414.237	−683.099	218.646	−2.155
5400	83.126	582.182	503.932	422.550	−684.281	235.672	−2.280
5500	83.126	583.707	505.369	430.862	−685.479	252.719	−2.400
5600	83.127	585.205	506.781	439.175	−686.695	269.788	−2.516
5700	83.128	586.676	508.170	447.488	−687.928	286.879	−2.629
5800	83.128	588.122	509.536	455.800	−689.180	303.992	−2.738
5900	83.129	589.543	510.880	464.113	−690.453	321.126	−2.843
6000	83.129	590.940	512.203	472.426	−691.749	338.282	−2.945

PREVIOUS: June 1965 (1 atm)   CURRENT. June 1965 (1 bar)

Trichlorosilane ($SiHCl_3$) IDEAL GAS M_r = 135.45244 Trichlorosilane ($SiHCl_3$) $Cl_3H_1Si_1(g)$

$S°(298.15\ K) = 313.717 \pm 0.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -491.15 \pm 4.2\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -496.22 \pm 4.2\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}
2261(1)	811(2)
499(1)	600(2)
254(1)	176(2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: Si–H = 1.4655 Å; Si–Cl = 2.0118 Å
Bond Angles: H–Si–Cl = 108.32°; Cl–Si–Cl = 110.60°
Product of the Moments of Inertia: $I_AI_BI_C = 7.59150 \times 10^{-113}\ g^3{\cdot}cm^6$

Enthalpy of Formation

$\Delta_fH°$(298.15 K) is calculated from that of $SiCl_4(g)$[1] using the difference $\Delta(\Delta_fH°) = 39.8\ kcal{\cdot}mol^{-1}$ taken from the analysis of Hunt and Sirtl.[2] The authors derived $\Delta_fH°(SiHCl_3$, g, 298.15 K) = $-116.9 \pm 0.7\ kcal{\cdot}mol^{-1}$ from six previously reported equilibrium studies. These were at temperatures (773–1200 K) and compositions where the dominant equilibrium was $SiHCl_3 + HCl = SiCl_4 + H_2$. Selected data[2] were either close to or extrapolated to infinite residence time. Equilibria were reduced to $\Delta_fH°$(298.15 K) using auxiliary data[2] which are similar to JANAF values,[1] except for $\Delta_fH°(SiCl_4$, g, 298.15 K). Since this is now 1.7 $kcal{\cdot}mol^{-1}$ more negative, we change $\Delta_fH°(SiHCl_3)$ accordingly. Our adopted value is 1.8 $kcal{\cdot}mol^{-1}$ more negative than that estimated by linear interpolation between $SiCl_4(g)$ and $SiH_4(g)$.[1]

We dismiss two calorimetric values due to probable bias. These include $\Delta_fH°(l) = -112\ kcal{\cdot}mol^{-1}$ from oxygen–bomb calorimetry[3] and $\Delta_fH°(g) = -117.4 \pm 1.7\ kcal{\cdot}mol^{-1}$ from solution calorimetry[4] in dilute aqueous NaOH. Revised auxiliary data[1,5] change these values to $\Delta_fH°(g) = -115$[3] and $-124\ kcal{\cdot}mol^{-1}$. Wagman *et al.*[5] adopted $-122.6\ kcal{\cdot}mol^{-1}$, presumably based on Wolf.[4] The combustion result is suspect because the chemical reaction was determined only qualitatively and included corrosion reactions of the bomb.[3] In our approximate revision of the solution result, we eliminate $Na_2SiO_3(cr)$ by taking the difference between the overall reactions[4] for $SiCl_4(l)$ and $SiHCl_3(g)$. This yields the difference $\Delta(\Delta_fH°) = \Delta_fH°(SiHCl_3, g) - \Delta_fH°(SiCl_4, g) = 34.6$ compared to 39.8 $kcal{\cdot}mol^{-1}$.[2] The solution result is suspect due to the possibility that the two hydrolyses did not proceed to equivalent degrees. Solution results[4] for $SiCl_4$, $SiBr_4(l)$ and $SiI_4(cr)$ also have a negative bias compared to our adopted values.[1]

Heat Capacity and Entropy

The molecular structure is based on microwave data of Mitzlaff *et al.*[6] for twleve isotopic forms of $SiHCl_3$ and $SiDCl_3$. Structural parameters are substitutional (r_s) values. They are in reasonable agreement with previous data[6] determined by various methods. The principal moments of inertia are $I_A = I_B = 34.3279 \times 10^{-39}$ and $I_C = 64.4220 \times 10^{-39}\ g{\cdot}cm^2$.

Vibrational frequencies are those selected by Shimanouchi[7] from gas–phase infrared spectra of Buerger and Ruoff.[8] Assignments are based on band contours and isotopic splittings and are consistent with recent liquid–phase Raman spectra.[9]

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from excited states should be unimportant, as discussed on the tables for SiH_2Cl_2, SiH_3Cl and SiH_3Br.[1]

References

[1] JANAF Thermochemical Tables: $Cl_4Si(g)$, 12–31–70; $Cl_2H_2Si(g)$, $ClH_3Si(g)$, BrH3Si(g), $Br_4Si(\ell)$, 12–31–76; $I_4Si(cr)$, $H_4Si(g)$, 6–30–76; 02Si(quartz), 6–30–67; ClH(g), 9–30–64; HNaO(cr), 12–31–70; ClNa(cr), 9–30–64.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−16.151	−491.151	−491.151	INFINITE
100	46.854	248.357	372.097	−12.374	−493.507	−484.572	253.115
200	63.216	286.041	320.258	−6.844	−495.059	−475.003	124.058
250	70.039	300.901	314.931	−3.507	−495.699	−469.914	98.183
298.15	75.455	313 717	313.717	0.	−496.222	−464.899	81.448
300	75.641	314.185	313.719	0.140	−496.241	−464.704	80.912
350	80.107	326.194	314.657	4.038	−496.680	−459.412	68.563
400	83.657	337.131	316.793	8.135	−497.025	−454.063	59.295
450	86.512	347.155	319.617	12.392	−497.286	−448.677	52.081
500	88.851	356.395	322.839	16.778	−497.478	−443.265	46.308
600	92.465	372.932	329.843	25.853	−497.691	−432.399	37.644
700	95.144	387.396	337.053	35.240	−497.729	−421.511	31.454
800	97.212	400.241	344.164	44.862	−497.642	−410.628	26.811
900	98.848	411.789	351.047	54.668	−497.466	−399.761	23.202
1000	100.164	422.275	357.654	64.621	−497.231	−388.917	20.315
1100	101.235	431.873	363.971	74.693	−496.960	−378.099	17.954
1200	102.115	440.721	370.003	84.862	−496.671	−367.306	15.988
1300	102.845	448.924	375.762	95.111	−496.381	−356.537	14.326
1400	103.455	456.569	381.264	105.427	−496.103	−345.790	12.902
1500	103.970	463.724	386.525	115.799	−495.845	−335.063	11.668
1600	104.406	470.449	391.562	126.218	−495.617	−324.352	10.589
1700	104.779	476.790	396.391	136.678	−545.602	−313.207	9.624
1800	105.100	482.788	401.026	147.172	−545.221	−299.548	8.693
1900	105.378	488.478	405.480	157.696	−544.843	−285.909	7.860
2000	105.620	493.890	409.766	168.247	−544.474	−272.291	7.112
2100	105.832	499.048	413.896	178.819	−544.116	−258.691	6.435
2200	106.018	503.976	417.879	189.412	−543.773	−245.107	5.820
2300	106.182	508.692	421.726	200.022	−543.450	−231.539	5.258
2400	106.328	513.214	425.444	210.648	−543.147	−217.984	4.744
2500	106.458	517.558	429.043	221.287	−542.870	−204.441	4.272
2600	106.575	521.735	432.528	231.939	−542.619	−190.909	3.835
2700	106.679	525.759	435.907	242.602	−542.398	−177.386	3.432
2800	106.774	529.641	439.186	253.275	−542.208	−163.871	3.057
2900	106.859	533.389	442.370	263.956	−542.050	−150.361	2.708
3000	106.936	537.013	445.464	274.646	−541.925	−136.857	2.383
3100	107.007	540.521	448.475	285.343	−541.834	−123.357	2.079
3200	107.071	543.919	451.404	296.047	−541.774	−109.859	1.793
3300	107.129	547.215	454.258	306.757	−541.746	−96.361	1.525
3400	107.183	550.414	457.039	317.473	−541.748	−82.865	1.273
3500	107.233	553.521	459.752	328.194	−541.778	−69.368	1.035
3600	107.278	556.543	462.399	338.919	−925.984	−45.409	0.659
3700	107.320	559.483	464.983	349.649	−925.647	−20.953	0.296
3800	107.359	562.345	467.508	360.383	−925.331	3.493	−0.048
3900	107.395	565.135	469.975	371.121	−925.032	27.932	−0.374
4000	107.428	567.854	472.388	381.862	−924.746	52.364	−0.684
4100	107.459	570.507	474.749	392.607	−924.468	76.788	−0.978
4200	107.488	573.097	477.060	403.354	−924.196	101.206	−1.259
4300	107.515	575.627	479.323	414.104	−923.924	125.617	−1.526
4400	107.541	578.099	481.540	424.857	−923.649	150.021	−1.781
4500	107.564	580.516	483.713	435.612	−923.367	174.420	−2.025
4600	107.586	582.880	485.843	446.370	−923.074	198.812	−2.258
4700	107.607	585.194	487.932	457.130	−922.767	223.197	−2.481
4800	107.627	587.460	489.982	467.891	−922.442	247.576	−2.694
4900	107.645	589.679	491.994	478.655	−922.097	271.948	−2.899
5000	107.662	591.854	493.970	489.420	−921.728	296.312	−3.096
5100	107.678	593.986	495.910	500.187	−921.333	320.670	−3.284
5200	107.694	596.077	497.816	510.956	−920.909	345.018	−3.466
5300	107.708	598.129	499.690	521.726	−920.455	369.359	−3.640
5400	107.722	600.142	501.531	532.497	−919.968	393.691	−3.808
5500	107.735	602.119	503.342	543.270	−919.446	418.013	−3.970
5600	107.747	604.060	505.124	554.044	−918.888	442.325	−4.126
5700	107.759	605.967	506.876	564.820	−918.293	466.627	−4.276
5800	107.770	607.841	508.601	575.596	−917.661	490.919	−4 421
5900	107.781	609.684	510.298	586.374	−916.989	515.199	−4.561
6000	107.791	611.495	511.970	597.152	−916.276	539.467	−4.696

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

Trichlorosilane ($SiHCl_3$) $Cl_3H_1Si_1(g)$

$S°(298.15 \text{ K}) = [335.747] \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = -997.47 \text{ kJ·mol}^{-1}$

$\Delta_f H°(298.15 \text{ K}) = -1004.72 \pm 20.9 \text{ kJ·mol}^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
[650](6)
[220](6)

Point Group: D_{3h} $\sigma = 6$

Bond Distance: Li–Cl = [2.2] Å

Bond Angle: Li–Cl–Li = [120]°

Product of the Moment of Inertia: $I_A I_B I_C = 2.67006 \times 10^{-112} \text{ g}^3\text{·cm}^6$

Enthalpy of Formation

The heat of sublimation at 298.15 K was chosen so as to give the correct ratio of monomer, dimer and trimer at 870 K. The value used was 52.6 kcal·mol^{-1} which compares very well with the value 53.6 kcal·mol^{-1} obtained from a third law analysis of the data of Nesmeyanov and Sazonov[1] in conjunction with the relative concentrations of monomer, dimer, and trimer at 870 K from the work of Miller and Kusch.[2]

Heat Capacity and Entropy

The postulated structure, bond lengths and frequencies were all taken from Hildenbrand *et al.*[3] The principal moments of inertia are: $I_A = I_B = 51.1090 \times 10^{-39}$ and $I_C = 102.2179 \times 10^{-39} \text{ g·cm}^2$.

References

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[2] R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1950).
[3] D. L. Hildenbrand, A. M. Saul, P. R. Basford, S. E. Stephanon, L. Larson and A. Uyehara, Aeronutronic Tenth Quarterly Report on Contract Nord 17980 Report C–898 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K$_f$
0	0.	0.	INFINITE	−20.383	−997.466	−997.466	INFINITE
100	56.629	250.069	413.649	−16.358	−999.293	−993.747	519.080
200	84.270	298.513	344.567	−9.211	−1002.228	−987.045	257.790
250	94.366	318.444	337.386	−4.735	−1003.565	−983.092	205.406
298.15	102.005	335.747	335.747	0.	−1004.721	−979.042	171.524
300	102.261	336.379	335.749	0.189	−1004.763	−978.883	170.439
350	108.285	352.616	337.017	5.459	−1005.859	−974.482	145.433
400	112.864	367.388	339.904	10.993	−1006.965	−969.925	126.659
450	116.369	380.893	343.719	16.728	−1008.164	−965.224	112.040
500	119.083	393.300	348.066	22.617	−1018.497	−959.462	100.234
600	122.907	415.376	357.491	34.731	−1020.781	−947.432	82.481
700	125.387	434.521	367.158	47.154	−1022.641	−935.055	69.775
800	127.072	451.381	376.653	59.782	−1024.251	−922.431	60.229
900	128.263	466.421	385.807	72.552	−1025.735	−909.613	52.793
1000	129.134	479.982	394.558	85.424	−1027.126	−896.636	46.835
1100	129.788	492.322	402.893	98.372	−1028.447	−883.522	41.955
1200	130.292	503.638	410.823	111.377	−1029.713	−870.291	37.883
1300	130.688	514.083	418.370	124.427	−1030.938	−856.956	34.433
1400	131.004	523.780	425.557	137.512	−1032.124	−843.528	31.472
1500	131.261	532.827	432.410	150.626	−1033.269	−830.017	28.904
1600	131.472	541.305	438.954	163.763	−1034.380	−816.430	26.654
1700	131.647	549.281	445.211	176.919	−1471.169	−781.247	24.005
1800	131.795	556.810	451.204	190.091	−1469.964	−740.698	21.494
1900	131.920	563.940	456.952	203.277	−1468.764	−700.216	19.250
2000	132.027	570.709	462.472	216.475	−1467.574	−659.797	17.232
2100	132.120	577.153	467.780	229.682	−1466.399	−619.437	15.408
2200	132.200	583.301	472.893	242.898	−1465.244	−579.133	13.750
2300	132.270	589.179	477.822	256.122	−1464.117	−538.880	12.238
2400	132.332	594.810	482.580	269.352	−1463.024	−498.676	10.853
2500	132.386	600.213	487.178	282.588	−1461.972	−458.517	9.580
2600	132.435	605.406	491.626	295.829	−1460.968	−418.398	8.406
2700	132.478	610.405	495.933	309.075	−1460.019	−378.318	7.319
2800	132.516	615.224	500.108	322.324	−1459.131	−338.271	6.311
2900	132.551	619.875	504.158	335.578	−1458.310	−298.255	5.372
3000	132.582	624.369	508.091	348.835	−1457.563	−258.266	4.497
3100	132.611	628.717	511.912	362.094	−1456.894	−218.301	3.678
3200	132.636	632.927	515.628	375.357	−1456.308	−178.356	2.911
3300	132.660	637.009	519.245	388.621	−1455.808	−138.428	2.191
3400	132.681	640.970	522.767	401.888	−1455.399	−98.514	1.513
3500	132.701	644.816	526.200	415.158	−1455.081	−58.610	0.875
3600	132.719	648.555	529.547	428.429	−1454.858	−18.714	0.272
3700	132.735	652.191	532.812	441.701	−1454.730	21.177	−0.299
3800	132.751	655.731	536.001	454.976	−1454.699	61.065	−0.839
3900	132.765	659.180	539.115	468.251	−1454.766	100.954	−1.352
4000	132.778	662.541	542.159	481.529	−1454.931	140.847	−1.839
4100	132.790	665.820	545.135	494.807	−1455.196	180.744	−2.303
4200	132.801	669.020	548.047	508.086	−1455.560	220.649	−2.744
4300	132.812	672.145	550.897	521.367	−1456.025	260.564	−3.165
4400	132.822	675.198	553.687	534.649	−1456.528	300.486	−3.567
4500	132.831	678.183	556.421	547.931	−1457.167	340.425	−3.952
4600	132.839	681.103	559.100	561.215	−1457.912	380.380	−4.319
4700	132.847	683.960	561.726	574.499	−1458.756	420.351	−4.672
4800	132.855	686.757	564.302	587.784	−1459.701	460.342	−5.010
4900	132.862	689.496	566.829	601.070	−1460.748	500.354	−5.334
5000	132.869	692.181	569.309	614.357	−1461.900	540.387	−5.645
5100	132.875	694.812	571.744	627.644	−1463.141	580.444	−5.945
5200	132.881	697.392	574.136	640.932	−1464.504	620.527	−6.233
5300	132.886	699.923	576.485	654.220	−1465.979	660.638	−6.511
5400	132.892	702.407	578.794	667.509	−1467.567	700.778	−6.779
5500	132.897	704.846	581.064	680.799	−1469.274	740.948	−7.037
5600	132.901	707.240	583.296	694.088	−1471.101	781.150	−7.286
5700	132.906	709.593	585.491	707.379	−1473.053	821.386	−7.527
5800	132.910	711.904	587.651	720.670	−1475.134	861.657	−7.760
5900	132.914	714.176	589.776	733.961	−1477.346	901.965	−7.985
6000	132.918	716.410	591.868	747.253	−1479.695	942.312	−8.204

PREVIOUS: June 1962 (1 atm) CURRENT· June 1962 (1 bar)

Phosphoryl Chloride ($OPCl_3$) IDEAL GAS $M_r = 153.33216$

$S°(298.15\ K) = 325.454\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -554.2 \pm 1.7\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -559.8 \pm 1.7\ kJ{\cdot}mol^{-1}$

Vibrational Levels and Multiplicities		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1290(1)	486(1)	337(1)
581(2)	267(2)	193(2)

Point Group: C_{3v} $\sigma = 3$
Bond Distances: P–O = 1.45 ± 0.03 Å; P–Cl = 1.99 ± .02 Å
Bond Angle: Cl–P–Cl = 103.6 ± 2°
Product of the Moments of Inertia: $I_AI_BI_C = 1.01841 \times 10^{-112}\ g^3{\cdot}cm^6$

Enthalpy of Formation

The $\Delta_fH°(298.15\ K)$ for $POCl_3(g)$ was derived from the $\Delta_fH°(298.15\ K)$ of $POCl_3(l)$ and the $\Delta_{vap}H°(298.15\ K)$. The $\Delta_fH°(298.15\ K)$ of the $POCl_3(l)$ was calculated from the heat of hydrolysis observed by Charnley and Skinner[1] for the reaction:

$$POCl_3(l) + (n+3)\ H_2O(l) \rightarrow [H_3PO_4 + 3\ HCl]\ \text{in}\ n\ H_2O(l)$$

The auxiliary thermochemical data, on the enthalpies of formation of water and aqueous solutions of HCl and of H_3PO_4, were taken from the NBS Circular 500,[2] and were adjusted for consistency with JANAF Tables. The heat of vaporization was measured and corrected to 298.15 K by Ott and Giauque.[3]

Heat Capacity and Entropy

The molecular constants are from the microwave spectral data of Williams *et al.*[4] In order to determine the structure Williams *et al.*[4] assumed the P–Cl distance equal to 1.99 Å. This was the smallest value allowed (2.02 ± 0.03 Å) by the electron diffraction work of Brockway and Beach.[5]

Ott and Giauque[3] have given the moments of inertia obtained from a weighted average of the isotopic species. $I_A \neq I_B$ due to isotopic loss of symmetry. The $S°(298.15\ K)$ calculated from calorimetric data by Ott and Giauque[3] was $77.75\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ and the $S°(298.15\ K)$, calculated from the spectral data was $77.77\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

The principal moments of inertia are: $I_A = I_B = 42.0514 \times 10^{-39}$ and $I_C = 57.5920 \times 10^{-39}\ g{\cdot}cm^2$.

References

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[3] J. B. Ott and W. F. Giauque, J. Amer. Chem. Soc. 82, 1308 (1960).
[4] Q. Williams, J. Sheridan and W. Gordy, J. Chem. Phys. 20, 164 (1952).
[5] L. O. Brockway and J. Y. Beach, J. Amer. Chem. Soc. 60, 1836 (1938).

Phosphoryl Chloride ($OPCl_3$) $Cl_3O_1P_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−17.880	−554.226	−554.226	INFINITE
100	50.035	251.381	392.051	−14.067	−557.121	−543.474	283.881
200	72.927	293.857	332.888	−7.806	−559.135	−529.144	138.198
250	79.947	310.927	326.826	−3.975	−559.553	−521.594	108.981
298.15	84.917	325.454	325.454	0.	−559.819	−514.257	90.096
300	85.082	325.980	325.456	0.157	−559.828	−513.975	89.491
350	88.953	339.399	326.507	4.512	−560.724	−506.246	75.553
400	91.957	351.481	328.886	9.038	−560.889	−498.451	65.091
450	94.338	362.455	332.016	13.698	−560.969	−490.641	56.952
500	96.257	372.497	335.569	18.464	−560.982	−482.825	50.440
600	99.115	390.317	343.246	28.242	−560.865	−467.202	40.674
700	101.093	405.753	351.098	38.258	−560.616	−451.610	33.700
800	102.506	419.349	358.797	48.442	−560.283	−436.060	28.472
900	103.544	431.485	366.211	58.747	−559.894	−420.555	24.408
1000	104.325	442.437	373.295	69.142	−559.467	−405.095	21.160
1100	104.925	452.410	380.041	79.606	−559.016	−389.680	18.504
1200	105.395	461.560	386.458	90.123	−622.120	−373.228	16.246
1300	105.770	470.012	392.564	100.682	−620.869	−352.537	14.165
1400	106.072	477.862	398.380	111.275	−619.619	−331.943	12.385
1500	106.320	485.189	403.926	121.895	−618.373	−311.439	10.845
1600	106.526	492.057	409.221	132.537	−617.133	−291.017	9.501
1700	106.697	498.521	414.286	143.199	−615.904	−270.672	8.317
1800	106.843	504.624	419.137	153.876	−614.688	−250.400	7.266
1900	106.967	510.404	423.790	164.567	−613.487	−230.194	6.328
2000	107.073	515.893	428.259	175.269	−612.303	−210.052	5.486
2100	107.165	521.119	432.557	185.981	−611.140	−189.968	4.725
2200	107.245	526.107	436.697	196.701	−610.000	−169.938	4.035
2300	107.315	530.876	440.689	207.429	−608.886	−149.961	3.406
2400	107.377	535.444	444.542	218.164	−607.800	−130.031	2.830
2500	107.432	539.829	448.267	228.905	−606.745	−110.146	2.301
2600	107.481	544.043	451.870	239.650	−605.723	−90.302	1.814
2700	107.524	548.100	455.359	250.400	−604.736	−70.497	1.364
2800	107.563	552.011	458.742	261.155	−603.784	−50.728	0.946
2900	107.598	555.787	462.023	271.913	−602.869	−30.992	0.558
3000	107.630	559.435	465.210	282.674	−601.992	−11.287	0.197
3100	107.658	562.965	468.307	293.439	−601.151	8.389	−0.141
3200	107.685	566.383	471.319	304.206	−600.346	28.038	−0.458
3300	107.708	569.697	474.250	314.976	−599.576	47.663	−0.754
3400	107.730	572.913	477.105	325.748	−598.838	67.266	−1.033
3500	107.750	576.036	479.887	336.522	−598.130	86.846	−1.296
3600	107.768	579.071	482.600	347.298	−597.449	106.408	−1.544
3700	107.785	582.024	485.247	358.075	−596.791	125.950	−1.778
3800	107.801	584.899	487.832	368.855	−596.154	145.475	−2.000
3900	107.815	587.699	490.357	379.635	−595.533	164.984	−2.210
4000	107.829	590.429	492.825	390.418	−594.925	184.476	−2.409
4100	107.841	593.092	495.238	401.201	−594.325	203.954	−2.598
4200	107.852	595.691	497.599	411.986	−593.730	223.417	−2.779
4300	107.863	598.229	499.910	422.772	−593.135	242.866	−2.950
4400	107.873	600.709	502.173	433.558	−592.538	262.301	−3.114
4500	107.883	603.133	504.389	444.346	−591.933	281.722	−3.270
4600	107.891	605.504	506.562	455.135	−591.317	301.130	−3.419
4700	107.900	607.825	508.692	465.924	−590.688	320.524	−3.562
4800	107.907	610.096	510.781	476.715	−590.042	339.905	−3.699
4900	107.915	612.321	512.830	487.506	−589.376	359.272	−3.830
5000	107.921	614.502	514.842	498.298	−588.689	378.625	−3.955
5100	107.928	616.639	516.817	509.090	−587.977	397.965	−4.076
5200	107.934	618.735	518.757	519.883	−587.238	417.289	−4.192
5300	107.940	620.791	520.663	530.677	−586.471	436.600	−4.303
5400	107.945	622.808	522.536	541.471	−585.675	455.896	−4.410
5500	107.950	624.789	524.377	552.266	−584.849	475.176	−4.513
5600	107.955	626.734	526.188	563.061	−583.990	494.442	−4.612
5700	107.959	628.645	527.968	573.857	−583.100	513.692	−4.707
5800	107.964	630.523	529.720	584.653	−582.177	532.926	−4.800
5900	107.968	632.368	531.445	595.450	−581.220	552.143	−4.888
6000	107.972	634.183	533.142	606.247	−580.231	571.344	−4.974

PREVIOUS: June 1962 (1 atm) CURRENT: June 1962 (1 bar)

Phosphorus Chloride (PCl_3) IDEAL GAS $M_r = 137.33276$ Phosphorus Chloride (PCl_3) $Cl_3P_1(g)$

$\Delta_fH°(0\text{ K}) = -285.50 \pm 5.4\text{ kJ·mol}^{-1}$

$S°(298.15\text{ K}) = 311.682 \pm .42\text{ J·K}^{-1}\text{·mol}^{-1}$ $\Delta_fH°(298.15\text{ K}) = -288.70 \pm 5.4\text{ kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
510 (1)	507 (2)
259 (1)	187 (2)

Ground State Quantum Weight = 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distance: P–Cl = 2.039 ± 0.0014 Å
Bond Angle: Cl–P–Cl = 100.27 ± 0.09°
Product of the Moments of Inertia: $I_AI_BI_C = 6.05196 \times 10^{-113}\text{ g}^3\text{·cm}^6$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−15.932	−285.497	−285.497	INFINITE
100	46.469	246.997	368.917	−12.192	−287.012	−281.592	147.088
200	62.949	284.738	317.995	−6.651	−288.291	−275.824	72.038
250	68.098	299.372	312.842	−3.368	−288.527	−272.679	56.973
298.15	71.581	311.682	311.682	0.	−288.696	−269.610	47.235
300	71.693	312.125	311.683	0.133	−288.702	−269.492	46.923
350	74.221	323.377	312.566	3.784	−289.564	−266.207	39.729
400	76.036	333.413	314.556	7.543	−289.749	−262.857	34.326
450	77.369	342.450	317.162	11.380	−289.892	−259.487	30.120
500	78.370	350.656	320.107	15.274	−290.007	−256.102	26.755
600	79.738	365.075	326.433	23.185	−290.177	−249.304	21.704
700	80.599	377.436	332.858	31.205	−290.297	−242.482	18.094
800	81.175	388.239	339.119	39.296	−290.388	−235.645	15.386
900	81.576	397.824	345.120	47.434	−290.463	−228.798	13.279
1000	81.867	406.435	350.828	55.607	−290.528	−221.943	11.593
1100	82.085	414.249	356.244	63.805	−290.587	−215.081	10.213
1200	82.251	421.398	361.380	72.022	−354.218	−207.136	9.016
1300	82.381	427.987	366.253	80.254	−353.502	−194.908	7.832
1400	82.485	434.096	370.884	88.498	−352.794	−182.735	6.818
1500	82.569	439.790	375.290	96.751	−352.094	−170.613	5.941
1600	82.638	445.121	379.489	105.011	−351.404	−158.537	5.176
1700	82.696	450.133	383.499	113.278	−350.723	−146.503	4.502
1800	82.744	454.861	387.333	121.550	−350.054	−134.510	3.903
1900	82.784	459.336	391.006	129.826	−349.397	−122.553	3.369
2000	82.819	463.583	394.530	138.107	−348.754	−110.631	2.889
2100	82.849	467.625	397.915	146.390	−348.127	−98.740	2.456
2200	82.875	471.479	401.172	154.676	−347.517	−86.879	2.063
2300	82.898	475.164	404.310	162.965	−346.927	−75.045	1.704
2400	82.918	478.692	407.336	171.256	−346.359	−63.236	1.376
2500	82.936	482.078	410.258	179.549	−345.814	−51.451	1.075
2600	82.951	485.331	413.084	187.843	−345.295	−39.687	0.797
2700	82.965	488.462	415.818	196.139	−344.803	−27.942	0.541
2800	82.978	491.479	418.466	204.436	−344.340	−16.215	0.302
2900	82.989	494.391	421.035	212.734	−343.907	−4.504	0.081
3000	82.999	497.205	423.527	221.034	−343.503	7.193	−0.125
3100	83.008	499.927	425.948	229.334	−343.128	18.877	−0.318
3200	83.017	502.562	428.301	237.635	−342.782	30.548	−0.499
3300	83.024	505.117	430.590	245.938	−342.464	42.210	−0.668
3400	83.031	507.595	432.819	254.240	−342.171	53.862	−0.827
3500	83.038	510.002	434.990	262.544	−341.902	65.506	−0.978
3600	83.043	512.342	437.106	270.848	−341.653	77.143	−1.119
3700	83.049	514.617	439.170	279.152	−341.422	88.773	−1.253
3800	83.054	516.832	441.185	287.458	−341.204	100.397	−1.380
3900	83.058	518.989	443.153	295.763	−340.998	112.015	−1.500
4000	83.063	521.092	445.075	304.069	−340.798	123.629	−1.614
4100	83.066	523.143	446.954	312.376	−340.601	135.237	−1.723
4200	83.070	525.145	448.792	320.682	−340.403	146.840	−1.826
4300	83.073	527.100	450.591	328.990	−340.200	158.439	−1.925
4400	83.077	529.010	452.351	337.297	−339.988	170.033	−2.019
4500	83.080	530.877	454.076	345.605	−339.764	181.622	−2.108
4600	83.082	532.703	455.765	353.913	−339.524	193.206	−2.194
4700	83.085	534.489	457.421	362.221	−339.265	204.784	−2.276
4800	83.087	536.239	459.045	370.530	−338.983	216.356	−2.354
4900	83.090	537.952	460.638	378.839	−338.676	227.923	−2.430
5000	83.092	539.631	462.201	387.148	−338.341	239.482	−2.502
5100	83.094	541.276	463.735	395.457	−337.975	251.036	−2.571
5200	83.096	542.890	465.242	403.767	−337.575	262.581	−2.638
5300	83.098	544.472	466.722	412.076	−337.141	274.118	−2.702
5400	83.099	546.026	468.176	420.386	−336.671	285.647	−2.763
5500	83.101	547.551	469.606	428.696	−336.161	297.167	−2.822
5600	83.102	549.048	471.011	437.007	−335.613	308.677	−2.879
5700	83.104	550.519	472.393	445.317	−335.023	320.177	−2.934
5800	83.105	551.964	473.753	453.627	−334.392	331.667	−2.987
5900	83.107	553.385	475.090	461.938	−333.718	343.145	−3.038
6000	83.108	554.782	476.407	470.249	−333.001	354.610	−3.087

PREVIOUS: June 1970 (1 atm) CURRENT. June 1970 (1 bar)

Enthalpy of Formation

Neale and Williams[1] measured the heat of hydrolysis of liquid phosphorus trichloride and reported a $\Delta_rH° = -67.5 \pm 0.3\text{ kcal·mol}^{-1}$ for the following reaction:

$$PCl_3(l) + (X_2 + 3)\,H_2O \rightarrow H_3PO_3(aq) + 3\,HCl(aq)$$

with X_2 in range 4500 to 7500. Combining this result with enthalpy of formation data for aqueous H_3PO_3, $-229.4\text{ kcal·mol}^{-1}$,[2,5,16] H_2O[2] and aqueous HCl,[2] we derive $\Delta_fH°(PCl_3, l, 0\text{ K}) = -76.7\text{ kcal·mol}^{-1}$. Charnley and Skinner[3] made an independent investigation of the hydrolysis of liquid phosphorus trichloride and obtained enthalpy data in very good agreement with Neale and Williams' results. Their results lead to $\Delta_fH°(PCl_3, l, 0\text{ K}) = -76.5\text{ kcal·mol}^{-1}$ when combined with heat of formation data.[2,5,16]

Neale and Williams[4] also investigated the hydrolysis of liquid phosphorus trichloride in aqueous bromine solution with the formation of phosphoric acid rather than phosphorus acid which results when hydrolysis occurs in water. They reported a $\Delta_rH° = -137.9\text{ kcal·mol}^{-1}$ for the following reaction:

$$PCl_3(l) + Br_2(aq) + (X_2 + 4)H_2O \rightarrow H_3PO_4(aq) + 3\,HCl(aq) + 2\,HBr(aq)$$

with X_2 in range 3500 to 6300. Combining this result with the following enthalpy of formation data: $\Delta_fH°(H_3PO_4 1\ H_2O) = -306.4 \pm 0.5\text{ kcal·mol}^{-1}$,[5] $\Delta_fH°(Br, aq) = -0.2\text{ kcal·mol}^{-1}$,[6] HCl(aq) and HBr(aq),[2] along with dilution data for $H_3PO_4(aq)$,[2] we derive $\Delta_fH°(PCl_3, 298.15\text{ K}) = -77.0\text{ kcal·mol}^{-1}$.

The enthalpy of formation from white phosphorus of gaseous PCl_3, $\Delta_fH°(PCl_3, g, 298.15\text{ K}) = -69.0 \pm 1.1\text{ kcal·mol}^{-1}$, is calculated from $\Delta_fH°(PCl_3, l, 298.15\text{ K}) = -76.7 \pm 1.0\text{ kcal·mol}^{-1}$, an average value of the three results given above, and the enthalpy of vaporization of PCl_3. $\Delta_{vap}H°(298.15\text{ K}) = 7.7 \pm 0.1\text{ kcal·mol}^{-1}$ is determined from a 2nd law analysis of the combined vapor pressure data of Nisel'son and Seryakov[7] and Regnault.[8] The smoothed vapor pressure data of Regnault as reported by Stull[9] were used.

An independent value for the heat of formation can be obtained from the work of Duus and Mykytiuk[17] on the reaction $1.5\,CaF_2 + PCl_3(g) \rightarrow 1.5\,CaCl_2 + PF_3(g)$. The authors reported $\Delta_rH°(630\text{ K}) = -2.97\text{ kcal·mol}^{-1}$. From a re-examination of their technique we believe that this heat evolution is likely to be too small, perhaps by 100%. The analytical results indicate that the reaction is 99% complete or better; thus, we can use this with JANAF entropies to calculate $\Delta_rH°(298.15\text{ K}) \le 3.55\text{ kcal·mol}^{-1}$. Finch *et al.*[18] have reported $\Delta_fH°(CaF_2, cr, 0\text{ K}) - \Delta_fH°(CaCl_2, cr, 0\text{ K}) = -100.87 \pm 0.02\text{ kcal·mol}^{-1}$; thus, we obtain $\Delta_fH°(PCl_3, g, 298.15\text{ K}) > -70.1 \pm 2.0\text{ kcal·mol}^{-1}$ from $\Delta_fH°(PF_3, g, 298.15\text{ K}) = -224.9 \pm 0.9\text{ kcal·mol}^{-1}$. This value is not adopted because of the lack of calorimeter calibration, but it offers an attractive possibility for further study.

Heat Capacity and Entropy

The molecular structure and bond length given above for PCl_3 are from the electron diffraction studies of Hedberg and Iwasahi.[11] The adopted values are in good agreement within experimental error with the following structural data reported by Kisliuk and Townes[12] from microwave studies: r(P–Cl) = 2.043 ± 0.003 Å, the angle Cl–P–Cl = 100°6′ ± 20′. The vibrational frequencies are from the recent infrared and Raman studies of Frankiss and Miller[13] and are in excellent agreement with those of Muller *et al.*[14] and Davis and Oetjen.[15] The principal moments of inertia are: $I_A = I_B = 32.3918 \times 10^{-39}$ and $I_C = 57.6799 \times 10^{-39}\text{ g·cm}^2$.

References

[1] E. Neale and L. T. D. Williams, J. Chem. Soc. 1952, 4535.
[2] U. S. Nat. Bur. Stand. Tech. Note 270-3, (1968).
[3] T. Charnley and H. A. Skinner, J. Chem. Soc. 1953, 450.
[4] E. Neale and L. T. D. Williams, J. Chem. Soc. 1954, 2156.
[5] R. J. Irving and H. McKerrell, Trans. Faraday Soc. 63, 2582 (1967).

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Thiophosphoryl Chloride (SPCl$_3$) IDEAL GAS $M_r = 169.39276$ Thiophosphoryl Chloride (SPCl$_3$) Cl$_3$P$_1$S$_1$(g)

$S°(298.15 \text{ K}) = 337.347 \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = [-376.2] \text{ kJ·mol}^{-1}$

$\Delta_f H°(298.15 \text{ K}) = [-380.0] \text{ kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
169(2)	[247](2)	247(1)
431(1)	540 (2)	751(1)

Ground State Quantum Weight: 1 $\sigma = 3$

Point Group: C_{3v}

Bond Distances: P–S = 1.85 ± 0.02 Å; P–Cl = 2.02 ± 0.01 Å

Bond Angle: Cl–P–Cl = 100.5° ± 1°

Product of the Moments of Inertia: $I_A I_B I_C = 2.06885 \times 10^{-112} \text{ g}^3\text{·cm}^6$

Enthalpy of Formation

$\Delta_f H°(298.15 \text{ K})$ was estimated by Henderson and Scheffee.[1] Henderson and Scheffee use white (α) phosphorus as a reference state.

Heat Capacity and Entropy

Ziomek and Piotrowski[2] have chosen the most probable values for the wave numbers from the infrared spectral data of Cilento *et al.*[3] and the Raman spectral data of Simon and Schulze,[4] Thatte,[5] Gerding and Westrick[6] and Delwaulle and Francois.[7] Ziomek and Piotrowski[2] found their normal coordinate treatments gave the listed wave numbers as fundamentals and lent support for the 247 cm^{-1} band missing from the Raman spectral data. The structure (bond distances and angles) was determined from microwave data by Williams *et al.*[8] The principal moments of inertia are: $I_A = 56.7997 \times 10^{-39}$, $I_B = I_C = 60.3519 \times 10^{-39} \text{ g·cm}^2$.

References

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[2] J. S. Ziomek and E. A. Piotrowski, J. Chem. Phys. 34, 1087 (1961).

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[7] M. Delwaulle and F. Francois, Compt. Rend. 220, 817 (1945).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.001	−376.202	−376.202	INFINITE
100	54.294	258.141	408.225	−15.008	−378.154	−372.596	194.624
200	77.707	303.800	345.230	−8.286	−379.893	−366.512	95.723
250	84.855	321.951	338.800	−4.212	−380.359	−363.110	75.868
298.15	89.847	337.347	337.347	0.	−380.744	−359.753	63.027
300	90.009	337.903	337.348	0.166	−380.758	−359.622	62.616
350	93.755	352.074	338.459	4.765	−381.839	−356.000	53.130
400	96.516	364.783	340.969	9.526	−384.453	−352.193	45.992
450	98.589	376.276	344.264	14.406	−385.479	−348.107	40.407
500	100.173	386.749	347.996	19.376	−386.520	−343.896	35.927
600	102.377	405.223	356.036	29.512	−388.049	−335.219	29.183
700	103.791	421.118	364.225	39.826	−389.223	−326.318	24.350
800	104.745	435.044	372.225	50.255	−390.187	−317.263	20.715
900	105.418	447.422	379.905	60.765	−444.146	−307.016	17.819
1000	105.908	458.556	387.223	71.333	−443.673	−291.805	15.242
1100	106.275	468.668	394.174	81.943	−443.192	−276.641	13.137
1200	106.558	477.928	400.773	92.585	−506.284	−260.443	11.337
1300	106.779	486.466	407.041	103.253	−505.035	−240.007	9.644
1400	106.956	494.386	413.000	113.940	−503.802	−219.667	8.196
1500	107.100	501.770	418.675	124.643	−502.585	−199.414	6.944
1600	107.218	508.686	424.087	135.359	−501.387	−179.242	5.852
1700	107.316	515.189	429.257	146.086	−500.210	−159.144	4.890
1800	107.398	521.326	434.203	156.821	−499.053	−139.115	4.037
1900	107.468	527.134	438.942	167.565	−497.919	−119.149	3.276
2000	107.528	532.648	443.491	178.315	−496.807	−99.243	2.592
2100	107.580	537.896	447.862	189.070	−495.721	−79.391	1.975
2200	107.625	542.902	452.069	199.830	−494.659	−59.591	1.415
2300	107.664	547.687	456.123	210.595	−493.626	−39.838	0.905
2400	107.698	552.269	460.035	221.363	−492.621	−20.130	0.438
2500	107.728	556.666	463.813	232.134	−491.646	−0.463	0.010
2600	107.755	560.892	467.466	242.909	−490.703	19.165	−0.385
2700	107.779	564.959	471.002	253.685	−489.792	38.759	−0.750
2800	107.801	568.879	474.428	264.464	−488.915	58.318	−1.088
2900	107.820	572.663	477.750	275.245	−488.072	77.847	−1.402
3000	107.838	576.318	480.975	286.028	−487.264	97.348	−1.695
3100	107.853	579.854	484.108	296.813	−486.488	116.822	−1.968
3200	107.868	583.279	487.154	307.599	−485.745	136.271	−2.224
3300	107.881	586.598	490.118	318.386	−485.034	155.699	−2.465
3400	107.893	589.819	493.003	329.175	−484.351	175.104	−2.690
3500	107.904	592.947	495.814	339.965	−483.696	194.491	−2.903
3600	107.914	595.987	498.555	350.756	−483.065	213.858	−3.103
3700	107.923	598.944	501.228	361.548	−482.455	233.209	−3.292
3800	107.931	601.822	503.837	372.340	−481.863	252.543	−3.471
3900	107.939	604.625	506.386	383.134	−481.285	271.862	−3.641
4000	107.947	607.358	508.876	393.928	−480.719	291.166	−3.802
4100	107.953	610.024	511.311	404.723	−480.159	310.457	−3.955
4200	107.960	612.625	513.692	415.519	−479.604	329.733	−4.101
4300	107.966	615.166	516.023	426.315	−479.048	348.997	−4.239
4400	107.971	617.648	518.304	437.112	−478.489	368.247	−4.372
4500	107.976	620.074	520.539	447.909	−477.922	387.484	−4.498
4600	107.981	622.448	522.729	458.707	−477.345	406.710	−4.618
4700	107.985	624.770	524.875	469.506	−476.755	425.922	−4.734
4800	107.990	627.043	526.980	480.304	−476.148	445.121	−4.844
4900	107.993	629.270	529.045	491.103	−475.522	464.308	−4.950
5000	107.997	631.452	531.071	501.903	−474.873	483.481	−5.051
5100	108.001	633.591	533.061	512.703	−474.201	502.642	−5.148
5200	108.004	635.688	535.014	523.503	−473.503	521.789	−5.241
5300	108.007	637.745	536.933	534.304	−472.776	540.922	−5.331
5400	108.010	639.764	538.819	545.104	−472.020	560.042	−5.417
5500	108.013	641.746	540.672	555.906	−471.232	579.147	−5.500
5600	108.015	643.692	542.495	566.707	−470.412	598.237	−5.580
5700	108.018	645.604	544.287	577.509	−469.558	617.313	−5.657
5800	108.020	647.483	546.050	588.311	−468.670	636.373	−5.731
5900	108.023	649.329	547.785	599.113	−467.747	655.418	−5.803
6000	108.025	651.145	549.492	609.915	−466.788	674.446	−5.872

PREVIOUS: September 1962 (1 atm) CURRENT September 1962 (1 bar)

Thiophosphoryl Chloride (SPCl$_3$) Cl$_3$P$_1$S$_1$(g)

Trichlorosilyl (SiCl$_3$) IDEAL GAS M_r = 134.4445 Trichlorosilyl (SiCl$_3$) Cl$_3$Si$_1$(g)

$S°(298.15\ K) = [-318.189 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -389.25 \pm 16.7\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -390.37 \pm 16.7\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
470 (1)
[254](1)
582 (2)
[176](2)

Ground State Quantum Weight = [2] $\sigma = 3$

Point Group: C_{3v}

Bond Distance: Si–Cl = [2.0118] Å

Bond Angle: Cl–Si–Cl = 110.9°

Product of the Moments of Inertia: $I_A I_B I_C = [7.36634 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted value for the heat of formation of SiCl$_3$(g) is based on the mass spectrometric study of the silicon subchlorides by Farber and Srivastava.[1] Our 2nd and 3rd law analysis of ten data points (1593–1792 K) for the equilibrium SiCl$_4$(g) + SiCl$_2$(g) = 2 SiCl$_3$(g) yield $\Delta_r H°$(298.15 K)(2nd law) = 6.4 ± 1.1 kcal·mol^{-1} and $\Delta_r H°$(298.15 K)(3rd law) = 12.0 ± 0.5 kcal·mol^{-1} with a drift of 3.3 ± 0.6 cal·K^{-1}·mol^{-1}. Using the 3rd law heat of reaction and auxiliary data,[2] we calculate and adopt $\Delta_f H°$(SiCl$_3$, g, 298.15 K) = −93.3 ± 2 kcal·mol^{-1}. This leads to $\Delta_a H°$(0 K) = 285.5 ± 2 kcal·mol^{-1} or an average bond energy of 95.2 kcal·mol^{-1}, a value which is within 0.5 kcal·mol^{-1} of the average bond energy in SiCl$_4$(g).

Many less definitive studies leading to the heat of formation of SiCl$_3$(g) are reported in the literature. These studies yield values which are 5–10 kcal·mol^{-1} less negative than our adopted value. These works include the relative reaction rates of SiCl$_3$ by Kerr *et al.*,[3] decomposition studies of SiCl$_4$ by adiabatic compression by Vurzel *et al.*,[4] interpretation of electron impact studies on several molecules by Steele *et al.*,[5] examination of infrared emission of a reaction involving SiCl$_3$(g) by Cadman *et al.*,[6] silane kinetic studies by Walsh and Wells,[7] and negative ion studies by Wang *et al.*[10] and Pabst *et al.*[11]

Heat Capacity and Entropy

Jacox and Milligan[8] studied the formation of SiCl$_3$ by photolysis of HSiCl$_3$ in matrices of argon, nitrogen and CO. The two stretching fundamentals were assigned from the infrared spectra. Isotopic splittings were found to be consistent with an angle of 72 ± 5° between the threefold axis and each of the Si–Cl bonds. This yields a bond angle of 110.9° which is similar to that of HSiCl$_3$. Non-planarity of SiCl$_3$ is consistent with the electron-spin-resonance studies of Roncin.[9]

We adopt the results of Jacox and Milligan[8] and estimate the bond length and two bending vibrations by analogy with HSiCl$_3$.[2] The ground state quantum weight is taken as two, but excited electronic levels are neglected. Jacox and Milligan[8] observed unstructured absorptions corresponding to excitation energies of 30000–34500 cm^{-1} and 41000–46000 cm^{-1}. The principal moments of inertia are: $I_A = I_B = 33.7539 \times 10^{-39}$ and $I_C = 64.6554 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0	0.	0.	INFINITE	−15.868	−389.246	−389.246	INFINITE
100	46.997	253.930	374.811	−12.088	−390.100	−386.759	202.022
200	62.205	291.584	324.423	−6.568	−390.315	−383.310	100.110
250	67.220	306.032	319.335	−3.326	−390.351	−381.554	79.721
298.15	70.733	318.189	318.189	0.	−390.367	−379.858	66.549
300	70.847	318.627	318.190	0.131	−390.368	−379.792	66.128
350	73.464	329.755	319.063	3.742	−390.369	−378.030	56.418
400	75.376	339.696	321.032	7.466	−390.359	−376.267	49.135
450	76.798	348.660	323.612	11.272	−390.342	−374.507	43.472
500	77.877	356.810	326.531	15.140	−390.320	−372.748	38.941
600	79.365	371.151	332.805	23.008	−390.276	−369.238	32.145
700	80.311	383.461	339.183	30.995	−390.245	−365.735	27.291
800	80.946	394.230	345.405	39.060	−390.238	−362.234	23.651
900	81.392	403.791	351.371	47.178	−390.263	−358.732	20.820
1000	81.715	412.384	357.050	55.334	−390.322	−355.226	18.555
1100	81.958	420.184	362.440	63.518	−390.419	−351.712	16.701
1200	82.143	427.324	367.554	71.724	−390.555	−348.188	15.156
1300	82.289	433.905	372.408	79.946	−390.732	−344.650	13.848
1400	82.405	440.007	377.021	88.181	−390.953	−341.097	12.727
1500	82.499	445.696	381.412	96.426	−391.218	−337.527	11.754
1600	82.576	451.023	385.598	104.680	−391.530	−333.938	10.902
1700	82.640	456.031	389.595	112.941	−442.066	−329.881	10.136
1800	82.694	460.756	393.419	121.208	−442.246	−323.277	9.381
1900	82.740	465.229	397.082	129.479	−442.434	−316.662	8.706
2000	82.779	469.474	400.596	137.755	−442.634	−310.038	8.097
2100	82.813	473.513	403.973	146.035	−442.847	−303.403	7.547
2200	82.842	477.366	407.222	154.318	−443.075	−296.757	7.046
2300	82.868	481.050	410.352	162.603	−443.320	−290.101	6.588
2400	82.890	484.577	413.372	170.891	−443.585	−283.434	6.169
2500	82.910	487.961	416.288	179.181	−443.872	−276.755	5.782
2600	82.928	491.213	419.108	187.473	−444.182	−270.064	5.426
2700	82.943	494.343	421.837	195.767	−444.518	−263.361	5.095
2800	82.957	497.360	424.481	204.062	−444.881	−256.645	4.788
2900	82.970	500.271	427.044	212.358	−445.272	−249.915	4.501
3000	82.981	503.084	429.532	220.656	−445.691	−243.172	4.234
3100	82.992	505.805	431.949	228.954	−446.137	−236.414	3.984
3200	83.001	508.440	434.298	237.254	−446.611	−229.641	3.749
3300	83.009	510.994	436.584	245.555	−447.111	−222.853	3.527
3400	83.017	513.473	438.809	253.856	−447.635	−216.050	3.319
3500	83.024	515.879	440.977	262.158	−448.181	−209.231	3.123
3600	83.031	518.218	443.090	270.461	−832.898	−191.935	2.785
3700	83.037	520.493	445.152	278.764	−833.065	−174.128	2.458
3800	83.043	522.708	447.164	287.068	−833.247	−156.317	2.149
3900	83.048	524.865	449.128	295.373	−833.439	−138.500	1.855
4000	83.052	526.968	451.048	303.678	−833.638	−120.678	1.576
4100	83.057	529.018	452.925	311.983	−833.839	−102.852	1.310
4200	83.061	531.020	454.761	320.289	−834.038	−85.021	1.057
4300	83.065	532.974	456.557	328.595	−834.232	−67.185	0.816
4400	83.068	534.884	458.315	336.902	−834.415	−49.344	0.586
4500	83.072	536.751	460.038	345.209	−834.585	−31.500	0.366
4600	83.075	538.577	461.725	353.516	−834.737	−13.651	0.155
4700	83.078	540.363	463.380	361.824	−834.869	4.199	−0.047
4800	83.080	542.113	465.002	370.132	−834.976	22.053	−0.240
4900	83.083	543.826	466.593	378.440	−835.056	39.909	−0.425
5000	83.085	545.504	468.154	386.748	−835.107	57.766	−0.603
5100	83.088	547.149	469.687	395.057	−835.125	75.624	−0.775
5200	83.090	548.763	471.193	403.366	−835.108	93.481	−0.939
5300	83.092	550.346	472.671	411.675	−835.056	111.338	−1.097
5400	83.094	551.899	474.124	419.984	−834.965	129.194	−1.250
5500	83.096	553.424	475.552	428.294	−834.834	147.048	−1.397
5600	83.097	554.921	476.956	436.603	−834.664	164.898	−1.538
5700	83.099	556.392	478.337	444.913	−834.451	182.746	−1.675
5800	83.100	557.837	479.695	453.223	−834.197	200.590	−1.807
5900	83.102	559.257	481.031	461.533	−833.900	218.428	−1.934
6000	83.103	560.654	482.347	469.843	−833.560	236.261	−2.057

PREVIOUS. December 1977 (1 atm) CURRENT: December 1977 (1 bar)

Titanium Chloride ($TiCl_3$) CRYSTAL $M_r = 154.239$

$S°(298.15\ K) = 139.750 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 220.1\ K$

$\Delta_f H°(0\ K) = -724.06 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -721.74 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(298.15\ K)$, of $TiCl_3(cr)$ has been measured by several investigators. The results of these measurements are as follows.

Source	Method	$\Delta_f H°(298.15\ K)$, $kcal \cdot mol^{-1}$
[1]Schaffer *et al.* (1954)	Calorimetric, $TiCl_4 + Hg = TiCl_3 + 1/2\ Hg_2Cl_2$	−171.9, − 172.4
[2]Clifton and MacWood (1956)	Solution calorimetric	−172.4
[3]Johnson *et al.* (1956)	Calorimetric, $TiCl_4(\ell) + HI(g) = TiCl_3(cr) + HCl(g) + 1/2\ I_2$	−172.5
[4]Krieve *et al.* (1956)	Solution calorimetric	−171.3
[5]Krieve and Mason (1956)	Equilibrium, $TiCl_3(cr) + HCl(g) = TiCl_4(g) + 1/2\ H_2(g)$	−172.9
[6]Altman *et al.* (1956)	Equilibrium, $Ti(cr) + 3\ TiCl_4(l) = 4\ TiCl_3(cr)$	−169.4, − 171.0
[7]Head (1960)	Equilibrium, $2\ TiCl_4(2) + H_2(g) = 2\ TiCl_3(cr) + 2\ HCl(g)$	−172.3
$TiCl_4(l) + Hg(l) = 1/2\ Hg_2Cl_2(cr) + TiCl_3(cr)$		
$TiCl_4(l) + Ag(cr) = AgCl(cr) + TiCl_3(cr)$		

The chosen value of $-172.5 \pm 1.0\ kcal \cdot mol^{-1}$ is that reported by Johnson *et al.*[3]

Heat Capacity and Entropy

The heat capacity and entropy of $TiCl_3(cr)$ has been measured over the temperature range 54 to 1000 K by King *et al.*[8] The value of $S°(298.15\ K)$ is calculated from these data based on $S°(51\ K) = 4.29\ cal \cdot K^{-1} \cdot mol^{-1}$.

Transition Data

A second order transition at 220.1 K was observed by King *et al.*[8] The heat capacity at this temperature is in excess of $146.8\ cal \cdot K^{-1} \cdot mol^{-1}$. King *et al.*[8] measured the value of $H°(240\ K)-H°(200\ K)$ as $1.213\ kcal \cdot mol^{-1}$.

Sublimation Data

The enthalpy of sublimation is calculated from the enthalpies of formation of $TiCl_3(cr)$ and $TiCl_3(g)$ at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta_r G° = 0$ for the process $TiCl_3(cr) = TiCl_3(g)$.

References

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Titanium Chloride ($TiCl_3$) $Cl_3Ti_1(cr)$

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−20.920	−724.059	−724.059	INFINITE
100	54.438	44.350	227.777	−18.343	−726.410	−701.668	366.514
200	101.926	95.504	149.101	−10.719	−725.260	−677.126	176.847
298.15	97.161	139.750	139.750	0.	−721.740	−654.469	114.660
300	97.195	140.351	139.752	0.180	−721.701	−654.052	113.881
400	98.959	168.557	143.585	9.989	−719.711	−631.807	82.506
500	100.577	190.816	150.882	19.967	−717.830	−610.050	63.731
600	102.048	209.285	159.120	30.099	−715.971	−588.668	51.248
700	103.248	225.106	167.443	40.364	−714.102	−567.598	42.355
800	104.426	238.970	175.535	50.748	−712.193	−546.799	35.702
900	105.583	251.337	183.283	61.249	−710.263	−526.241	30.542
1000	106.704	262.519	190.656	71.863	−708.375	−505.896	26.425
1100	107.818	272.742	197.661	82.589	−706.589	−485.735	23.066
1200	108.926	282.171	204.315	93.426	−708.889	−465.613	20.268
1300	110.029	290.933	210.645	104.374	−706.581	−445.433	17.898
1400	111.125	299.127	216.676	115.432	−704.254	−425.432	15.873
1500	112.215	306.831	222.432	126.599	−701.924	−405.597	14.124

PREVIOUS: March 1964 CURRENT: June 1968

Titanium Chloride ($TiCl_3$) IDEAL GAS $M_r = 154.239$ Titanium Chloride ($TiCl_3$) $Cl_3Ti_1(g)$

$S°(298.15\ K) = [316.895 \pm 4.2]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -536.09 \pm 6.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -539.32 \pm 6.3\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[2]	[4000]	[2]
[600]	[2]	[10000]	[2]
[1500]	[2]		

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[530](1)	[590](2)
[275](1)	[260](2)

Point Group: $[C_{3v}]$ $\sigma = 3$
Bond Distance: Ti–Cl = [2.3] Å
Bond Angle: Cl–Ti–Cl = [100]°
Products of the Moments of Inertia: $I_A I_B I_C = [1.34297 \times 10^{-112}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation of $TiCl_3(g)$ is calculated from the heats of reaction for the processes, (A) $3TiCl_4(g) + Ti(cr) = 4TiCl_3(g)$, and (B) $TiCl_3(cr) = TiCl_3(g)$, combined with auxiliary JANAF heats of formation for $TiCl_4(g)$, $TiCl_3(cr)$ and Ti(cr). Equilibrium measurements of reaction (A) have been reported by Gross and Levi.[1] Vapor pressure measurements for reaction (B) have been reported by Sanderson and MacWood[2] and by Farber and Darnell.[3] Second and third law analyses of these data yield the following results.

Source	Reaction	Data Points	T/K	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Gross and Levi[1]	A	3	1223		31.6 ± 2.0		−128.5
Sanderson and MacWood[2]	B	9*	628–823	42.8 ± 1.1	42.8	−0.1 ± 1.5	−129.3
Farber and Darnell[3]	B	8	636–723	45.3 ± 2.1	45.8	0.8 ± 3.1	−126.2

*One point rejected due to failure of statistical test.

The chosen value of $\Delta_f H°(298.15\ K)$ is − 128.9 kcal·mol^{-1}. This value is the average of the first two determinations.

Heat Capacity and Entropy

The *interatomic distance is estimated* from that of the solid, given as 2.46 Å by Natta *et al.*,[4] and from comparisons of bond distances of crystal and gas phase tetrahalides of titanium. The pyramidal bond angle is estimated assuming $TiCl_3(g)$ similar to the group V trihalides. The principal moments of inertia are: $I_A = I_B = 42.8614 \times 10^{-39}$ and $I_C = 73.1025 \times 10^{-39}\ g·cm^2$. The vibrational frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti^{+3}.[5]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.375	−536.091	−536.091	INFINITE
100	42.233	254.787	373.049	−11.826	−537.471	−533.773	278.814
200	61.090	290.122	323.216	−6.619	−538.737	−529.527	138.298
250	67.847	304.518	318.065	−3.387	−539.097	−527.179	110.148
298.15	72.567	316.895	316.895	0.	−539.318	−524.862	91.954
300	72.719	317.344	316.896	0.134	−539.324	−524.773	91.371
350	76.177	328.828	317.795	3.862	−539.462	−522.335	77.954
400	78.645	339.171	319.831	7.736	−539.541	−519.883	67.890
450	80.423	348.542	322.509	11.715	−539.584	−517.423	60.061
500	81.717	357.086	325.546	15.770	−539.604	−514.959	53.797
600	83.362	372.145	332.092	24.032	−539.616	−510.029	44.402
700	84.264	385.070	338.759	32.418	−539.626	−505.097	37.691
800	84.774	396.358	345.268	40.872	−539.646	−500.163	32.657
900	85.073	406.362	351.511	49.366	−539.724	−495.224	28.742
1000	85.258	415.336	357.453	57.883	−539.933	−490.270	25.609
1100	85.378	423.468	363.090	66.415	−540.341	−485.285	23.044
1200	85.457	430.900	368.436	74.957	−544.936	−480.135	20.900
1300	85.509	437.743	373.507	83.506	−545.026	−474.732	19.075
1400	85.543	444.081	378.325	92.059	−545.205	−469.318	17.510
1500	85.563	449.984	382.908	100.614	−545.486	−463.889	16.154
1600	85.572	455.506	387.274	109.171	−545.884	−458.437	14.966
1700	85.575	460.694	391.442	117.728	−546.412	−452.956	13.918
1800	85.571	465.585	395.427	126.285	−547.085	−447.439	12.984
1900	85.564	470.212	399.242	134.842	−547.917	−441.882	12.148
2000	85.555	474.600	402.901	143.398	−563.609	−435.822	11.383
2100	85.544	478.774	406.415	151.953	−565.551	−429.385	10.680
2200	85.533	482.753	409.796	160.507	−567.512	−422.855	10.040
2300	85.521	486.555	413.051	169.060	−569.494	−416.236	9.453
2400	85.509	490.195	416.190	177.611	−571.499	−409.529	8.913
2500	85.497	493.685	419.221	186.162	−573.530	−402.739	8.415
2600	85.486	497.038	422.149	194.711	−575.587	−395.867	7.953
2700	85.474	500.264	424.983	203.259	−577.673	−388.915	7.524
2800	85.463	503.373	427.728	211.806	−579.788	−381.885	7.124
2900	85.453	506.371	430.388	220.351	−581.934	−374.779	6.751
3000	85.442	509.268	432.969	228.896	−584.109	−367.599	6.400
3100	85.431	512.070	435.476	237.440	−586.315	−360.346	6.072
3200	85.420	514.782	437.912	245.982	−588.550	−353.021	5.762
3300	85.409	517.410	440.282	254.524	−590.813	−345.626	5.471
3400	85.397	519.960	442.588	263.064	−593.103	−338.162	5.195
3500	85.385	522.435	444.834	271.603	−595.416	−330.630	4.934
3600	85.373	524.840	447.023	280.141	−597.750	−323.031	4.687
3700	85.360	527.179	449.158	288.678	−1009.200	−307.580	4.342
3800	85.347	529.455	451.241	297.213	−1010.333	−288.602	3.967
3900	85.333	531.672	453.275	305.747	−1011.531	−269.594	3.611
4000	85.319	533.832	455.262	314.280	−1012.792	−250.554	3.272
4100	85.304	535.939	457.205	322.811	−1014.108	−231.481	2.949
4200	85.289	537.994	459.104	331.341	−1015.475	−212.376	2.641
4300	85.274	540.001	460.962	339.869	−1016.887	−193.238	2.347
4400	85.257	541.961	462.781	348.395	−1018.339	−174.067	2.066
4500	85.241	543.877	464.561	356.920	−1019.824	−154.863	1.798
4600	85.224	545.750	466.306	365.444	−1021.338	−135.624	1.540
4700	85.206	547.583	468.016	373.965	−1022.875	−116.354	1.293
4800	85.188	549.377	469.692	382.485	−1024.431	−97.049	1.056
4900	85.170	551.133	471.337	391.003	−1025.999	−77.712	0.828
5000	85.152	552.854	472.950	399.519	−1027.576	−58.344	0.610
5100	85.133	554.540	474.533	408.033	−1029.156	−38.943	0.399
5200	85.114	556.193	476.088	416.545	−1030.737	−19.512	0.196
5300	85.095	557.814	477.614	425.056	−1032.313	−0.051	0.
5400	85.075	559.404	479.114	433.564	−1033.880	19.441	−0.188
5500	85.056	560.965	480.588	442.071	−1035.437	38.961	−0.370
5600	85.036	562.497	482.037	450.575	−1036.979	58.510	−0.546
5700	85.016	564.002	483.462	459.078	−1038.503	78.085	−0.716
5800	84.996	565.481	484.864	467.579	−1040.007	97.688	−0.880
5900	84.976	566.933	486.242	476.077	−1041.488	117.316	−1.039
6000	84.956	568.361	487.599	484.574	−1042.944	136.969	−1.192

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

Zirconium Chloride ($ZrCl_3$) CRYSTAL $M_r = 197.579$ Zirconium Chloride ($ZrCl_3$) $Cl_3Zr_1(cr)$

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = [145.812 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-714.21 \pm 62.8]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Turnbull and Watts[1] determined the equilibrium pressures for the disproportionation of $ZrCl_3(cr)$ in the temperature range from 613 K to 723 K by a modified dew point technique. 2nd and 3rd law analyses of their vapor pressure–temperature equation give the same enthalpy of reaction $\Delta_r H°(298.15\ K) = 30.7\ kcal \cdot mol^{-1}$ for $2ZrCl_3(cr) \rightarrow ZrCl_2(cr) + ZrCl_4(g)$. The adopted value, $\Delta_f H°(ZrCl_3, cr, 298.15\ K) = -170.7\ kcal \cdot mol^{-1}$, is calculated from the enthalpy of reaction at 298.15 K, and $\Delta_f H°(ZrCl_4, g, 298.15\ K) = -207.77\ kcal \cdot mol^{-1}$ [2] and $\Delta_f H°(ZrCl_2, cr, 298.15\ K) = -103\ kcal \cdot mol^{-1}$.[3] The assigned uncertainty, $\pm 15\ kcal \cdot mol^{-1}$ is mainly due to the uncertainty in the enthalpy of formation of $ZrCl_2(cr)$, and also the dew point technique used.

Heat Capacity and Entropy

The heat capacities of $ZrCl_3(cr)$ are estimated from the $C_p°$ values of $ZrCl_4(cr)$ by deduction of one Cl atom $C_p°$ contributions which are calculated as $1/4[C_p°(ZrCl_4, cr) - C_p°(Zr, cr)]$. The $S°(298.15\ K)$ is calculated as $34.85\ cal \cdot K^{-1} \cdot mol^{-1}$ based on the assumption that $S°(ZrCl_3, cr, 298.15\ K) = S°(ZrCl_4, cr, 298.15\ K) - 1/4[S°(ZrCl_4, cr, 298.15\ K) - S°(Zr, cr, 298.15\ K)]$.

Sublimation Data

The enthalpy of sublimation is calculated from the difference in the enthalpies of formation of gas and crystal at 298.15 K. The sublimation temperature is taken as the point at which $\Delta_r G = 0$ for $ZrCl_3(cr) = ZrCl_3(g)$.

References

[1] A. G. Turnbull and J. A. Watts, Aust. J. Chem. 16, 947 (1963).
[2] JANAF Thermochemical Table: $ZrCl_4(g)$, 12–31–69.
[3] JANAF Thermochemical Table: $ZrCl_2(cr)$, 12–31–69.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
0							
100							
200							
298.15	96.190	145.812	145.812	0.	−714.209	−646.327	113.234
300	96.311	146.408	145.814	0.178	−714.172	−645.906	112.462
400	100.705	174.755	149.649	10.042	−712.072	−623.463	81.416
500	103.470	197.536	157.023	20.257	−709.839	−601.567	62.845
600	105.583	216.593	165.406	30.712	−707.523	−580.129	50.505
700	107.378	233.005	173.918	41.361	−705.149	−559.083	41.719
800	109.052	247.454	182.224	52.184	−702.725	−538.382	35.153
900	110.596	260.388	190.203	63.166	−700.270	−517.986	30.063
1000	112.081	272.121	197.817	74.304	−697.794	−497.865	26.006
1100	113.177	282.855	205.067	85.567	−695.328	−477.992	22.698
1200	114.223	292.748	211.967	96.937	−696.602	−458.120	19.941
1300	115.269	301.932	218.538	108.412	−693.654	−438.366	17.614
1400	116.315	310.514	224.805	119.992	−690.657	−418.840	15.627
1500	117.152	318.567	230.790	131.666	−687.633	−399.530	13.913
1600	117.989	326.155	236.515	143.424	−684.602	−380.422	12.420
1700	118.700	333.329	242.001	155.258	−681.581	−361.504	11.108
1800	119.453	340.137	247.266	167.168	−678.583	−342.762	9.947
1900	119.872	346.607	252.325	179.135	−675.638	−324.186	8.912
2000	120.290	352.766	257.195	191.143	−672.773	−305.763	7.986

PREVIOUS: June 1964 CURRENT· December 1969

Zirconium Chloride ($ZrCl_3$) IDEAL GAS M_r = 197.579 Zirconium Chloride ($ZrCl_3$) $Cl_3Zr_1(g)$

$S°(298.15\ K) = [339.340 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -522.60 \pm 20.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -524.26 \pm 20.9\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[1800]	[2]
[4500]	[2]
[12000]	[2]
[30000]	[2]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[490](1)	[333](2)
[185](1)	[131](2)

Point Group: [C_{3v}] σ = [3]
Bond Distance: Zr–Cl = [2.3] Å
Bond Angle: Cl–Zr–Cl = [100]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.54256 \times 10^{-112}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Potter[1] investigated mass spectrometrically the equilibrium *$CaCl(g) + ZrCl_4(g) \rightarrow CaCl_2(g) + ZrCl_3(g)$ in the temperature range* 1163–1157 K. Ion intensities were measured 2.5 eV above threshold and they were used in the calculation of equilibrium constants. Using the reported equilibrium constants, the enthalpies of reaction at 298 K are evaluated by the 3rd law and 2nd law methods as −3.69 and −16.67 kcal·mol^{-1}, respectively. The 3rd law drift is 9.31 ± 1.25 cal·K^{-1}·mol^{-1}. Using the 3rd law $\Delta_r H°(298.15\ K) = -3.69$ kcal·mol^{-1}, $\Delta_f H°(ZrCl_4, g, 298.15\ K) = -207.77$ kcal·mol^{-1},[2] $\Delta_f H°(CaCl, g, 298.15\ K) = -28.8$ kcal·mol^{-1}[3] and $\Delta_f H°(CaCl_2, g, 298.15\ K) = -115.0$ kcal·mol^{-1},[4] we obtain $\Delta_f H°(ZrCl_3, g, 298.15\ K) = -125.3$ kcal·mol^{-1}, which is adopted in the tabulation.

Farber *et al.*[5] also studied mass spectrometrically the reaction $Zr(cr) + 3\ ZrCl_4(g) \rightarrow 4\ ZrCl_3(g)$ in the temperature range from 1579 K to 1729 K. They reported a second law heat of reaction as $\Delta_r H°(298.15\ K) = 59.2 \pm 1.6$ kcal·mol^{-1}. Since the attainment of equilibrium was questionable in their studies, the heat of reaction obtained from the third law method is generally more reliable. Using their reported ion intensities of run 3 (temperature range from 1667 K to 1896 K, five points), we have calculated the equilibrium constants $K_1 = (I_{ZrCl2})^2/(I_{ZrCl3})(I_{ZrCl})$ for reaction (1) $ZrCl_3(g) + ZrCl(g) \rightarrow 2\ ZrCl_2(g)$; and $K_2 = (I_{ZrCl3})^2/(I_{ZrCl4})(I_{ZrCl2})$ for reaction (2) $ZrCl_4(g) + ZrCl_2 \rightarrow 2\ ZrCl_3(g)$. Third law analyses of the equilibrium constants give $\Delta_r H°(298.15\ K) = -11.0$ kcal·mol^{-1} for reaction (1) and its drift 4.1 ± 1.7 cal·K^{-1}·mol^{-1}; and $\Delta_r H°(298.15\ K) = 1.4$ kcal·mol^{-1} for reaction (2) and its drift 11.1 ± 1.2 cal·K^{-1}·mol^{-1}. Using the 3rd law heats of reaction, and $\Delta_f H°(ZrCl, g, 298.15\ K) = 49.1$ kcal·mol^{-1}[2] and $\Delta_f H°(ZrCl_4, g, 298.15\ K) = -207.77$ kcal·mol^{-1},[2] we obtain $\Delta_f H°(ZrCl_3, g, 298.15\ K) = -124.9$ kcal·mol^{-1} and $\Delta_f H°(ZrCl_2, g, 298.15\ K) = -43.4$ kcal·mol^{-1} which are in good agreement with the values adopted.

Heat Capacity and Entropy

The molecular structure is assumed to be a pyramid similar to the group VA trichlorides. The bond distance is assumed to be the same as that of $ZrCl_4(g)$. The principal moments of inertia are: $I_A = I_B = 45.9362 \times 10^{-39}$ and $I_C = 73.1025 \times 10^{-39}$ g·cm^2. The electronic levels are estimated as three times higher than those of $TiCl_3(g)$, based on the ratio of the first splitting interval between Ti(IV) and Zr(IV), given by Moore.[6] The quantum weights are assumed to be the same as those of $TiCl_3(g)$.

Vibrational frequencies are calculated from the estimated force constants by the valence force method.[7] The force constants are estimated from those of PCl_3, $AsCl_3$ and $SbCl_3$ listed by Herzberg.[7]

References

[1] N. D. Potter, Aeronutronic Div., Philco-Ford Corp., Newport Beach, Calif., private communication, dated (December 4, 1969).

[2] JANAF Thermochemical Table: ZrCl(g) and $ZrCl_4(g)$, 12–31–69.

[3] The enthalpy of formation and the free energy functions of CaCl(g) are preliminary values calculated by the Physicochemical Laboratory, The Dow Chemical Company, Midland, Michigan.

[4] The enthalpy of formation and the free energy functions of $CaCl_2(g)$ are preliminary values calculated by the Physicochemical Studies, The Dow Chemical Company, Midland, Michigan.

[5] M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Monrovia, Calif., Rep. No. AFRPL–TR–67–244, Contract FO4611–67–C–0010, (November, 1967).

[6] C. E. Moore, U.S. Nat. Bur. Stand. Circ. 467, (1949).

[7] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc., New York, (1945).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−17.615	−522.602	−522.602	INFINITE
100	54.064	267.133	402.036	−13.490	−523.731	−520.688	271.979
200	69.657	310.172	346.126	−7.191	−524.181	−517.416	135.135
250	73.530	326.163	340.579	−3.604	−524.239	−515.717	107.753
298.15	76.025	339.340	339.340	0.	−524.255	−514.074	90.064
300	76.104	339.811	339.342	0.141	−524.255	−514.011	89.497
350	77.945	351.688	340.276	3.994	−524.251	−512.304	76.457
400	79.367	362.192	342.371	7.928	−524.232	−510.598	66.677
450	80.536	371.610	345.106	11.927	−524.203	−508.895	59.071
500	81.533	380.148	348.190	15.979	−524.163	−507.197	52.986
600	83.156	395.163	354.801	24.217	−524.064	−503.812	43.861
700	84.387	408.079	361.511	32.597	−523.959	−500.445	37.344
800	85.308	419.410	368.055	41.084	−523.871	−497.093	32.457
900	85.986	429.499	374.332	49.651	−523.833	−493.748	28.656
1000	86.482	438.586	380.310	58.275	−523.869	−490.404	25.616
1100	86.842	446.846	385.989	66.943	−523.998	−487.053	23.128
1200	87.101	454.414	391.380	75.641	−527.945	−483.463	21.045
1300	87.281	461.394	396.501	84.360	−527.752	−479.764	19.277
1400	87.402	467.867	401.370	93.095	−527.601	−476.079	17.763
1500	87.475	473.899	406.007	101.839	−527.507	−472.402	16.451
1600	87.511	479.546	410.428	110.589	−527.483	−468.730	15.302
1700	87.518	484.852	414.652	119.340	−527.546	−465.056	14.289
1800	87.502	489.854	418.692	128.091	−527.706	−461.376	13.389
1900	87.470	494.584	422.563	136.840	−527.979	−457.684	12.583
2000	87.426	499.070	426.277	145.585	−528.377	−453.975	11.857
2100	87.372	503.334	429.846	154.325	−528.913	−450.242	11.199
2200	87.313	507.397	433.279	163.059	−550.923	−445.735	10.583
2300	87.251	511.277	436.587	171.787	−552.190	−440.925	10.014
2400	87.187	514.989	439.777	180.509	−553.486	−436.060	9.491
2500	87.123	518.547	442.857	189.225	−554.811	−431.140	9.008
2600	87.060	521.963	445.834	197.934	−556.169	−426.166	8.562
2700	86.999	525.247	448.715	206.637	−557.560	−421.140	8.147
2800	86.940	528.410	451.505	215.334	−558.986	−416.061	7.762
2900	86.883	531.460	454.210	224.025	−560.446	−410.931	7.402
3000	86.829	534.404	456.834	232.711	−561.941	−405.750	7.065
3100	86.778	537.251	459.383	241.391	−563.470	−400.519	6.749
3200	86.729	540.005	461.859	250.066	−565.033	−395.238	6.452
3300	86.683	542.673	464.268	258.737	−566.627	−389.907	6.172
3400	86.639	545.260	466.612	267.403	−568.251	−384.527	5.908
3500	86.597	547.771	468.895	276.065	−569.901	−379.100	5.658
3600	86.558	550.210	471.120	284.723	−571.576	−373.624	5.421
3700	86.520	552.581	473.290	293.376	−573.271	−368.103	5.197
3800	86.484	554.888	475.407	302.027	−574.983	−362.535	4.983
3900	86.450	557.134	477.474	310.673	−576.709	−356.922	4.780
4000	86.418	559.322	479.493	319.317	−578.443	−351.264	4.587
4100	86.386	561.456	481.466	327.957	−580.183	−345.563	4.403
4200	86.356	563.537	483.396	336.594	−581.924	−339.819	4.226
4300	86.327	565.569	485.283	345.228	−583.663	−334.034	4.058
4400	86.300	567.553	487.130	353.860	−585.394	−328.209	3.896
4500	86.273	569.492	488.939	362.488	−587.115	−322.345	3.742
4600	86.247	571.388	490.711	371.114	−588.822	−316.442	3.593
4700	86.222	573.243	492.447	379.738	−590.511	−310.502	3.451
4800	86.197	575.058	494.150	388.359	−1153.115	−292.910	3.188
4900	86.174	576.835	495.819	396.977	−1154.411	−274.975	2.931
5000	86.151	578.576	497.457	405.593	−1155.697	−257.015	2.685
5100	86.129	580.281	499.064	414.207	−1156.969	−239.028	2.448
5200	86.107	581.954	500.642	422.819	−1158.224	−221.017	2.220
5300	86.087	583.594	502.192	431.429	−1159.458	−202.982	2.001
5400	86.066	585.203	503.714	440.037	−1160.667	−184.924	1.789
5500	86.047	586.782	505.210	448.642	−1161.850	−166.844	1.585
5600	86.028	588.332	506.681	457.246	−1163.003	−148.742	1.387
5700	86.009	589.854	508.127	465.848	−1164.123	−130.621	1.197
5800	85.991	591.350	509.549	474.448	−1165.210	−112.479	1.013
5900	85.974	592.820	510.948	483.046	−1166.260	−94.320	0.835
6000	85.957	594.265	512.324	491.643	−1167.271	−76.143	0.663

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

Cobalt Chloride ((CoCl$_2$)$_2$) IDEAL GAS M_r = 259.6784 Cobalt Chloride ((CoCl$_2$)$_2$) Cl$_4$Co$_2$(g)

$S°(298.15\ K) = [450.400 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -352.91 \pm 29.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -350.62 \pm 29.3\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]
[210]	[8]
[2804]	[8]
[10425]	[4]
[14197]	[8]
[21270]	[8]

Vibrational Frequencies and Degeneracies

υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[50](1)	[125](1)	323 (1)
[75](1)	[150](1)	[143] (1)
[100](1)	[175](1)	289 (1)
[110](1)	[200](1)	432.5(1)

Point Group: [D$_{2h}$] σ = 4
Bond Distances: Co–Cl = [2.09] Å; Co–Cl'(bridge) = [2.2] Å
Bond Angles: Co–Cl'(bridge)–Co = [90]°; Cl'(bridge)–Co–Cl = [135]°; Cl'(bridge)–Co–Cl'(bridge) = [90]°
Product of Moments of Inertia: $I_A I_B I_C = [1.34964 \times 10^{-111}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Mass spectrometric studies[1,2] have indicated the presence of small amounts of dimer in the saturated vapor over CoCl$_2$(cr). The existence of the dimeric species was inferred from the ion current intensities observed for $Co_2Cl_4^+$. This ion is believed to be produced by simple ionization of the dimer molecules. Schoonmaker *et al.*[1] have combined their mass spectral data with results of effusion vapor pressure measurements to give partial pressures for the monomer and dimer at 817 K. These results are analyzed by the third law method with JANAF free energy functions to give ΔH(dimerization, 298.15 K) = −38.99 kcal·mol^{-1} for the process 2 CoCl$_2$(g) = Co$_2$Cl$_4$(g). This result is combined with $\Delta_f H°$(CoCl$_2$, g, 298.15 K) = −22.4 ± 2.0 kcal·mol^{-1} [3] to give $\Delta_f H°$(Co$_2$Cl$_4$, g, 298.15 K) = −83.8 kcal·mol^{-1} (350.619 ± 29.3 kJ·mol^{-1}) which we adopt. The uncertainty assigned to $\Delta_f H°$ is estimated to be ± 7.0 kcal·mol^{-1} and arises mainly from uncertainties in the values of $S°$(298.15 K) for dimer and $\Delta_f H°$ for the monomer.

Heat Capacity and Entropy

A bridge–bond structure of D$_{2h}$ symmetry is assigned to Co$_2$Cl$_4$. A similar structure has been proposed for Be$_2$Cl$_4$[3] and other dimeric transition–metal dihalides.[3-5] The Co$_2$Cl$_2$ ring system is assumed to be square and planar. The Cl–Co–Cl'(bridge) bond angle is estimated as 135°. The outer Co–Cl bond lengths are estimated from that for CoCl$_2$,[3] while the ring Co–Cl'(bridge) bond lengths are estimated to be somewhat larger. The principal moments of inertia are: $I_A = 28.4941 \times 10^{-39}$, $I_B = 203.8550 \times 10^{-39}$, and $I_C = 232.3490 \times 10^{-39}$ g·cm^2.

The three observed vibrational frequencies (υ_9, υ_{11}, and υ_{12}) are taken from the matrix–infrared study of Thompson and Carlson.[5] The rest of the frequencies except for υ_{10} are estimated by comparison with similar data for other dimeric molecules.[3] The value for υ_{10} (143 cm^{-1}) was obtained by Thompson and Carlson[5] from a simplified normal coordinate analysis. Also, Leroi *et al.*[4] obseved a band at 422 ± 10 cm^{-1} in the infrared spectrum of gaseous CoCl$_2$ near 1000 K. The band was assigned to an outer–bond stretching frequency of the dimer. This interpretation agrees with our adopted results. The electronic levels and quantum weights are arbitrarily taken equal to those for the monomer.[3]

References

[1] R. C. Schoonmaker, A. H. Friedman and R. F. Porter, J. Chem. Phys. 31, 1586 (1959).
[2] S. D. Hill, C. A. Cleland, A. Adams, A. Landsberg and F. E. Block, J. Chem. Eng. Data 14, 84 (1969).
[3] JANAF Thermochemical Tables: CoCl$_2$(g), 12–31–73; Be$_2$Cl$_4$(g), 6–30–65; Fe$_2$Cl$_4$(g), 12–31–70; Mg$_2$Cl$_4$(g), 12–31–69.
[4] G. E. Leroi, T. C. Jones, J. T. Hougen and W. Klemperer, J. Chem. Phys. 36, 2879 (1962).
[5] K. R. Thompson and K. D. Carlson, J. Chem. Phys. 49, 4379 (1968).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0	0.	0.	INFINITE	−30.198	−352.913	−352.913	INFINITE
100	100.830	322.221	559.182	−23.696	−353.278	−346.163	180.817
200	121.951	400.502	461.920	−12.283	−351.761	−339.640	88.705
250	125.421	428.124	452.488	−6.091	−351.117	−336.687	70.347
298.15	127.432	450.400	450.400	0.	−350.619	−333.955	58.507
300	127.493	451.189	450.403	0.236	−350.601	−333.851	58.129
350	128.835	470.949	451.960	6.646	−350.154	−331.096	49.413
400	129.766	488.217	455.436	13.113	−349.800	−328.399	42.885
450	130.455	503.543	459.946	19.619	−349.543	−325.740	37.811
500	131.001	517.317	465.006	26.156	−349.376	−323.106	33.755
600	131.862	541.281	475.780	39.301	−349.283	−317.865	27.673
700	132.569	561.662	486.629	52.523	−349.477	−312.617	23.328
800	133.183	579.405	497.141	65.811	−350.788	−307.199	20.058
900	133.716	595.123	507.171	79.157	−351.571	−301.707	17.511
1000	134.167	609.236	516.684	92.552	−352.794	−296.106	15.467
1100	134.536	622.041	525.689	105.988	−354.531	−290.358	13.788
1200	134.829	633.760	534.213	119.457	−356.857	−284.426	12.381
1300	135.052	644.562	542.291	132.951	−360.073	−278.267	11.181
1400	135.216	654.576	549.958	146.465	−364.438	−271.817	10.142
1500	135.330	663.909	557.248	159.993	−366.787	−265.114	9.232
1600	135.406	672.646	564.190	173.530	−368.637	−258.274	8.432
1700	135.451	680.856	570.814	187.073	−370.301	−251.325	7.722
1800	135.473	688.599	577.144	200.619	−404.514	−243.691	7.072
1900	135.478	695.924	583.205	214.167	−406.721	−234.696	6.452
2000	135.472	702.873	589.016	227.714	−408.948	−225.585	5.892
2100	135.460	709.483	594.596	241.261	−411.199	−216.362	5.382
2200	135.443	715.784	599.963	254.806	−413.476	−207.030	4.916
2300	135.426	721.804	605.130	268.350	−415.781	−197.595	4.488
2400	135.410	727.567	610.113	281.891	−418.117	−188.059	4.093
2500	135.396	733.095	614.922	295.432	−420.486	−178.424	3.728
2600	135.385	738.405	619.570	308.971	−422.891	−168.695	3.389
2700	135.378	743.514	624.067	322.509	−425.333	−158.871	3.074
2800	135.375	748.438	628.421	336.046	−427.814	−148.957	2.779
2900	135.377	753.188	632.642	349.584	−430.333	−138.954	2.503
3000	135.384	757.778	636.737	363.122	−432.891	−128.863	2.244
3100	135.394	762.217	640.714	376.661	−435.487	−118.686	2.000
3200	135.410	766.516	644.578	390.201	−1187.745	−104.879	1.712
3300	135.429	770.683	648.337	403.743	−1187.558	−71.042	1.125
3400	135.451	774.726	651.995	417.287	−1187.407	−37.211	0.572
3500	135.478	778.653	655.558	430.833	−1187.289	−3.383	0.050
3600	135.507	782.470	659.030	444.382	−1187.203	30.441	−0.442
3700	135.539	786.183	662.417	457.935	−1187.148	64.264	−0.907
3800	135.573	789.798	665.722	471.490	−1187.120	98.085	−1.348
3900	135.609	793.320	668.948	485.049	−1187.119	131.906	−1.767
4000	135.647	796.754	672.101	498.612	−1187.140	165.728	−2.164
4100	135.686	800.104	675.182	512.179	−1187.182	199.550	−2.542
4200	135.726	803.374	678.196	525.749	−1187.242	233.374	−2.902
4300	135.768	806.568	681.144	539.324	−1187.316	267.199	−3.246
4400	135.809	809.690	684.030	552.903	−1187.402	301.026	−3.574
4500	135.851	812.742	686.857	566.486	−1187.498	334.854	−3.887
4600	135.893	815.729	689.626	580.073	−1187.600	368.686	−4.187
4700	135.935	818.652	692.340	593.665	−1187.708	402.519	−4.473
4800	135.977	821.514	695.002	607.260	−1187.818	436.355	−4.749
4900	136.018	824.318	697.612	620.860	−1187.930	470.193	−5.012
5000	136.059	827.067	700.174	634.464	−1188.041	504.033	−5.266
5100	136.098	829.761	702.688	648.072	−1188.152	537.876	−5.509
5200	136.137	832.404	705.158	661.683	−1188.260	571.720	−5.743
5300	136.175	834.998	707.583	675.299	−1188.366	605.567	−5.968
5400	136.212	837.544	709.966	688.918	−1188.468	639.416	−6.185
5500	136.247	840.043	712.309	702.541	−1188.568	673.267	−6.394
5600	136.282	842.499	714.612	716.168	−1188.666	707.119	−6.596
5700	136.315	844.911	716.876	729.798	−1188.762	740.973	−6.790
5800	136.346	847.282	719.104	743.431	−1188.858	774.830	−6.978
5900	136.377	849.613	721.297	757.067	−1188.864	808.680	−7.160
6000	136.406	851.906	723.455	770.706	−1188.939	842.537	−7.335

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

Iron Chloride (Fe_2Cl_4) IDEAL GAS $M_r = 253.506$ Iron Chloride ($(FeCl_2)_2$) $Cl_4Fe_2(g)$

$S°(298.15\ K) = [464.382 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -433.864 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -431.370 \pm 4.2\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i
0	[10]
[4600]	[10]
[7140]	[5]

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[30](1)	[90](1)	[150](1)	249(1)
[50](1)	110 (1)	[180](1)	325(1)
[80](1)	[125](1)	[200](1)	438(1)

Ground State Quantum Weight: [10] $\sigma = [4]$
Point Group: [D_{2h}]
Bond Distances: Fe–Cl = [2.17] Å; $Fe–Cl'_{(bridge)} = [2.30]$ Å
Bond Angles: $Fe–Cl'_{(bridge)}–Fe = [90°]$; $Cl'_{(bridge)}–Fe–Cl'_{(bridge)} = [90°]$
$Cl–Fe–Cl'_{(bridge)} = [135°]$
Product of the Moments of Inertia: $I_A I_B I_C\ [1.7005] \times 10^{-111}\ g^3 \cdot cm^6$

Heat of Formation

Beusman[1] reported the partial pressures of the monomer and dimer in the temperature range from 980–1167 K using both a static method to determine the total pressures of these two species and a transpiration method to determine the ratio of monomer to dimer. Schoonmaker and Porter[2] determined mass spectrometrically the partial pressures of the monomer and dimer in the temperature range from 621–658 K. Based on the combination of these two sets of partial pressure data, we have derived a smoothed equation $\log K_p(\text{atm}) = -7549/T + 6.506$ for $Fe_2Cl_4(g) = 2\ FeCl_2(g)$. Second law analysis of the equilibrium constants gives the heat and the entropy of the dimerization at 298 K as $\Delta_d H° = -35.7\ kcal \cdot mol^{-1}$ and $\Delta_d S° = -32.0\ cal \cdot K^{-1} \cdot mol^{-1}$ which lead to the adopted $\Delta_f H°$(Fe Cl , g, 298.15 K) = −103.1 kcal·mol^{-1} (−431.370 ± 4.2 kJ·mol^{-1}) and $S°$(FeCl,g,298.15K) = 111.0 cal·K^{-1}·mol^{-1}, using $\Delta_f H°(FeCl_2, g, 298.15\ K) = -33.7\ kcal \cdot mol^{-1}$ and $S°(FeCl_2, g, 298.15\ K) = 71.50\ cal \cdot K^{-1} \cdot mol^{-1}$.[3]

The equilibrium constants derived from the two different experimental techniques are reasonably consistent considering the uncertainties inherent in the problems. Combination of these two sets of data leads to reliable second law heat and entropy since the temperature ranges are different by 400 K.

Heat Capacity and Entropy

A planar structure with D_{2h} symmetry was suggested by Leroi *et al.*,[4] Thompson and Carlson.[5] Two iron and two chlorine atoms form a square. The outer Fe–Cl distance is estimated to be the same as in $FeCl_2(g)$ and the square Fe–Cl' distance is assumed to be slightly larger. The $Cl–Fe–Cl'_{bridge}$ angle is estimated to be 135°. The three principal moments of inertia are: $I_A = 31.13 \times 10^{-39}$, $I_B = 218.68 \times 10^{-39}\ g \cdot cm^2$ and $I_C = I_A + I_B$. The electronic levels and quantum weights were arbitrarily estimated to be the same as in $FeCl_2(g)$.

There are only four vibrational frequencies observed in the matrix isolated infrared spectrum, $\nu_{10} = 110\ cm^{-1}$ and $\nu_{12} = 436.2\ cm^{-1}$,[5] $\nu_9 = 325\ cm^{-1}$, $\nu_{11} = 249\ cm^{-1}$ and $\nu_{12} = 438\ cm^{-1}$.[6] The other eight fundamental vibrational frequencies were estimated by comparison with other dimer molecules and also adjusted so that they give $S°(Fe_2Cl_4, g, 298.15\ K) = 111.0\ cal \cdot K^{-1} \cdot mol^{-1}$ which has been discussed in the earlier heat of formation part. The order of the frequencies listed above is arbitrary and not related to their species types.

References

[1] C. Beusman, Oak Ridge National Lab. ORNL−2323, (June 1957).
[2] R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 29, 116 (1958).
[3] JANAF Thermochemical Table: $FeCl_2(g)$, 12-31-70.
[4] G. E. Leroi, T. C. James, J. T. Hougen and W. Klemperer, J. Chem. Phys. 36, 2879 (1962).
[5] K. R. Thompson and K. D. Carlson, J. Chem. Phys. 49, 4379 (1968).
[6] R. A. Frey, R. D. Werder and H. H. Gunthard, J. Mol. Spectrosc. 35, 260 (1970).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0	0.	0.	INFINITE	−29.849	−433.845	−433.845	INFINITE
100	97.710	339.737	570.950	−23.121	−433.786	−428.745	223.953
200	119.006	415.490	475.843	−12.071	−432.348	−424.281	110.811
250	123.307	442.549	466.563	−6.004	−431.794	−422.331	88.241
298.15	125.875	464.503	464.503	0.	−431.370	−420.548	73.678
300	125.953	465.282	464.506	0.233	−431.356	−420.481	73.212
350	127.673	484.836	466.046	6.576	−431.022	−418.697	62.487
400	128.846	501.966	469.488	12.991	−430.794	−416.953	54.448
450	129.679	517.193	473.958	19.455	−430.676	−415.231	48.199
500	130.290	530.889	478.978	25.955	−430.677	−413.516	43.200
600	131.116	554.723	489.674	39.029	−431.040	−410.058	35.699
700	131.659	574.977	500.450	52.169	−431.895	−406.500	30.333
800	132.077	592.586	510.890	65.357	−433.336	−402.782	26.299
900	132.451	608.164	520.849	78.583	−435.607	−398.837	23.148
1000	132.822	622.138	530.292	91.847	−439.312	−394.572	20.610
1100	133.205	634.816	539.226	105.148	−444.796	−389.804	18.510
1200	133.604	646.423	547.683	118.489	−449.159	−384.650	16.743
1300	134.013	657.133	555.695	131.869	−450.210	−379.233	15.238
1400	134.424	667.080	563.300	145.291	−451.406	−373.729	13.944
1500	134.830	676.368	570.532	158.754	−452.747	−368.135	12.820
1600	135.221	685.082	577.422	172.257	−454.232	−362.447	11.833
1700	135.591	693.291	583.998	185.797	−457.765	−356.623	10.958
1800	135.935	701.051	590.288	199.374	−460.217	−350.604	10.174
1900	136.249	708.409	596.313	212.983	−491.018	−343.040	9.431
2000	136.531	715.405	602.094	226.623	−494.258	−335.168	8.754
2100	136.780	722.073	607.650	240.288	−497.494	−327.134	8.137
2200	136.996	728.441	612.997	253.977	−500.732	−318.945	7.573
2300	137.181	734.535	618.149	267.687	−503.976	−310.610	7.054
2400	137.335	740.376	623.121	281.413	−507.232	−302.133	6.576
2500	137.460	745.985	627.924	295.153	−510.506	−293.520	6.133
2600	137.559	751.379	632.570	308.904	−513.804	−284.775	5.721
2700	137.633	756.572	637.067	322.664	−517.129	−275.903	5.338
2800	137.685	761.578	641.425	336.430	−520.485	−266.908	4.979
2900	137.718	766.410	645.652	350.200	−523.876	−257.792	4.643
3000	137.732	771.079	649.755	363.973	−527.304	−248.558	4.328
3100	137.731	775.596	653.742	377.746	−530.770	−239.209	4.031
3200	137.716	779.968	657.619	391.518	−1230.874	−214.901	3.508
3300	137.690	784.206	661.391	405.289	−1230.615	−183.156	2.899
3400	137.653	788.315	665.064	419.056	−1230.458	−151.417	2.326
3500	137.607	792.305	668.642	432.819	−1230.402	−119.682	1.786
3600	137.554	796.181	672.132	446.577	−1230.445	−87.946	1.276
3700	137.494	799.949	675.535	460.329	−1230.586	−56.209	0.794
3800	137.430	803.615	678.858	474.076	−1230.823	−24.466	0.336
3900	137.361	807.184	682.103	487.815	−1231.152	7.284	−0.098
4000	137.289	810.660	685.273	501.548	−1231.571	39.045	−0.510
4100	137.214	814.050	688.373	515.273	−1232.076	70.816	−0.902
4200	137.137	817.355	691.405	528.990	−1232.666	102.601	−1.276
4300	137.059	820.581	694.372	542.700	−1233.337	134.401	−1.633
4400	136.980	823.731	697.276	556.402	−1234.085	166.217	−1.973
4500	136.901	826.809	700.120	570.096	−1234.909	198.051	−2.299
4600	136.821	829.817	702.907	583.782	−1235.805	229.905	−2.611
4700	136.741	832.758	705.639	597.460	−1236.771	261.778	−2.909
4800	136.662	835.636	708.317	611.131	−1237.806	293.673	−3.196
4900	136.584	838.453	710.945	624.793	−1238.907	325.590	−3.471
5000	136.507	841.212	713.522	638.448	−1240.074	357.530	−3.735
5100	136.430	843.914	716.053	652.094	−1241.305	389.494	−3.989
5200	136.355	846.563	718.537	665.734	−1242.600	421.483	−4.234
5300	136.281	849.160	720.977	679.365	−1243.960	453.497	−4.469
5400	136.209	851.706	723.375	692.990	−1245.384	485.538	−4.697
5500	136.137	854.205	725.731	706.607	−1246.875	517.606	−4.916
5600	136.068	856.657	728.047	720.217	−1248.434	549.702	−5.127
5700	135.999	859.065	730.324	733.821	−1250.064	581.825	−5.332
5800	135.933	861.430	732.565	747.417	−1251.767	613.979	−5.529
5900	135.868	863.753	734.768	761.007	−1253.547	646.162	−5.721
6000	135.804	866.036	736.937	774.591	−1255.409	678.375	−5.906

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

Magnesium Chloride ((MgCl$_2$)$_2$) IDEAL GAS $M_r = 190.422$

$S°(298.15\ K) = [418.810 \pm 20.9]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -954.41 \pm 29.3\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -954.37 \pm 29.3\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[500](1)	[240](1)	[130](2)
[400](1)	[200](1)	[100](2)
295(1)	[150](1)	[80](2)

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: [D_{2h}]
Bond Distance: Mg–Cl = [2.18] Å; Mg–Cl′(ring) = [2.3] Å
Bond Angles: Cl′–Mg–Cl′(in ring) = [90°]; Cl–Mg–Cl′ = [135°]
Product of the Moments of Inertia: $I_A I_B I_C = 1.3313 \times 10^{-111}\ g^3{\cdot}cm^6$

Enthalpy of Formation

References relative to the monomer–dimer ratio in magnesium chloride vapor are given in the discussion for monomeric ideal gas. The selected best value for the enthalpy of dimerization at 900 K is −39.2 kcal·mol^{-1}. Combined with enthalpy of formation data for the monomer and the heat capacity of the dimer, this yields $\Delta_f H°(298.15\ K) = -228.10\ kcal{\cdot}mol^{-1}$.

Heat Capacity and Entropy

A planar structure with D_{2h} symmetry was assumed, with the outer Mg–Cl distance the same as in MgCl$_2$ and the ring Mg–Cl distance slightly larger. The ring was taken to be square, and the Cl–Mg–Cl′ angle 135°. This structure gives individual moments of inertia of $I_A = 31.12 \times 10^{-39}$, $I_B = 191.86 \times 10^{-39}$, and $I_C = I_A + I_B$ g·cm^2.

A reasonable set of frequencies was estimated by comparison with MgCl$_2$ monomer and other dimer molecules. The single observed frequency is from Buchler and Klemperer[1] who erroneously ascribed it to the bending mode of the monomer. The estimated values were adjusted until the entropy of dimerization at 900 K was −29.9 kcal·mol^{-1}, as selected in the discussion for ideal monomeric gas. The calculated thermodynamic properties of monomer and dimer give total vapor pressures in good agreement with experiment and yield a boiling point for magnesium chloride of 1624 K at one atmosphere pressure.

References

[1] A. Buchler and W. Klemperer, J. Chem. Phys. 29, 121 (1958).

Magnesium Chloride ((MgCl$_2$)$_2$) Cl$_4$Mg$_2$(g)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−28.396	−954.409	−954.409	INFINITE
100	91.553	298.917	522.238	−22.332	−955.452	−945.642	493.953
200	115.181	371.122	430.020	−11.780	−954.989	−935.971	244.451
250	120.397	397.431	420.950	−5.880	−954.669	−931.253	194.575
298.15	123.611	418.931	418.931	0.	−954.370	−926.771	162.366
300	123.710	419.696	418.933	0.229	−954.359	−926.600	161.335
350	125.913	438.942	420.448	6.473	−954.077	−921.996	137.600
400	127.437	455.861	423.839	12.809	−953.830	−917.430	119.804
450	128.529	470.937	428.250	19.209	−953.622	−912.893	105.966
500	129.335	484.523	433.209	25.657	−953.457	−908.377	94.897
600	130.418	508.208	443.792	38.649	−953.264	−899.382	78.298
700	131.090	528.366	454.470	51.727	−953.274	−890.404	66.443
800	131.534	545.902	464.827	64.860	−953.517	−881.409	57.550
900	131.842	561.413	474.713	78.029	−954.025	−872.368	50.631
1000	132.065	575.316	484.091	91.225	−972.015	−861.830	45.017
1100	132.230	587.911	492.965	104.441	−973.162	−850.756	40.399
1200	132.357	599.422	501.364	117.670	−974.317	−839.577	36.546
1300	132.456	610.021	509.320	130.911	−975.483	−828.302	33.282
1400	132.534	619.840	516.868	144.161	−1231.477	−810.602	30.244
1500	132.598	628.986	524.041	157.417	−1229.960	−780.592	27.183
1600	132.650	637.545	530.870	170.680	−1228.454	−750.683	24.507
1700	132.693	645.588	537.384	183.947	−1226.961	−720.869	22.150
1800	132.729	653.174	543.608	197.218	−1225.482	−691.141	20.056
1900	132.760	660.351	549.566	210.493	−1224.020	−661.496	18.186
2000	132.786	667.161	555.276	223.770	−1222.575	−631.927	16.504
2100	132.809	673.641	560.760	237.050	−1221.150	−602.429	14.985
2200	132.829	679.819	566.032	250.332	−1219.748	−572.999	13.605
2300	132.846	685.724	571.109	263.615	−1218.372	−543.633	12.346
2400	132.861	691.379	576.003	276.901	−1217.026	−514.325	11.194
2500	132.874	696.802	580.727	290.188	−1215.713	−485.073	10.135
2600	132.886	702.014	585.293	303.476	−1214.435	−455.873	9.159
2700	132.896	707.029	589.709	316.765	−1213.198	−426.720	8.255
2800	132.906	711.863	593.986	330.055	−1212.004	−397.614	7.418
2900	132.914	716.527	598.132	343.346	−1210.856	−368.549	6.638
3000	132.922	721.033	602.154	356.638	−1209.756	−339.523	5.912
3100	132.929	725.391	606.059	369.930	−1208.708	−310.532	5.232
3200	132.935	729.612	609.855	383.223	−1207.712	−281.575	4.596
3300	132.941	733.703	613.546	396.517	−1206.770	−252.648	3.999
3400	132.946	737.671	617.139	409.811	−1205.884	−223.749	3.437
3500	132.951	741.525	620.638	423.106	−1205.053	−194.875	2.908
3600	132.955	745.271	624.048	436.401	−1204.279	−166.023	2.409
3700	132.959	748.913	627.374	449.697	−1203.560	−137.193	1.937
3800	132.963	752.459	630.619	462.993	−1202.898	−108.382	1.490
3900	132.966	755.913	633.788	476.290	−1202.291	−79.586	1.066
4000	132.969	759.280	636.883	489.586	−1201.740	−50.806	0.663
4100	132.972	762.563	639.908	502.884	−1201.243	−22.039	0.281
4200	132.975	765.767	642.867	516.181	−1200.800	6.717	−0.084
4300	132.978	768.896	645.762	529.479	−1200.411	35.462	−0.431
4400	132.980	771.953	648.595	542.776	−1200.074	64.200	−0.762
4500	132.982	774.942	651.370	556.075	−1199.790	92.930	−1.079
4600	132.984	777.865	654.088	569.373	−1199.558	121.655	−1.381
4700	132.986	780.725	656.752	582.671	−1199.379	150.374	−1.671
4800	132.988	783.525	659.364	595.970	−1199.251	179.091	−1.949
4900	132.990	786.267	661.926	609.269	−1199.176	207.806	−2.215
5000	132.991	788.953	664.440	622.568	−1199.153	236.519	−2.471
5100	132.993	791.587	666.907	635.867	−1199.183	265.233	−2.717
5200	132.994	794.170	669.330	649.167	−1199.267	293.947	−2.953
5300	132.996	796.703	671.709	662.466	−1199.403	322.664	−3.180
5400	132.997	799.189	674.047	675.766	−1199.596	351.384	−3.399
5500	132.998	801.629	676.345	689.066	−1199.843	380.108	−3.610
5600	132.999	804.026	678.603	702.365	−1200.148	408.837	−3.813
5700	133.000	806.380	680.824	715.665	−1200.512	437.572	−4.010
5800	133.001	808.693	683.009	728.965	−1200.935	466.314	−4.200
5900	133.002	810.966	685.159	742.266	−1201.420	495.064	−4.383
6000	133.003	813.202	687.274	755.566	−1201.967	523.822	−4.560

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

Molybdenum Chloride ($MoCl_4$) CRYSTAL $M_r = 237.752$ Molybdenum Chloride ($MoCl_4$) $Cl_4Mo_1(cr)$

$\Delta_fH°(0\ K)$ = Unknown

$S°(298.15\ K) = [223.84 \pm 12.6]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(298.15\ K) = -477.0 \pm 8\ kJ{\cdot}mol^{-1}$

$T_{fus} = 590\ K$

$\Delta_{fus}H° = [16.736 \pm 8]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_fH°(298.15\ K) = 114\ kcal{\cdot}mol^{-1}$ was determined by Shchukarev *et al.*[1] by solution calorimetry. The authors measured the enthalpy of solution of $MoCl_4$ in the aqueous solvent $FeCl_3 + HCl$ and obtained the enthalpy of formation from a comparison with the enthalpy of solution of $MoCl_5$ measured in the same solvent.

The decomposition pressures of $2MoCl_5(cr) = 2MoCl_4(cr) + Cl_2(g)$ (80–150°C) were measured manometrically by Saeki and Matsuzaki[2]. From the reported data we evaluate the enthalpy change for the above reaction by 3rd law analysis. Based on $\Delta_fH°(MoCl_5$, cr, $298.15\ K) = -126\ kcal{\cdot}mol^{-1}$ and the 3rd law $\Delta_rH°(298.15\ K) = 24.132\ kcal{\cdot}mol^{-1}$, we obtain $\Delta_fH°(MoCl_4$, cr, $298.15\ K) = -113.94\ kcal{\cdot}mol^{-1}$, which is in very good agreement with the value reported by Shchukarev *et al.*[1]

Heat Capacity and Entropy

The heat capacity is estimated by comparison with that of $WCl_4(cr)$. The estimated $S°(298.15\ K) = 53.5\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ is based on the assumption that the entropy difference between $MoCl_4(cr)$ and $MoCl_5(cr)$ is about the same as that between $WCl_4(cr)$ and $WCl_5(cr)$. The entropy obtained from the second law analysis of the data of Saeki and Matsuzaki[2] agrees with the adopted one within the error of the vapor pressure data.

Fusion Data

Refer to the liquid table for details.

References

[1] S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin and A. K. Baev, Russ. J. Inorg. Chem. 5, 802 (1960).

[2] Y. Saeki and R. Matsuzaki, Denki Kagaku 33, 155–8 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	129.704	223.844	223.844	0.	−476.976	−402.164	70.458
300	129.704	224.646	223.846	0.240	−476.906	−401.700	69.942
400	135.143	262.705	228.999	13.482	−473.059	−377.207	49.258
500	140.582	293.445	238.908	27.269	−468.964	−353.711	36.952
590.000	145.478	317.108	249.072	40.141	--- CRYSTAL <--> LIQUID ---		
600	146.022	319.557	250.226	41.599	−464.515	−331.072	28.822
700	151.461	342.470	261.799	56.469	−459.661	−309.210	23.074
800	157.318	363.082	273.192	71.912	−454.339	−288.074	18.809
900	162.758	381.937	284.242	87.926	−448.531	−267.635	15.533
1000	166.942	399.306	294.891	104.415	−442.329	−247.865	12.947
1100	170.707	415.397	305.124	121.301	−435.806	−228.731	10.862
1200	174.054	430.400	314.945	138.546	−429.003	−210.205	9.150
1300	176.565	444.434	324.372	156.080	−421.994	−192.255	7.725
1400	178.657	457.595	333.423	173.841	−414.847	−174.850	6.524
1500	180.749	469.993	342.118	191.811	−407.583	−157.960	5.501

PREVIOUS: CURRENT: December 1968

Molybdenum Chloride ($MoCl_4$) $Cl_4Mo_1(cr)$

Molybdenum Chloride ($MoCl_4$) LIQUID $M_r = 237.752$ Molybdenum Chloride ($MoCl_4$) $Cl_4Mo_1(l)$

$S°(298.15\ K) = [245.525]\ J \cdot K^{-1} \cdot mol^{-1}$

$T_{fus} = 590\ K$

$\Delta_f H°(298.15\ K) = [-462.837]\ kJ \cdot mol^{-1}$

$\Delta_{fus} H° = [16.736 \pm 8]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(MoCl_4, l, 298.15\ K)$ is calculated from $\Delta_f H°(MoCl_4, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(590\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacities are assumed to be constant at 7 $cal \cdot K^{-1}\ g \cdot atom^{-1}$. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} is taken from Gutmann.[1] $\Delta_{fus} H°$ is estimated such that the derived $\Delta_f G°$ for $MoCl_4(l)$ yields a reasonable boiling point which is expected to be between 600 and 700 K from comparisons with related compounds.

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change ($\Delta_r G°$) of the following process $MoCl_4(l) = MoCl_4(g)$ is zero. The difference between $\Delta_f H°$ for $MoCl_4(l)$ and $MoCl_4(g)$ at T_{vap} is the enthalpy of vaporization.

Reference

[1] V. Gutmann, "Halogen Chemistry," Vol. 3, Academic Press, New York, (1967).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	146.440	245.525	245.525	0.	−462.837	−394.490	69.113
300	146.440	246.431	245.528	0.271	−462.736	−394.066	68.613
400	146.440	288.559	251.271	14.915	−457.488	−371.977	48.575
500	146.440	321.236	262.118	29.559	−452.535	−351.178	36.687
590.000	146.440	345.474	273.036	42.739	--- CRYSTAL <--> LIQUID ---		
600	146.440	347.935	274.264	44.203	−447.772	−331.356	28.847
700	146.440	370.509	286.442	58.847	−443.144	−312.321	23.306
800	146.440	390.063	298.200	73.491	−438.621	−293.941	19.192
900	146.440	407.311	309.384	88.135	−434.184	−276.124	16.026
1000	146.440	422.740	319.961	102.779	−429.826	−258.796	13.518
1100	146.440	436.698	329.950	117.423	−425.545	−241.901	11.487
1200	146.440	449.440	339.384	132.067	−421.343	−225.392	9.811
1300	146.440	461.161	348.306	146.711	−417.224	−209.230	8.407
1400	146.440	472.013	356.760	161.355	−413.194	−193.383	7.215
1500	146.440	482.117	364.784	175.999	−409.257	−177.820	6.192

PREVIOUS: CURRENT: December 1968

Molybdenum Chloride (MoCl$_4$) CRYSTAL-LIQUID

0 to 590 K crystal
above 590 K *liquid*

Refer to the individual tables for details.

M_r = 237.752 Molybdenum Chloride (MoCl$_4$) Cl$_4$Mo$_1$(cr,l)

Enthalpy Reference Temperature = T_r = 298.15 K | Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0							
100							
200							
298.15	129.704	223.844	223.844	0.	−476.976	−402.164	70.458
300	129.704	224.646	223.846	0.240	−476.906	−401.700	69.942
400	135.143	262.705	228.999	13.482	−473.059	−377.207	49.258
500	140.582	293.445	238.908	27.269	−468.964	−353.711	36.952
590.000	145.478	317.108	249.072	40.141	CRYSTAL <--> LIQUID TRANSITION		
590.000	146.440	345.474	249.072	56.877			
600	146.440	347.935	250.699	58.342	−447.772	−331.356	28.847
700	146.440	370.509	266.244	72.986	−443.144	−312.321	23.306
800	146.440	390.063	280.526	87.630	−438.621	−293.941	19.192
900	146.440	407.311	293.674	102.274	−434.184	−276.124	16.026
1000	146.440	422.740	305.823	116.918	−429.826	−258.796	13.518
1100	146.440	436.698	317.096	131.562	−425.545	−241.901	11.487
1200	146.440	449.440	327.601	146.206	−421.343	−225.392	9.811
1300	146.440	461.161	337.430	160.850	−417.224	−209.230	8.407
1400	146.440	472.013	346.661	175.494	−413.194	−193.383	7.215
1500	146.440	482.117	355.358	190.138	−409.257	−177.820	6.192

PREVIOUS: CURRENT: December 1968

Molybdenum Chloride (MoCl$_4$) IDEAL GAS M_r = 237.752

$S°(298.15\ \mathrm{K}) = [371.941]\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$

$\Delta_f H°(0\ \mathrm{K}) = [-384.25 \pm 12.6]\ \mathrm{kJ \cdot mol^{-1}}$
$\Delta_f H°(298.15\ \mathrm{K}) = [-384.93 \pm 12.6]\ \mathrm{kJ \cdot mol^{-1}}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[10000]	[3]
[30000]	[3]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[390](1)	[410](3)
[120](2)	[120](3)

Point Group: T$_d$ σ = [12]
Bond Distance: Mo–Cl = [2.27] Å
Bond Angle: Cl–Mo–Cl = [109.4712]°
Product of the Moments of Inertia: $I_A I_B I_C = [5.29405 \times 10^{-112}]\ \mathrm{g^3 \cdot cm^6}$

Enthalpy of Formation

Shchukarev *et al.*,[1] derived the value $\Delta_f H°(\mathrm{MoCl_4}$, g, 298.15 K) = −89 kcal·mol^{-1} from the decomposition pressures of $2\mathrm{MoCl_3(cr)} = \mathrm{MoCl_2(cr)} + \mathrm{MoCl_4(g)}$, 480–600°C, measured by a transpiration method. However, this value is adjusted to be −92 ± 3 kcal·mol^{-1}, in order to obtain a reasonable boiling point (see the liquid table for details).

Heat Capacity and Entropy

Vibrational frequencies and quantum weights are estimated by comparison with those of WCl$_4$(g). The molecular configuration is assumed to be tetrahedral similar to those of WCl$_4$(g), SiCl$_4$(g), TiCl$_4$(g) and PbCl$_4$(g). The bond distance is estimated to be the same as that of MoCl$_5$(g). The principal moments of inertia are $I_A = I_B = I_C = 80.8964 \times 10^{-39}\ \mathrm{g \cdot cm^2}$. The low lying electronic levels are estimated to be 0, 10000, and 30000, all triplets, by comparison with those of WCl$_4$(g).

Reference

[1] S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B N. Sharupin and A. K. Baev, Zh, Neorg. Khim. 5, 1650–4 (1960).

Molybdenum Chloride (MoCl$_4$) Cl$_4$Mo$_1$(g)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0	.000	.000	INFINITE	−22.265	−384.247	−384.247	INFINITE
100	69.235	279.286	452.572	−17.329	−385.625	−375.050	195.906
200	89.478	334.366	380.690	−9.265	−385.479	−364.471	95.190
250	94.767	354.944	373.540	−4.649	−385.219	−359.248	75.061
298.15	98.109	371.941	371.941	.000	−384.928	−354.272	62.067
300	98.213	372.548	371.943	.182	−384.916	−354.081	61.651
350	100.529	387.873	373.148	5.154	−384.595	−348.967	52.081
400	102.140	401.408	375.851	10.223	−384.271	−343.900	44.909
450	103.298	413.509	379.375	15.360	−383.950	−338.873	39.335
500	104.154	424.439	383.344	20.548	−383.637	−333.881	34.880
600	105.306	443.539	391.830	31.026	−383.040	−323.987	28.206
700	106.021	459.830	400.409	41.594	−382.488	−314.189	23.445
800	106.494	474.020	408.743	52.222	−381.981	−304.467	19.880
900	106.822	486.583	416.707	62.888	−381.521	−294.806	17.110
1000	107.060	497.851	424.268	73.583	−381.112	−285.193	14.897
1100	107.238	508.064	431.429	84.298	−380.760	−275.619	13.088
1200	107.377	517.401	438.210	95.029	−380.471	−266.074	11.582
1300	107.491	526.000	444.636	105.773	−380.253	−256.550	10.308
1400	107.589	533.970	450.736	116.527	−380.113	−247.040	9.217
1500	107.678	541.396	456.535	127.290	−380.056	−237.538	8.272
1600	107.765	548.348	462.059	138.063	−380.091	−228.036	7.445
1700	107.853	554.884	467.329	148.843	−380.222	−218.529	6.715
1800	107.946	561.051	472.366	159.633	−380.459	−209.011	6.065
1900	108.044	566.890	477.188	170.433	−380.809	−199.477	5.484
2000	108.150	572.435	481.813	181.242	−381.280	−189.922	4.960
2100	108.263	577 714	486.255	192.063	−381.883	−180.340	4.486
2200	108.384	582.753	490.528	202.895	−382.628	−170.725	4.054
2300	108.513	587.574	494.643	213.740	−383.526	−161.074	3.658
2400	108.647	592.195	498.612	224.598	−384.589	−151.380	3.295
2500	108.787	596.633	502.445	235.470	−385.830	−141.638	2.959
2600	108.931	600.902	506.150	246.356	−387.274	−131.843	2.649
2700	109.079	605.016	509.736	257.256	−388.961	−121.987	2.360
2800	109.228	608.986	513.210	268.171	−390.954	−112.064	2.091
2900	109.377	612.821	516.579	279.102	−429.221	−102.014	1.837
3000	109.527	616.532	519.850	290.047	−430.037	−90.717	1.580
3100	109.675	620.126	523.027	301.007	−430.877	−79.392	1.338
3200	109.821	623.610	526.116	311.982	−431.739	−68.041	1.111
3300	109.964	626.992	529.122	322.971	−432.624	−56.661	.897
3400	110.103	630.276	532.049	333.974	−433.527	−45.255	.695
3500	110.237	633.470	534.901	344.991	−434.447	−33.822	.505
3600	110.367	636.577	537.682	356.022	−435.380	−22.362	.324
3700	110.492	639.603	540.396	367.065	−436.322	−10.876	.154
3800	110.612	642.551	543.046	378.120	−437.270	.635	−.009
3900	110.726	645.426	545.634	389.187	−438.220	12.171	−.163
4000	110.834	648.231	548.164	400.265	−439.166	23.732	−.310
4100	110.937	650.969	550.639	411.354	−440.105	35.316	−.450
4200	111.034	653.643	553.059	422.452	−441.031	46.923	−.584
4300	111.125	656.257	555.429	433.560	−441.940	58.551	−.711
4400	111.211	658.813	557.750	444.677	−442.827	70.201	−.833
4500	111.291	661.313	560.023	455.802	−443.688	81.870	−.950
4600	111.366	663.760	562.252	466.935	−444.519	93.559	−1.062
4700	111.436	666.155	564.437	478.075	−445.316	105.264	−1.170
4800	111.501	668.502	566.581	489.222	−446.075	116.987	−1.273
4900	111.562	670.802	568.685	500.375	−446.792	128.725	−1.372
5000	111.618	673.056	570.750	511.534	−1038.849	146.208	−1.527
5100	111.670	675.267	572.777	522.699	−1041.153	169.933	−1.740
5200	111.718	677.436	574.769	533.868	−1043.554	193.702	−1.946
5300	111.763	679.565	576.726	545.042	−1046.045	217.519	−2.144
5400	111.804	681.654	578.650	556.221	−1048.625	241.384	−2.335
5500	111.841	683.706	580.542	567.403	−1051.288	265.298	−2.520
5600	111.876	685.721	582.402	578.589	−1054.031	289.260	−2.698
5700	111.907	687.702	584.232	589.778	−1056.849	313.273	−2.871
5800	111.936	689.648	586.033	600.970	−1059.740	337.335	−3.038
5900	111.963	691.562	587.805	612.165	−1062.697	361.447	−3.200
6000	111.987	693.444	589.550	623.363	−1065.721	385.610	−3.357

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

Molybdenum Chloride (MoCl$_4$) Cl$_4$Mo$_1$(g)

Tungsten Chloride Oxide ($OWCl_4$) CRYSTAL $M_r = 351.6614$ Tungsten Chloride Oxide ($OWCl_4$) $Cl_4O_1W_1(cr)$

$S°(298.15 K) = [172.8 \pm 16.7]$ J·K^{-1}·mol^{-1}
$T_{fus} = 484$ K

$\Delta_f H°(0 K)$ = Unknown
$\Delta_f H°(298.15 K) = -671.11 \pm 8.4$ kJ·mol^{-1}
$\Delta_{fus} H° = 45.380 \pm 12.6$ kJ·mol^{-1}

Enthalpy of Formation

Shchukarev *et al.*[1] measured calorimetrically the enthalpies of reaction (1) and (2) at 298.15 K as −131.5 ± 0.3 and −13.6 ± 0.11 kcal·mol^{-1}, respectively. The reactions are given as follows:

(1) $WOCL_4(cr) + 6\ NaOH(aq, 16.3\ H_2O) \rightarrow Na_2WO_4(aq, 190000\ H_2O) + 4\ NaCl(aq, 50000\ H_2O) + 3\ H_2O(l)$
(2) $H_2WO_4(cr) + 2\ NaOH(aq, 16.3\ H_2O) \rightarrow Na_2WO_4(aq, 20000\ H_2O) + 2\ H_2O(l)$

Based on these data and the enthalpies of dilution for NaOH(aq),[2] and Na_2WO_4(aq),[3] we obtain $\Delta_r H°(298.15 K) = -118.0 \pm 1.6$ kcal·mol^{-1} for $WOCl_4(cr) + 4OH^-(aq, \infty) \rightarrow H_2WO_4(cr) + 4\ Cl^-(aq, \infty) + H_2O(l)$. This leads to $\Delta_f H°(WOCl_4, cr, 298.15 K) = 160.4 \pm 2$ kcal·mol^{-1}, using $\Delta_f H°(H_2WO_4, cr, 298.15 K) = -270.5 \pm 0.4$ kcal·mol^{-1}.[5]

Heat Capacity and Entropy

$C°_p(300 K) = 35.0$ cal·K^{-1}·mol^{-1} is estimated using Kopp's rule. Since the melting point of $WOCl_4$(cr) is approximately 500 K, which is relatively low for oxygen to reach its maximum contribution, we estimate $C°_p(500 K) = 40.0$ cal·K^{-1}·mol^{-1} based on the values for WO_2(cr), WO_3(cr) and WCl_6(cr).

The entropy, $S°(298.15 K) = 41.3$ cal·K^{-1}·mol^{-1}, is calculated from $\Delta S°(457 K) = 44.5$ cal·K^{-1}·mol^{-1} for $WOCl_4(cr) \rightarrow WOCl_4(g)$ obtained from the 2nd law analysis of the vapor pressure equation given by Shchukarev and Suvorov.[4] See $WOCl_4$(g) table (March 31, 1967) for details.

It is surprising that this entropy is smaller than the corresponding value for WOF_4(cr). See WOF_4(cr) table (March 31, 1967) for details.

Fusion Data

T_{fus} is calculated as the temperature at which the Gibbs energies of formation of crystal and liquid are equal. The difference between the enthalpies of formation of crystal and liquid at the melting point is $\Delta_{fus}H°$. This $\Delta_{fus}H°$ is derived from 2nd law analyses of the vapor pressure equation determined by Shchukarev and Suvorov.[4] See $WOCl_4$(l, g) tables (March 31, 1967) for details.

References

[1] S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov, Zh. Neorg. Khim. 3, 2642 (1958).
[2] V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2, U. S. Nat. Bur. Stand., (1965).
[3] We have assumed $\Delta H°$ dil = 0 ± 0.5 kcal·mol^{-1} for $Na_2WO_4(aq, 20000\ H_2O) \rightarrow Na_2WO_4(aq, 190000\ H_2O)$.
[4] S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Earlier data reported by Shchukarev *et al.*, Zh. Neorg. Khim 1, 357 (1956); 3, 2630 (1958); 5, 1650 (1960); have been revised and they are not used here.
[5] JANAF Thermochemical Tables: H_2WO_4(cr), 3–31–67.

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C°_p$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	146.248	172.799	172.799	0.	−671.114	−549.292	96.234
300	146.440	173.704	172.802	0.271	−671.041	−548.536	95.509
400	156.900	217.265	178.671	15.438	−666.763	−508.327	66.381
484.000	165.686	247.984	188.095	28.986	--- CRYSTAL <--> LIQUID ---		
500	167.360	253.400	190.099	31.651	−661.736	−469.283	49.026
600	177.820	284.879	203.325	48.932	−655.856	−431.331	37.551
700	185.560	312.904	217.015	67.122	−649.238	−394.425	29.432
800	190.790	338.049	230.600	85.959	−642.114	−358.504	23.408
900	193.719	360.694	243.818	105.188	−634.717	−323.495	18.775
1000	196.230	381.238	256.549	124.689	−627.155	−289.319	15.112

PREVIOUS: September 1962   CURRENT: March 1967

Tungsten Chloride Oxide ($OWCl_4$) LIQUID M_r = 341.6614 Tungsten Chloride Oxide ($OWCl_4$) $Cl_4O_1W_1(l)$

$S°(298.15\ K) = [253.565]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = [-630.573]\ kJ{\cdot}mol^{-1}$

$T_{fus} = 484\ K$ $\Delta_{fus}H° = 45.380 \pm 12.6\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(WOCl_4, l, 298.15\ K)$, is calculated from that of the gas by subtracting the enthalpy of vaporization, $\Delta_{vap}H°(298.15\ K) = 13.643\ kcal{\cdot}mol^{-1}$. The latter is obtained by the 3rd law method from the vapor pressure equation given by Shchukarev and Surorov.[1] 2nd law analysis gives $\Delta_{vap}H°(501.9\ K) = 10.32\ kcal{\cdot}mol^{-1}$ [($\Delta_{vap}H°(298.15\ K) = 13\ 643\ kcal{\cdot}mol^{-1}$] and the boiling point $T_{vap} = 493$ K. Earlier data reported by Shchukarev *et al.*[2] have been revised and they are not used here.

Heat Capacity and Entropy

The heat capacity is assumed to be constant at $7.25\ cal{\cdot}K^{-1}\ g{\cdot}atom^{-1}$ as suggested by Kubaschewski and Evans.[3]

The entropy, $S°(298.15\ K) = 60.6\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, is calculated from $\Delta S°(501.9\ K) = 20.9\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ for $WOCl_4(l) \rightarrow WOCl_4(g)$ obtained from the 2nd law analysis of the vapor pressure equation given by Shchukarev and Suvorov.[1]

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is calculated as the temperature at which the Gibbs energies of formation of liquid and gas are equal. The difference between the enthalpies of formation of liquid and gas at the boiling point is $\Delta_{vap}H°$.

References

[1] S. A. Shchukarev and A. V. Surorov, Vestn. Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).

[2] A. Shchukarev *et al.*, Zh. Neorg. Khim. 1, 357 (1956); 3, 2630 (1958); and 5, 1650 (1960).

[3] O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	182.004	253.565	253.565	0.	−630.573	−532.832	93.350
300	182.004	254.691	253.569	0.337	−630.434	−532.226	92.669
400	182.004	307.050	260.708	18.537	−623.123	−500.601	65.372
484.000	182.004	341.744	271.857	33.825	--- CRYSTAL <--> LIQUID ---		
500	182.004	347.663	274.188	36.738	−616.109	−470.788	49.183
600	182.004	380.847	289.283	54.938	−609.310	−442.365	38.511
700	182.004	408.903	304.419	73.138	−602.682	−415.067	30.973
800	182.004	433.206	319.032	91.339	−596.194	−388.709	25.380
900	182.004	454.643	332.933	109.539	−589.826	−363.157	21.077
1000	182.004	473.819	346.079	127.740	−583.563	−338.309	17.671

PREVIOUS: CURRENT: March 1967

Tungsten Chloride Oxide (OWCl$_4$) CRYSTAL-LIQUID

0	to	484	K crystal
above		484	K liquid

Refer to the individual tables for details.

M_r = 351.6614 Tungsten Chloride Oxide (OWCl$_4$) Cl$_4$O$_1$W$_1$(cr,l)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0							
100							
200							
298.15	146.248	172.799	172.799	0.	−671.114	−549.292	96.234
300	146.440	173.704	172.802	0.271	−671.041	−548.536	95.509
400	156.900	217.265	178.671	15.438	−666.763	−508.327	66.381
484.000	165.686	247.984	188.095	28.986	CRYSTAL <--> LIQUID TRANSITION		
484.000	182.004	341.744	188.095	74.366			
500	182.004	347.663	193.107	77.278	−616.109	−470.788	49.183
600	182.004	380.847	221.716	95.478	−609.310	−442.365	38.511
700	182.004	408.903	246.504	113.679	−602.682	−415.067	30.973
800	182.004	433.206	268.357	131.879	−596.194	−388.709	25.380
900	182.004	454.643	287.888	150.080	−589.826	−363.158	21.077
1000	182.004	473.819	305.539	168.280	−583.563	−338.309	17.671

PREVIOUS: CURRENT: March 1967

Tungsten Chloride Oxide ($OWCl_4$) IDEAL GAS $M_r = 341.6614$ Tungsten Chloride Oxide ($OWCl_4$) $Cl_4O_1W_1(g)$

$S°(298.15 \text{ K}) = [377.079]\ \text{J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = -568.09 \pm 20.9\ \text{kJ·mol}^{-1}$
$\Delta_f H°(298.15 \text{ K}) = -573.49 \pm 20.9\ \text{kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[1000](1)	[350](1)	[200](1)
[1000](1)	[350](1)	[200](1)
[480](1)	[300](1)	[100](1)
[480](1)	[300](1)	[100](1)

Ground State Quantum Weight = 1 $\sigma = [2]$
Point Group: [C_{2v}]
Bond Distances: W–Cl = [2.26] Å; W–O = [1.81] Å
Bond Angles: Cl*–W–O* = Cl*–W–Cl* = [120]°
Cl*–W–Cl** = Cl**–W–O* = [90]°
Cl**–W–Cl** = [180]°
*Equatorial **Axial
Product of the Moments of Inertia: $I_AI_BI_C = [5.87434 \times 10^{-112}]\ \text{g}^3\text{·cm}^6$

Enthalpy of Formation

The enthalpy formation, $\Delta_f H°(WOCl_4, g, 298.15 \text{ K}) = -137.0\ \text{kcal·mol}^{-1}$, is calculated from $\Delta_r H°(298.15 \text{ K}) = 23.4\ \text{kcal·mol}^{-1}$ for $WOCl_4(cr) \rightarrow WOCl_4(g)$. The latter is obtained by the 3rd law method from the vapor pressure equation given by Shchukarev and Suvorov.[1] Second law analysis gives $\Delta_r H°(457.2 \text{ K}) = 21.9\ \text{kcal·mol}^{-1}((\Delta_r H°(298.15 \text{ K}) = 23.4\ \text{kcal·mol}^{-1})$.

*Earlier data reported by Shchukarev *et al.*[2] have been revised and they are not used here.

Heat Capacity and Entropy

The molecular configuration is assumed to be a trigonal bipyramid similar to that of $SOF_4(g)$, reported by Goggin *et al.*[3] The bond distances W–O and W–Cl are estimated to be the same as those in $WO_3(g)$ and $WCl_6(g)$, respectively. The principal moments of inertia are: $I_A = 67.5706 \times 10^{-39}$, $I_B = 82.6053 \times 10^{-39}$ and $I_C = 105.2432 \times 10^{-39}\ \text{g·cm}^2$.

All vibrational frequencies are estimated by comparison with those observed in the infrared and Raman spectra for $SOF_4(g)$,[3] $MoOCl_4(g)$,[4] $WO_2Cl_2(g)$,[5] $CrO_2Cl_2(g)$,[6,7] $WO_3(g)$,[8] and $WCl_6(g)$.[8] The frequencies are not listed in point group order.

References

[1] S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).
[2] S. A. Shchukarev *et al.*, Zh. Neorg. Khim. 1, 357 (1956), 3, 2630 (1956), 5, 1650 (1960).
[3] P. L. Goggin, H. L. Roberts and L. A. Woodward, Trans. Faraday Soc. 57, 1877 (1961).
[4] T. V. Iorns and F. E. Stafford, J. Amer. Chem. Soc. 88, 4819 (1966).
[5] C. G. Barraclough and J. Stals, Aust. J. Chem. 19, 741 (1966).
[6] F. A. Miller, G. L. Carlson and W. B. White, Spectrochim. Acta 1959, 709 (1959).
[7] H. Stammreich, K. Kawai and Y. Tavares, Spectrochim. Acta 1959, 438 (1959).
[8] JANAF Thermochemical Tables: $WO_3(g)$, 9–30–66; $WCl_6(g)$, 12–31–66.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−22.271	−568.087	−568.087	INFINITE
100	63.815	283.395	460.920	−17.752	−571.497	−552.408	288.549
200	92.057	337.421	386.393	−9.794	−573.077	−532.573	139.094
250	100.261	358.894	378.796	−4.975	−573.382	−522.407	109.151
298.15	106.138	377.079	377.079	0.	−573.493	−512.577	89.801
300	106.335	377.736	377.081	0.197	−573.494	−512.199	89.182
350	110.987	394.492	378.394	5.635	−573.456	−501.984	74.917
400	114.621	409.559	381.364	11.278	−573.301	−491.783	64.220
450	117.495	423.232	385.268	17.084	−573.058	−481.607	55.904
500	119.794	435.735	389.698	23.018	−572.747	−471.462	49.253
600	123.162	457.895	399.265	35.178	−571.990	−451.274	39.287
700	125.440	477.062	409.041	47.615	−571.125	−431.222	32.178
800	127.036	493.922	418.619	60.243	−570.209	−411.298	26.855
900	128.188	508.955	427.836	73.007	−569.277	−391.490	22.721
1000	129.045	522.508	436.637	85.871	−568.352	−371.786	19.420
1100	129.697	534.839	445.012	98.809	−567.447	−352.173	16.723
1200	130.203	546.147	452.975	111.805	−566.573	−332.642	14.480
1300	130.604	556.585	460.549	124.846	−565.738	−313.181	12.584
1400	130.926	566.276	467.759	137.924	−564.948	−293.784	10.961
1500	131.188	575.318	474.632	151.030	−564.207	−274.441	9.557
1600	131.405	583.792	481.192	164.160	−563.520	−255.146	8.330
1700	131.586	591.764	487.464	177.309	−562.890	−235.893	7.248
1800	131.739	599.289	493.469	190.476	−562.321	−216.674	6.288
1900	131.868	606.416	499.228	203.656	−561.817	−197.486	5.429
2000	131.980	613.183	504.758	216.849	−561.382	−178.322	4.657
2100	132.076	619.624	510.076	230.052	−561.019	−159.178	3.959
2200	132.159	625.770	515.196	243.264	−560.731	−140.050	3.325
2300	132.232	631.647	520.132	256.483	−560.524	−120.933	2.746
2400	132.297	637.276	524.897	269.710	−560.400	−101.824	2.216
2500	132.353	642.678	529.501	282.942	−560.363	−82.717	1.728
2600	132.404	647.870	533.954	296.180	−560.412	−63.611	1.278
2700	132.449	652.868	538.266	309.423	−560.578	−44.500	0.861
2800	132.489	657.685	542.446	322.670	−560.896	−25.380	0.473
2900	132.526	662.335	546.500	335.921	−561.407	−6.247	0.113
3000	132.559	666.828	550.437	349.175	−562.138	12.909	−0.225
3100	132.588	671.175	554.262	362.432	−563.133	32.093	−0.541
3200	132.615	675.385	557.981	375.693	−564.422	51.313	−0.838
3300	132.640	679.467	561.601	388.955	−566.028	70.579	−1.117
3400	132.662	683.427	565.126	402.221	−567.983	89.898	−1.381
3500	132.683	687.273	568.562	415.488	−570.349	109.281	−1.631
3600	132.702	691.011	571.911	428.757	−573.218	128.738	−1.868
3700	132.719	694.647	575.180	442.028	−611.453	148.474	−2.096
3800	132.736	698.186	578.370	455.301	−612.028	169.020	−2.323
3900	132.750	701.634	581.487	468.575	−612.622	189.582	−2.539
4000	132.764	704.996	584.533	481.851	−613.230	210.159	−2.744
4100	132.777	708.274	587.511	495.128	−613.845	230.751	−2.940
4200	132.789	711.474	590.425	508.406	−614.462	251.359	−3.126
4300	132.800	714.598	593.276	521.686	−615.077	271.981	−3.304
4400	132.810	717.652	596.068	534.966	−615.685	292.617	−3.474
4500	132.820	720.636	598.803	548.248	−616.279	313.267	−3.636
4600	132.829	723.556	601.484	561.530	−616.857	333.930	−3.792
4700	132.837	726.412	604.112	574.814	−617.412	354.605	−3.941
4800	132.845	729.209	606.689	588.098	−617.942	375.292	−4.084
4900	132.853	731.948	609.217	601.383	−618.442	395.990	−4.221
5000	132.860	734.632	611.699	614.668	−618.909	416.697	−4.353
5100	132.866	737.263	614.135	627.955	−619.340	437.414	−4.480
5200	132.873	739.844	616.528	641.241	−619.732	458.138	−4.602
5300	132.879	742.375	618.879	654.529	−620.083	478.870	−4.720
5400	132.884	744.858	621.189	667.817	−620.390	499.608	−4.833
5500	132.889	747.297	623.459	681.106	−620.653	520.351	−4.942
5600	132.894	749.691	625.692	694.395	−620.869	541.099	−5.047
5700	132.899	752.043	627.888	707.685	−621.038	561.849	−5.149
5800	132.904	754.355	630.049	720.975	−621.159	582.604	−5.247
5900	132.908	756.627	632.175	734.265	−621.231	603.358	−5.342
6000	132.912	758.861	634.268	747.556	−621.254	624.114	−5.433

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

Tungsten Chloride Oxide ($OWCl_4$) $Cl_4O_1W_1(g)$

Lead Chloride ($PbCl_4$) IDEAL GAS $M_r = 349.012$ Lead Chloride ($PbCl_4$) $Cl_4Pb_1(g)$

$S°(298.15\ K) = [381.659 \pm 12.6]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-550.6 \pm 84]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-552.4 \pm 84]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
331 (1)
90 (2)
352 (3)
103 (3)

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distance: Pb–Cl = 2.43 Å
Bond Angle: Cl–Pb–Cl = [109.4712°]
Product of the Moments of Inertia: $I_A I_B I_C = [7.96655 \times 10^{-112}]\ g^3·cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(0\ K) = -131.6 \pm 20\ kcal·mol^{-1}$ is derived from the dissociation energy for the process $PbCl_4(g) = Pb(g) + 4Cl(g)$. $D° = 12.70$ eV is estimated from an intercomparison of the lead mono-, di-, and tetra- halides.[1] The adopted $D°$ value for $PbCl_4(g)$ is greater than the $D°$ value for $PbCl_2(g)$ by a factor of 2.02. The auxiliary values $\Delta_f H°(Pb, g, 0\ K) = 46.91\ kcal·mol^{-1}$ [1] and $\Delta_f H°(Cl, g, 0\ K) = 28.587\ kcal\ mol^{-1}$ [1] are used. $\Delta_f H°(PbCl, g, 298.15\ K) = -132.0 \pm 20\ kcal·mol^{-1}$ is calculated from $\Delta_f H°(0\ K)$.

Heat Capacity and Entropy

The bond distance is given by Lister and Sutton.[2] The vibrational frequencies are those determined by Clark and Hunter[3] from Raman spectra of $PbCl_4$ in n-pentane solution. Clark and Hunter[3] also observed an electronic transition at 35, 250 cm^{-1} which they claim is the lowest allowed electronic transition of the molecule. The present calculations assume a singlet electronic gound state.

The principal moments of inertia are: $I_A = I_B = I_C = 92.7022 \times 10^{-39}\ g·cm^2$.

References

[1] JANAF Thermochemical Tables: PbF(g), $PbF_2(g)$, $PBF_4(g)$, PbBr(g), $PbBr_2(g)$, PbI(g), and $PbI_2(g)$,12–31–73; PbCl(g) and $PbCl_2(g)$, 6–30–73; Pb(g), 3–31–62;Cl(g), 6–30–72.

[2] M. W. Lister and L. E. Sutton, Trans. Faraday Soc. 37, 393 (1941).

3. R. J. H. Clark and B. K. Hunter, J. Mol. Struct. 9, 354 (1971).

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	.000	.000	INFINTE	−23.449	−550.612	−550.612	INFINITE
100	74.317	284.403	465.502	−18.110	−552.863	−539.819	281.973
200	93.443	342.811	390.673	−9.572	−552.926	−526.648	137.546
250	97.857	364.177	383.300	−4.781	−552.677	−520.106	108.670
298.15	100.536	381.659	381.659	.000	−552.403	−513.857	90.026
300	100.618	382.281	381.661	.186	−552.393	−513.618	89.429
350	102.426	397.936	382.893	5.265	−552.105	−507.179	75.692
400	103.662	411.699	385.651	10.419	−551.829	−500.780	65.395
450	104.540	423.962	389.239	15.625	−551.571	−494.414	57.390
500	105.184	435.011	393.273	20.869	−551.335	−488.076	50.989
600	106.044	454.271	401.881	31.434	−550.923	−475.465	41.393
700	106.573	470.661	410.565	42.067	−555.456	−462.117	34.484
800	106.922	484.916	418.987	52.743	−555.196	−448.800	29.304
900	107.163	497.525	427.027	63.448	−554.917	−435.517	25.277
1000	107.337	508.825	434.651	74.174	−554.620	−422.267	22.057
1100	107.466	519.061	441.867	84.914	−554.304	−409.046	19.424
1200	107.564	528.417	448.695	95.666	−553.970	−395.856	17.231
1300	107.641	537.029	455.163	106.426	−553.625	−382.694	15.377
1400	107.702	545.009	461.299	117.193	−553.284	−369.558	13.788
1500	107.752	552.441	467.130	127.966	−552.957	−356.446	12.413
1600	107.792	559.397	472.682	138.743	−552.652	−343.355	11.209
1700	107.826	565.933	477.977	149.524	−552.374	−330.283	10.148
1800	107.854	572.097	483.036	160.308	−552.127	−317.226	9.206
1900	107.878	577.929	487.879	171.095	−551.914	−304.182	8.363
2000	107.898	583.463	492.521	181.884	−551.740	−291.148	7.604
2100	107.916	588.727	496.978	192.675	−728.828	−271.007	6.741
2200	107.931	593.748	501.263	203.467	−728.350	−249.218	5.917
2300	107.944	598.546	505.389	214.261	−727.986	−227.447	5.165
2400	107.956	603.140	509.367	225.056	−727.740	−205.691	4.477
2500	107.966	607.547	513.207	235.852	−727.617	−183.942	3.843
2600	107.975	611.782	516.917	246.649	−727.617	−162.195	3.259
2700	107.983	615.857	520.507	257.447	−727.740	−140.446	2.717
2800	107.991	619.785	523.983	268.245	−727.985	−118.690	2.214
2900	107.997	623.574	527.352	279.045	−728.349	−96.924	1.746
3000	108.003	627.236	530.621	289.845	−728.825	−75.143	1.308
3100	108.008	630.777	533.795	300.645	−729.408	−53.344	.899
3200	108.013	634.206	536.879	311.447	−730.090	−31.525	.515
3300	108.018	637.530	539.879	322.248	−730.862	−9.683	.153
3400	108.022	640.755	542.799	333.050	−731.715	12.184	−.187
3500	108.025	643.886	545.643	343.852	−732.640	34.076	−.509
3600	108.029	646.929	548.414	354.655	−733.624	55.997	−.812
3700	108.032	649.889	551.117	365.458	−734.659	77.945	−1.100
3800	108.035	652.770	553.754	376.262	−735.733	99.921	−1.374
3900	108.037	655.577	556.329	387.065	−736.836	121.926	−1.633
4000	108.040	658.312	558.845	397.869	−737.957	143.960	−1.880
4100	108.042	660.980	561.303	408.673	−739.087	166.022	−2.115
4200	108.044	663.583	563.708	419.477	−740.215	188.112	−2.340
4300	108.046	666.126	566.060	430.282	−741.334	210.228	−2.554
4400	108.048	668.610	568.363	441.087	−742.433	232.370	−2.759
4500	108.050	671.038	570.617	451.892	−743.506	254.536	−2.955
4600	108.051	673.413	572.826	462.697	−744.545	276.727	−3.142
4700	108.053	675.736	574.991	473.502	−745.543	298.939	−3.322
4800	108.054	678.011	577.114	484.307	−746.495	321.172	−3.495
4900	108.056	680.239	579.196	495.113	−747.395	343.425	−3.661
5000	108.057	682.422	581.239	505.918	−748.239	365.695	−3.820
5100	108.058	684.562	583.244	516.724	−749.022	387.982	−3.974
5200	108.059	686.660	585.212	527.530	−749.740	410.283	−4.121
5300	108.060	688.719	587.146	538.336	−750.392	432.597	−4.264
5400	108.061	690.739	589.046	549.142	−750.974	454.924	−4.401
5500	108.062	692.722	590.913	559.948	−751.484	477.260	−4.533
5600	108.063	694.669	592.748	570.755	−751.922	499.605	−4.660
5700	108.064	696.581	594.553	581.561	−752.285	521.957	−4.783
5800	108.065	698.461	596.328	592.367	−752.574	544.315	−4.902
5900	108.066	700.308	598.075	603.174	−752.787	566.677	−5.017
6000	108.066	702.124	599.794	613.980	−752.926	589.041	−5.128

PREVIOUS: December 1973 (1 atm)   CURRENT· December 1973 (1 bar)

$S°(298.15\ K) = 330.945 \pm 0.21\ J{\cdot}K^{-1}$

$\Delta_fH°(0\ K) = -660.57 \pm 1.3\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -662.75 \pm 1.3\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
425 ± 1 (1)	620 ± 1 (3)
149 ± 2 (2)	220 ± 4 (3)

Ground State Quantum Weight: 1 $\sigma = 12$
Point Group: T_d
Bond Distance: Si–Cl = 2.0173 ± 0.0034 Å
Bond Angle: Cl–Si–Cl = 109.4712°
Product of the Moments of Inertia: $I_AI_BI_C = 2.60769 \times 10^{-112}\ g^3{\cdot}cm^6$

Enthalpy of Formation

Gross *et al.*[1] measured the enthalpy of formation of $SiCl_4(l)$ by the direct chlorination of silicon in a bomb calorimeter. Corrections for the difference in enthalpy content between liquid and gaseous chlorine at 25 °C and 1 atm led to the value of $\Delta_fH°(SiCl_4, l, 298.15\ K) = -165.49 \pm 0.16\ kcal{\cdot}mol^{-1}$. Combination of $\Delta_fH°(l, 298.15\ K)$ with $\Delta_{vap}H°(298.15\ K) = 7.09\ kcal{\cdot}mol^{-1}$ gives $\Delta_fH°(SiCl_4, g, 298.15\ K) = -158.4 \pm 0.3\ kcal{\cdot}mol^{-1}$ which is adopted in the tabulation.

Schafer and Heine[2] measured both enthalpy of solution of Si(cr) and $SiCl_4(l)$ in HF solution containing AgF which gave $\Delta_rH°(298.15\ K) = 42.7 \pm 0.4\ kcal{\cdot}mol^{-1}$ for the overall reaction $SiCl_4(l) + 4Ag(cr) = Si(cr) + 4AgCl(cr)$ and led to $\Delta_fH°(SiCl_4, l, 298.15\ K) = -164.18\ kcal{\cdot}mol^{-1}$ in agreement with the value adopted, using $\Delta_fH°(AgCl, cr, 298.15\ K) = -30.37\ kcal{\cdot}mol^{-1}$.[3]

Wolf[4] determined the heats of solution of $SiCl_4(l)$ and $Na_2SiO_3{\cdot}8H_2O(cr)$ in NaOH solution and derived $\Delta_rH°(298.15\ K) = -129.3\ kcal{\cdot}mol^{-1}$ for $SiCl_4(l) + 13NaOH(27.8\ H_2O) = Na_2SiO_3(cr) + 4NaCl + 3H_2O(l) + 7NaOH(52.14\ H_2O)$ which leads to $\Delta_fH°(SiCl_4, l, 298.15\ K) = -166.7 \pm 2\ kcal{\cdot}mol^{-1}$, using all JANAF auxiliary data and heats of dilution of NaOH from Parker.[5] However, Wolf's data are suspect due to uncertainties in how he converted his data from Na_2SiO_3(calorimetric solution) to $Na_2SiO_3(cr)$. Beezer and Mortimer[6] measured the heat of solution $\Delta_rH°(298.15\ K) = -97.0\ kcal{\cdot}mol^{-1}$ for $SiCl_4(l) + 185\ HF(4.335\ H_2O) = 4HCl(11\ H_2O) + [H_2SiF_6, 179\ HF, 758\ H_2O]$ and combined with those of Good *et al.*[7] for $[H_2SiF_6, 41\ HF, 174\ H_2O]$ solution by neglecting the unknown heats of dilution between the two calorimetric solutions and obtained $\Delta_fH°(l, 298.15\ K) = -169.9\ kcal{\cdot}mol^{-1}$ which is in poor agreement with the value adopted. In both the measurements of Woof[4] and Beezer and Mortimer,[6] the final state of the calorimetric solution is not well defined or not well known, thus it leads to large uncertainties in their results.

Other calorimetric studies involving aqueous hydrolysis of $SiCl_4(l)$ to form SiO_2(colloidal solution) have been reviewed by Gross *et al.*[1] Since the SiO_2(colloidal solution) is an ill–defined state, the heat of formation of $SiCl_4(l)$ derived from hydrolysis data is quite unreliable.

Heat Capacity and Entropy

Morino and Murata[8] measured the adopted bond distance by electron diffraction. Their value was confirmed by Ryan and Hedberg.[9] Morino *et al.*[10] observed the adopted vibrational frequencies from the infrared and Raman spectra from the vapor. Infrared data of Smith[11] confirm that ν_3 is about 12 cm^{-1} larger in the vapor than in the liquid. The principal moments of inertia are: $I_A = I_B = I_C = 63.8879 \times 10^{-39}\ g{\cdot}cm^2$.

Vaporization Data

Vapor pressure data ranging from 20° below T_{fus}(supercooled liquid) to 10° above T_{vap} are in reasonable agreement as summarized below. The analysis is based on fugacities calculated from vapor pressures by the approximation of Lewis *et al.*[19] using $T_c = 506\ K$,[20] $P_c = 37.1\ atm$[21] and $\omega = 0.26$. At 298.15 K the calculated f/P is 0.982 compared with 0.984 observed by Wood.[22] The analysis also presumes a linear variation of the liquid phase C_p based on 33.3 cal·K^{-1}·mol^{-1} at 210 K and 34.2 at 300 K. The latter value is from data of Vold[17] since earlier data (77–294 K) of Latimer[18] appear to have large positive bias below T_{fus}. The C_p at 210 K assumes Latimer's value to have about 1% bias by analogy with his data for $CCl_4(l)$.

Source	Data Points	T/K	$\Delta_{vap}S°(298.15\ K)$, cal·K^{-1}·mol^{-1}	$\Delta_{vap}H°(298.15\ K)$, kcal·mol^{-1}
Combined[14,15,22]	19	275–341	21.45 ± 0.04	7.09 ± 0.01
[12]	Equation	183–204	21.13	7.19
[13]	6	303–323	20.85 ± 0.13	6.89 ± 0.04
[14]	12	298–341	21.48 ± 0.09	7.10 ± 0.03
[15]	6	275–330	21.40 ± 0.05	7.08 ± 0.01
[16]	13	273–333	21.55 ± 0.08	7.13 ± 0.03

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$ (kJ·mol^{-1})	$\Delta_fG°$ (kJ·mol^{-1})	log K$_f$
0	0.	0.	INFINITE	−19.404	−660.570	−660.570	INFINITE
100	57.203	250.191	402.620	−15.243	−662.499	−649.333	339.177
200	78.605	297.154	338.877	−8.344	−662.854	−635.967	166.097
250	85.418	315.465	332.406	−4.235	−662.833	−629.246	131.474
298.15	90.261	330.945	330.945	0.	−662.746	−622.784	109.109
300	90.420	331.504	330.947	0.167	−662.741	−622.536	108.393
350	94.081	345.732	332.062	4.784	−662.596	−615.846	91.910
400	96.788	358.480	334.582	9.559	−662.410	−609.179	79.551
450	98.820	370.003	337.888	14.452	−662.194	−602.538	69.941
500	100.372	380.499	341.632	19.433	−661.957	−595.922	62.256
600	102.529	399.005	349.693	29.587	−661.443	−582.763	50.734
700	103.910	414.921	357.901	39.914	−660.908	−569.692	42.511
800	104.841	428.861	365.918	50.354	−660.376	−556.697	36.349
900	105.495	441.249	373.613	60.873	−659.860	−543.769	31.560
1000	105.972	452.390	380.943	71.447	−659.370	−530.896	27.731
1100	106.329	462.508	387.905	82.063	−658.910	−518.071	24.601
1200	106.604	471.772	394.513	92.710	−658.485	−505.287	21.995
1300	106.819	480.314	400.789	103.382	−658.099	−492.536	19.790
1400	106.991	488.236	406.756	114.073	−657.754	−479.814	17.902
1500	107.130	495.623	412.437	124.779	−657.454	−467.114	16.266
1600	107.245	502.541	417.854	135.498	−657.200	−454.434	14.836
1700	107.340	509.045	423.029	146.227	−707.173	−441.320	13.560
1800	107.420	515.183	427.980	156.966	−706.790	−425.693	12.353
1900	107.488	520.993	432.724	167.711	−706.419	−410.087	11.274
2000	107.546	526.508	437.276	178.463	−706.061	−394.500	10.303
2100	107.596	531.756	441.651	189.220	−705.721	−378.930	9.425
2200	107.639	536.762	445.862	199.982	−705.400	−363.376	8.628
2300	107.677	541.548	449.919	210.747	−705.102	−347.837	7.900
2400	107.710	546.131	453.833	221.517	−704.830	−332.309	7.233
2500	107.740	550.529	457.613	232.289	−704.587	−316.793	6.619
2600	107.766	554.755	461.269	243.065	−704.375	−301.285	6.053
2700	107.789	558.823	464.807	253.842	−704.197	−285.785	5.529
2800	107.810	562.743	468.235	264.622	−704.054	−270.291	5.042
2900	107.829	566.527	471.560	275.404	−703.948	−254.802	4.589
3000	107.845	570.182	474.786	286.188	−703.880	−239.315	4.167
3100	107.861	573.719	477.921	296.973	−703.848	−223.830	3.772
3200	107.875	577.144	480.969	307.760	−703.853	−208.346	3.401
3300	107.887	580.463	483.933	318.548	−703.892	−192.860	3.053
3400	107.899	583.684	486.820	329.337	−703.963	−177.374	2.725
3500	107.909	586.812	489.633	340.128	−704.064	−161.885	2.416
3600	107.919	589.852	492.374	350.919	−1088.341	−135.931	1.972
3700	107.928	592.809	495.049	361.712	−1088.075	−109.479	1.546
3800	107.936	595.687	497.660	372.505	−1087.827	−83.034	1.141
3900	107.944	598.491	500.209	383.299	−1087.592	−56.595	0.758
4000	107.951	601.224	502.701	394.094	−1087.366	−30.162	0.394
4100	107.958	603.890	505.136	404.889	−1087.143	−3.735	0.048
4200	107.964	606.491	507.519	415.685	−1086.917	22.687	−0.282
4300	107.969	609.032	509.850	426.482	−1086.683	49.104	−0.596
4400	107.975	611.514	512.133	437.279	−1086.435	75.514	−0.896
4500	107.980	613.941	514.368	448.077	−1086.169	101.919	−1.183
4600	107.984	616.314	516.559	458.875	−1085.880	128.318	−1.457
4700	107.989	618.636	518.706	469.674	−1085.564	154.710	−1.719
4800	107.993	620.910	520.812	480.473	−1085.215	181.096	−1.971
4900	107.996	623.137	522.877	491.272	−1084.830	207.473	−2.212
5000	108.000	625.319	524.904	502.072	−1084.405	233.842	−2.443
5100	108.003	627.457	526.894	512.872	−1083.938	260.203	−2.665
5200	108.007	629.555	528.848	523.673	−1083.424	286.553	−2.878
5300	108.010	631.612	530.768	534.473	−1082.862	312.894	−3.084
5400	108.012	633.631	532.654	545.275	−1082.250	339.223	−3.281
5500	108.015	635.613	534.508	556.076	−1081.584	365.541	−3.472
5600	108.018	637.559	536.331	566.878	−1080.865	391.846	−3.655
5700	108.020	639.471	538.124	577.679	−1080.090	418.137	−3.832
5800	108.022	641.350	539.887	588.482	−1079.259	444.415	−4.002
5900	108.025	643.196	541.623	599.284	−1078.370	470.678	−4.167
6000	108.027	645.012	543.331	610.087	−1077.423	496.924	−4.326

PREVIOUS: December 1970 (1 atm) CURRENT· December 1970 (1 bar)

Titanium Chloride ($TiCl_4$) CRYSTAL $M_r = 189.712$ Titanium Chloride ($TiCl_4$) $Cl_4Ti_1(cr)$

$S°(298.15\ K) = 209.069 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 249.05\ K$

$\Delta_f H°(0\ K) = [-818.797]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-815.025]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 9.966\ kJ \cdot mol^{-1}$

Heat of Formation

The enthalpy of formation, $\Delta_f H°(298.15\ K)$, of $TiCl_4(cr)$ is calculated from the corresponding quantity for $TiCl_4(l)$ and the values of $H°(249.05\ K)–H°(298.15\ K)$ for both crystal and liquid.

Heat Capacity and Entropy

The heat capacity of $TiCl_4(cr)$ has been reported by Latimer[1] and by Furukawa.[2] The data from the latter investigation are adopted. These data lead to a value of 44.5 $cal \cdot K^{-1} \cdot mol^{-1}$ for $S°(249.05\ K)$. This compares with Latimer's value[1] of 43.8 $cal \cdot K^{-1} \cdot mol^{-1}$ for the same quantity. The heat capacity of the solid is extrapolated to a value of 18R at 600 K, based on the known heat capacities of $TiBr_4(cr)$ and $TiI_4(cr)$. The hypothetical entropy at 298.15 K is base don the integration of the extrapolated curve and the value at the melting point.

Melting Data

The triple point is reported to be 249.05 K, with a measured enthalpy of fusion of 2.382 $kcal \cdot mol^{-1}$, by Furukawa.[2] Latimer[1] reported values of 248.0 K and 2.233 $kcal \cdot mol^{-1}$ for these quantities. The former data are adopted.

References

[1] W. M. Latimer, J. Amer. Chem. Soc. 44, 90 (1922).
[2] G. T. Furukawa, personal communication, U. S. Nat. Bur. Stand., (1964).

Enthalpy Reference Temperature = T_r = 298.15 K | Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−26.963	−818.797	−818.797	INFINITE
100	84.480	92.582	312.283	−21.970	−820.188	−790.818	413.081
200	112.380	160.341	220.513	−12 034	−818.244	−762.082	199.035
249.046	124.710	186.262	211.264	−6.227	--- CRYSTAL <--> LIQUID ---		
298.15	129.460	209.069	209.069	.000	−815.025	−735.166	128.798
300	129.704	209.871	209.072	.240	−814.958	−734.671	127.918
400	139.540	248.622	214.288	13.733	−811.018	−708.487	92.519
500	145.600	280.480	224.436	28.022	−806.612	−683.357	71.390

PREVIOUS: March 1964 CURRENT: December 1967

Titanium Chloride ($TiCl_4$) $Cl_4Ti_1(cr)$

Titanium Chloride ($TiCl_4$) LIQUID $M_r = 189.692$

$S°(298.15 \text{ K}) = 252.38 \pm 0.4 \text{ J·K}^{-1}\text{·mol}^{-1}$
$T_{fus} = 249.05 \text{ K}$

$\Delta_f H°(298.15 \text{ K}) = -804.2 \pm 4.2 \text{ kJ·mol}^{-1}$
$\Delta_{fus}H° = 9.966 \text{ kJ·mol}^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(TiCl_4, \text{l}, 298.15 \text{ K})$, is calculated from that of $TiCl_4(g)$ and the value of $\Delta_{vap}H°(298.15 \text{ K})$. The value of $\Delta_{vap}H°(298.15 \text{ K})$ is determined from 2nd and 3rd law analyses of fugacity as follows.

Source	Method	T/K	Data Points	$\Delta_{vap}H°(298.15 \text{ K})$ 2nd law	3rd law	Drift cal·K⁻¹·mol⁻¹	$\Delta_f H°(298.15 \text{ K})$ kcal·mol⁻¹
Pike and Foster[1]	Manometric	363−415	18*	9.82 ± 0.02	9.83	0.0 ± 0.1	−192.2
Seryakov *et al.*[2]	Manometric	358−412	8	9.79 ± 0.03	9.84	0.1 ± 0.1	−192.2
Schafer and Zeppenick[3]	Isoteniscope	313−358	17*	9.86 ± 0.02	9.82	−0.1 ± 0.0	−192.2
Schafer and Zeppenick[3]	Isoteniscope	313−357	16**	9.80 ± 0.01	9.82	0.0 ± 0.0	−192.2
Schafer and Zeppenick[3]	Isoteniscope	313−357	16	9.91 ± 0.02	9.83	−0.2 ± 0.1	−192.2
Schafer and Zeppenick[3]	Isoteniscope	312−359	17	9.90 ± 0.02	9.83	−0.2 ± 0.1	−192.2
Weed[4]	Manometric	298−319	***	9.79 ± 0.01	9.82	0.1 ± 0.0	−192.2
Weed[4]	Manometric	298−319	***	9.81 ± 0.01	9.82	0.0 ± 0.0	−192.2
Weed[4]	Spectra	250−302	***	9.69 ± 0.01	9.80	0.4 ± 0.0	−192.2

* Two Points rejected to failure of a statistical test
** Three points rejected due to failure of a statistical test
*** Selected points from extensive data

3rd law analyses of the several vapor pressure sets result in drifts which are proportional to the mean temperatures. Conversion of these data to fugacity eliminates this temperature dependence and the drifts are then scattered randomly about a constant value. This constant value is made to be essentially zero by methods described on the $TiCl_4(g)$ table. The conversion to fugacity was made using Pitzer's method for normal fluids.[5] The calculation was carried out using the value of 45.7 atm. for the critical pressure, P_c, reported by Minzer[6] and estimated values of 643 ± 15 K for the critical temperature, T_c, and 0.23 ± 0.03 for the acentric constant, ω. Schafer *et al.*[7] reported a calorimetric determination of $\Delta_{vap}H°(298.15 \text{ K})$. Their value of 9.9 ± 0.02 kcal·mol⁻¹ was used to check the reliability of their equipment, assuming that the vapor pressure data[3] gave a more accurate determination of $\Delta_{vap}H°(298.15 \text{ K})$. The adopted value of $\Delta_{vap}H°(298.15 \text{ K})$ is 9.82 ± 0.02 kcal·mol⁻¹.

Heat Capacity and Entropy

The entropy and heat capacity of $TiCl_4(l)$ has been measured by Furukawa.[8] His reported values are adopted.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is taken as the temperature at which $K_p = 1$ for the reaction $TiCl_4(l) = TiCl_4(g)$. The vapor pressure data are discussed above.

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Titanium Chloride ($TiCl_4$) $Cl_4Ti_1(l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0							
100							
200	144.710	194.513	265.642	−14.226	−809.576	−760.247	198.556
249.046	144.910	226.279	254.876	−7.121	--- CRYSTAL <--> LIQUID ---		
298.15	145.205	252.379	252.379	.000	−804.165	−737.219	129.158
300	145.220	253.277	252.382	.269	−804.069	−736.804	128.289
400	146.170	295.195	258.090	14.842	−799.049	−715.147	93.389
500	147.080	327.909	268.901	29.504	−794.269	−694.728	72.578
600	147.985	354.805	281.043	44.258	−789.606	−675.260	58.787
700	148.892	377.685	293.255	59.101	−784.994	−656.567	48.994
800	149.800	397.626	305.081	74.036	−780.383	−638.535	41.692
900	150.709	415.323	316.365	89.061	−775.789	−621.080	36.047
1000	151.620	431.249	327.071	104.178	−771.267	−604.133	31.557

PREVIOUS: March 1964 CURRENT: December 1967

Titanium Chloride ($TiCl_4$) CRYSTAL-LIQUID

0 to 249.05 K crystal
above 249.05 K liquid

Refer to the individual tables for details.

M_r = 189.692 Titanium Chloride ($TiCl_4$) $Cl_4Ti_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−37.824	−818.798	−818.798	INFINITE
100	84.480	92.582	420.895	−32.831	−820.189	−790.820	413.082
200	112.380	160.341	274.819	−22.896	−818.245	−762.083	199.036
249.046	124.710	186.262	254.876	−17.088	___ CRYSTAL <−−> LIQUID ___		
249.046	144.910	226.279	254.876	−7.122	TRANSITION		
298.15	145.205	252.379	252.379	.000	−804.165	−737.219	129.158
300	145.220	253.277	252.382	.269	−804.069	−736.804	128.289
400	146.170	295.195	258.090	14.842	−799.049	−715.147	93.389
500	147.080	327.909	268.901	29.504	−794.269	−694.728	72.578
600	147.985	354.805	281.043	44.258	−789.606	−675.260	58.787
700	148.892	377.685	293.255	59.101	−784.994	−656.567	48.994
800	149.800	397.626	305.081	74.036	−780.383	−638.535	41.692
900	150.709	415.323	316.365	89.061	−775.789	−621.080	36.047
1000	151.620	431.249	327.071	104.178	−771.267	−604.133	31.557

PREVIOUS: CURRENT: December 1967

Titanium Chloride ($TiCl_4$) $Cl_4Ti_1(cr,l)$

Titanium Chloride (TiCl$_4$) IDEAL GAS M_r = 189.692 Titanium Chloride (TiCl$_4$) Cl$_4$Ti$_1$(g)

$S°(298.15 \text{ K}) = 354.889 \pm 2.9 \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = -761.58 \pm 3.8 \text{ kJ·mol}^{-1}$

$\Delta_f H°(298.15 \text{ K}) = -763.16 \pm 3.8 \text{ kJ·mol}^{-1}$

Vibrational Frequences and Degeneracies ν, cm^{-1}	ν, cm^{-1}
368 (1)	498.5(3)
111 (2)	131 (3)

Ground State Quantum Weight: 1 $\sigma = 12$
Point Group: T$_d$
Bond Distance: Ti–Cl = 2.185 Å
Bond Angle: Cl–Ti–Cl = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = 4.21057 \times 10^{-112}$ g^3·cm^6

Enthalpy of Formation

$\Delta_f H°(298.15 \text{ K})$ of TiCl$_4$(g) and TiCl$_4$(l) has been measured by several investigators. The results of these measurements are as follows.

Source	Method	Reaction	$\Delta_f H°$(298.15 K), kcal·mol^{-1} TiCl$_4$(l)	TiCl$_4$(g)
Johnson *et al.*[1]	Calorimetric	$Ti(cr) + 2\ Cl_2(g) = TiCl_4(g)$	(−192.2)	−182.4 ± 0.7
Farber and Darnell[2]	Equilibrium	$TiO_2(cr) + 4\ HCl(g) = TiCl_4(g) + 2\ H_2O(g)$	(−192.7)	−182.9 ± 0.5
Skinner and Ruehrwein[3]	Calorimetric	$Ti(cr) + xCl_2(g) = [TiCl_4 + (x-2)Cl_2]$ soln	−190.3 ± 3.0	(−180.5)
Gross *et al.*[4]	Calorimetric	$Ti(cr) + xCl_2(\ell) = [TiCl_4 + (x-2)Cl_2]$ soln	−191.5 ± 0.3	(−181.7)
Krieve *et al.*[5]	Calorimetric	$Ti(cr) + xCl_2(g) = [TiCl_4 + (x-2)Cl_2]$ soln	−190.0 ± 0.4	(−180.2)
Thomsen[6]		$TiCl_4(l) + 2\ H_2O(l) = 4\ HCl_{(0.002\ m)} + TiO_2(cr)$	−194.5	(−184.7)

The chosen value of $\Delta_f H°(298.15 \text{ K})$ is that reported by Johnson *et al.*[1] This investigation has the advantage of being independent of the enthalpy of vaporization of chlorine and any heats of solution in deriving the value of the enthalpy of formation.

Heat Capacity and Entropy

The adopted value for the interatomic distance is that reported by Kimura *et al.*[7] The tetrahedral structure was established by the Raman work of Bhagavantam.[8] The vibrational frequencies determined from the infrared and Raman spectra of TiCl$_4$ by Hawkins and Carpenter[9] are adjusted downward 8 cm^{-1} for ν_2 and ν_4 so that the enthalpies of vaporization determined by both 2nd and 3rd law methods are in agreement. See TiCl$_4$(l) table for details. The principal moments of inertia are: $I_A = I_B = I_C = 74.9515 \times 20^{-39}$ g·cm^2.

References

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0	0.	0.	INFINITE	−21.613	−761.583	−761.583	INFINITE
100	67.436	265.427	432.828	−16.740	−763.094	−751.010	392.287
200	86.118	318.509	363.378	−8.974	−763.321	−738.791	192.953
250	91.800	338.374	356.444	−4.517	−763.265	−732.664	153.082
298.15	95.614	354.889	354.889	0.	−763.162	−726.779	127.329
300	95.735	355.481	354.891	0.177	−763.157	−726.553	126.504
350	98.486	370.458	356.068	5.037	−763.022	−720.463	107.523
400	100.452	383.744	358.712	10.013	−762.875	−714.393	93.290
450	101.892	395.663	362.167	15.073	−762.724	−708.342	82.222
500	102.970	406.457	366.065	20.196	−762.574	−702.307	73.370
600	104.441	425.371	374.417	30.572	−762.288	−690.281	60.094
700	105.366	441.546	382.880	41.066	−762.026	−678.301	50.615
800	105.982	455.658	391.114	51.635	−761.781	−666.358	43.509
900	106.412	468.167	398.994	62.256	−761.591	−654.442	37.983
1000	106.723	479.396	406.482	72.914	−761.528	−642.542	33.563
1100	106.956	489.579	413.581	83.598	−761.659	−630.638	29.947
1200	107.134	498.893	420.307	94.303	−765.972	−618.594	26.927
1300	107.273	507.474	426 687	105.024	−765.777	−606.321	24.362
1400	107.384	515.428	432.745	115.757	−765.666	−594.060	22.165
1500	107.474	522.840	438.507	126.500	−765.655	−581.804	20.260
1600	107.547	529.779	443.997	137.251	−765.758	−569.544	18.594
1700	107.609	536.301	449.237	148.009	−765.990	−557.274	17.123
1800	107.660	542.453	454.246	158.773	−766.366	−544.987	15.815
1900	107.703	548.275	459.043	169.541	−766.900	−532.674	14.644
2000	107.741	553.801	463.644	180.313	−782.294	−519.876	13.578
2100	107.773	559.058	468.063	191.089	−783.940	−506.714	12.604
2200	107.801	564.072	472.314	201.867	−785.606	−493.474	11.717
2300	107.825	568.865	476.409	212.649	−787.297	−480.157	10.905
2400	107.846	573.454	480.357	223.432	−789.015	−466.767	10.159
2500	107.865	577.857	484.170	234.218	−790.762	−453.304	9.471
2600	107.882	582.088	487.855	245.005	−792.542	−439.771	8.835
2700	107.897	586.160	491.421	255.794	−794.357	−426.168	8.245
2800	107.910	590.084	494.875	266.584	−796.208	−412.498	7.695
2900	107.922	593.871	498.224	277.376	−798.097	−398.761	7.182
3000	107.933	597.530	501.474	288.169	−800.024	−384.958	6.703
3100	107.943	601.069	504.630	298.963	−801.988	−371.090	6.253
3200	107.951	604.496	507.697	309.757	−803.989	−357.158	5.830
3300	107.960	607.818	510.681	320.553	−806.025	−343.163	5.432
3400	107.967	611.041	513.586	331.349	−808.093	−329.106	5.056
3500	107.974	614.171	516.415	342.146	−810.191	−314.988	4.701
3600	107.980	617.213	519.173	352.944	−812.315	−300.809	4.365
3700	107.986	620.171	521.863	363.742	−1223.559	−278.783	3.936
3800	107.991	623.051	524.488	374.541	−1224.487	−253.236	3.481
3900	107.996	625.857	527.051	385.340	−1225.483	−227.664	3.049
4000	108.000	628.591	529.556	396.140	−1226.541	−202.066	2.639
4100	108.004	631.258	532.004	406.940	−1227.654	−176.440	2.248
4200	108.008	633.860	534.398	417.741	−1228.815	−150.787	1.875
4300	108.012	636.402	536.741	428.542	−1230.017	−125.105	1.520
4400	108.015	638.885	539.034	439.343	−1231.253	−99.395	1.180
4500	108.019	641.312	541.280	450.145	−1232.517	−73.657	0.855
4600	108.021	643.687	543.481	460.947	−1233.802	−47.890	0.544
4700	108.024	646.010	545.638	471.749	−1235.101	−22.096	0.246
4800	108.027	648.284	547.752	482.552	−1236.408	3.726	−0.041
4900	108.029	650.512	549.827	493.355	−1237.718	29.576	−0.315
5000	108.032	652.694	551.863	504.158	−1239.024	55.452	−0.579
5100	108.034	654.833	553.861	514.961	−1240.322	81.355	−0.833
5200	108.036	656.931	555.823	525.765	−1241.605	107.283	−1.078
5300	108.038	658.989	557.750	536.568	−1242.871	133.235	−1.313
5400	108.040	661.009	559.643	547.372	−1244.113	159.211	−1.540
5500	108.041	662.991	561.504	558.176	−1245.329	185.210	−1.759
5600	108.043	664.938	563.334	568.980	−1246.515	211.230	−1.970
5700	108.044	666.850	565.134	579.785	−1247.666	237.272	−2.174
5800	108.046	668.729	566.904	590.589	−1248.781	263.333	−2.372
5900	108.047	670.576	568.645	601.394	−1249.857	289.413	−2.562
6000	108.049	672.392	570.359	612.199	−1250.891	315.511	−2.747

PREVIOUS: December 1967 (1 atm)   CURRENT: December 1967 (1 bar)

Tungsten Chloride (WCl_4) CRYSTAL $M_r = 325.662$ Tungsten Chloride (WCl_4) $Cl_4W_1(cr)$

$\Delta_fH°(0\ K)$ = Unknown
$\Delta_fH°(298.15\ K) = -443.086 \pm 62.8\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = [198.322]\ J\cdot K^{-1}\cdot mol^{-1}$
$T_d = [771]\ K$

Heat of Formation

The heat of formation, $\Delta_fH°(WCl_4$, cr, 298.15 K) = $-105.9\ kcal\cdot mol^{-1}$, is calculated from $\Delta_rH°(298.15\ K) = 58\ 9\ kcal\cdot mol^{-1}$ for $3\ WCl_4(cr) = WCl_2(cr) + 2\ WCl_5(g)$ The value of $\Delta_rH°$(298 15 K) is calculated by the third law method from decomposition pressure data in the temperature range from 354 °C to 436 °C reported by Shchukarev *et al.*[1] The second law, $\Delta_rH°(298.15\ K) = 73.6 \pm 7.9\ kcal\cdot mol^{-1}$ and the third law drift is $-24 \pm 12\ cal\cdot K^{-1}\cdot mol^{-1}$ which would correspond to a total entropy discrepancy of $-8 \pm 4\ cal\cdot K^{-1}\cdot mol^{-1}$ per mole of WCl_4. This entropy discrepancy is probably within the combined uncertainty of the data and the estimated entropies for the three species. Shchukarev *et al.*[2] have shown that decomposition pressures are essentially independent of the composition in the solid phase until WCl_4(cr) is almost completely decomposed to WCl_2(cr). This is consistent with the assumption of solid phase activities of unity which we have used in the equilibrium analysis.

Heat Capacity and Entropy

$C_p°(298.15\ K) = 6.2\ cal\cdot K^{-1}\ g\cdot atom^{-1}$ and $C_p°(700\ K) = 7.25\ cal\cdot K^{-1}\ g\cdot atom^{-1}$ are estimated using the method described by Kubaschewski and Evans.[3] Between 298 and 700 K, which is near the decomposition temperature, the heat capacity is obtained by linear interporation.

The entropy of WCl_4(cr), $S°(298.15\ K) = 47.4\ cal\cdot K^{-1}\cdot mol^{-1}$, is estimated by the method of Latimer.[4]

Temperature of Decomposition

$T_{dcm} = 771$ K (f = atm) is calculated as the temperature at which the Gibbs energy change of the reaciton $3\ WCl_4(cr) = WCl_2(cr) + 2\ WCl_5(g)$ approaches zero. We have also derived an approximate value of decomposition temperature, $T_{dcm} = 744$ K, by extrapolation to one atmosphere total pressure of a log P versus $1/T$ fit of the decomposition pressure data reported by Shchukarev *et al.*[5] The difference between the two decomposition temperatures is related to the second law entropy and the adopted entropy.

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	129.704	198.322	198.322	0.	−443.086	−359.456	62.975
300	129.830	199.124	198.324	0.240	−443.016	−358.937	62.496
400	135.290	237.222	203.482	13.496	−439.164	−331.485	43.288
500	140.750	267.997	213.401	27.298	−435.019	−305.038	31.867
600	146.210	294.142	224.732	41.646	−430.492	−279.460	24.329
700	151.670	317.090	236.319	56.540	−425.543	−254.673	19.004
800	157.130	337.700	247.724	71.981	−420.147	−230.626	15.058
900	162.507	356.526	258.782	87.970	−414.287	−207.283	12.030
1000	167.025	373.888	269.436	104.452	−408.012	−184.616	9.643
1100	170.875	389.994	279.672	121.353	−401.390	−162.594	7.721
1200	173.929	404.997	289.498	138.598	−394.493	−141.188	6.146
1300	176.439	419.019	298.928	156.119	−387.387	−120.366	4.836
1400	178.657	432.178	307.981	173.876	−380.110	−100.098	3.735
1500	180.623	444.572	316.678	191.841	−372.689	−80.355	2.798
1600	182.422	456.287	325.040	209.995	−365.145	−61.111	1.995
1700	184.096	467.397	333.090	228.321	−357.493	−42.343	1.301
1800	185 770	477.967	340.848	246.815	−349.738	−24.028	0.697
1900	187.276	488.052	348.332	265.468	−341.892	−6.147	0.169
2000	188.698	497.695	355.561	284.268	−333.969	11.319	−0.296

PREVIOUS: September 1962   CURRENT: December 1966

Tungsten Chloride (WCl$_4$) IDEAL GAS $M_r = 325.662$ Tungsten Chloride (WCl$_4$) Cl$_4$W$_1$(g)

$S°(298.15\ K) = 379.171\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -335.256 \pm 33\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -335.975 \pm 33\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i
0	[3]
[10000]	[3]
[30000]	[3]

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
[380](1)	[390](3)
[110](2)	[115](3)

Ground State Quantum Weight: [3] $\sigma = [12]$
Point Group: [T$_d$]
Bond Distance: W–Cl = [2.26] Å
Bond Angle: Cl–W–Cl = [109.47]°
Product of the Moments of Inertia: $I_A I_B I_C = [5.154 \times 10^{-112}]\ g^3 \cdot cm^6$

Heat of Formation

The heat of formation, $\Delta_f H°(WCl_4, g, 298.15\ K) = -80.3\ kcal \cdot mol^{-1}$, is calculated from $\Delta_r H° = 37.7\ kcal \cdot mol^{-1}$ for $WCl_6(g) \rightarrow WCl_4(g) + Cl_2(g)$. The value of $\Delta_f H°(298.15\ K)$ is calculated by the third law method from the equation for log K_p given by Shchukarev and Suvorov.[1] The second law $\Delta_f H°(298.15\ K)$ is 43.6 kcal·mol^{-1} and the third law drift is $-9.6\ cal \cdot K^{-1} \cdot mol^{-1}$.

Heat Capacity and Entropy

The molecular configuration is assumed to be tetrahedral similar to those of SiCl$_4$, TiCl$_4$, VCl$_4$, GeCl$_4$, ZrCl$_4$, SnCl$_4$, PbCl$_4$. The bond distance is estimated to be the same as that in WCl$_6$(g). The three principal moments of inertia are: $I_A = I_B = I_C = 80.18 \times 10^{-39}\ g \cdot cm^2$.

All vibrational frequencies are estimated from those of SiCl$_4$, TiCl$_4$, VCl$_4$, GeCl$_4$, SnCl$_4$ and PbCl$_4$ given by Nakamoto.[2]

If it is considered that the metal atoms are effectively ionized, then the W^{4+} will have 2 d electrons in a field of chloride ions. The electronic splitting would be roughly the inverse of that in NiCl$_2$(g), as given by DeKock and Gruen,[3] where Ni has a d^8 configuration. By analogy with the splitting in NiCl$_2$, the low lying electronic levels are estimated to be 10000 cm^{-1} and 30000 cm^{-1}, both triplets.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0	0.	0.	INFINITE	−22.616	−335.256	−335.256	INFINITE
100	70.716	285.257	460.891	−17.563	−336.680	−326.443	170.516
200	90.681	341.319	388.116	−9.359	−336.559	−316.182	82.578
250	95.721	362.138	380.897	−4.690	−336.284	−311.119	65.005
298.15	98.865	379.285	379.285	0.	−335.975	−306.300	53.662
300	98.963	379.897	379.287	0.183	−335.963	−306.115	53.299
350	101.124	395.325	380.501	5.189	−335.619	−301.168	44.947
400	102.620	408.932	383.221	10.284	−335.265	−296.270	38.689
450	103.691	421.084	386.765	15.444	−334.910	−291.417	33.827
500	104.481	432.052	390.754	20.649	−334.557	−286.604	29.941
600	105.540	451.203	399.279	31.154	−333.874	−277.078	24.122
700	106.197	467.525	407.891	41.744	−333.229	−267.664	19.973
800	106.630	481.736	416.253	52.386	−332.630	−258.338	16.868
900	106.931	494.314	424.241	63.065	−332.081	−249.085	14.457
1000	107.148	505.592	431.822	73.770	−331.584	−239.891	12.531
1100	107.312	515.812	439.000	84.493	−331.140	−230.744	10.957
1200	107.439	525.155	445.796	95.231	−330.750	−221.634	9.647
1300	107.544	533.759	452.236	105.980	−330.415	−212.555	8.541
1400	107.635	541.732	458.347	116.739	−330.136	−203.500	7.593
1500	107.719	549.161	464.156	127.507	−329.913	−194.463	6.772
1600	107.801	556.116	469.689	138.283	−329.746	−185.438	6.054
1700	107.885	562.654	474.967	149.067	−329.636	−176.423	5.421
1800	107.974	568.823	480.011	159.860	−329.583	−167.412	4.858
1900	108.069	574.663	484.841	170.662	−329.588	−158.403	4.355
2000	108.173	580.209	489.472	181.474	−329.651	−149.392	3.902
2100	108.284	585.489	493.919	192.297	−329.776	−140.376	3.492
2200	108.403	590.529	498.197	203.131	−329.962	−131.353	3.119
2300	108.530	595.351	502.317	213.978	−330.212	−122.320	2.778
2400	108.663	599.973	506.290	224.838	−330.529	−113.275	2.465
2500	108.802	604.411	510.127	235.711	−330.913	−104.215	2.177
2600	108.945	608.681	513.836	246.598	−331.365	−95.138	1.911
2700	109.091	612.796	517.425	257.500	−331.913	−86.042	1.665
2800	109.239	616.766	520.903	268.416	−332.593	−76.924	1.435
2900	109.388	620.602	524.275	279.348	−333.444	−67.778	1.221
3000	109.537	624.313	527.548	290.294	−334.495	−58.600	1.020
3100	109.684	627.907	530.728	301.255	−335.789	−49.383	0.832
3200	109.830	631.391	533.819	312.231	−337.355	−40.120	0.655
3300	109.972	634.773	536.827	323.221	−339.218	−30.803	0.488
3400	110.110	638.058	539.757	334.225	−341.410	−21.425	0.329
3500	110.245	641.252	542.611	345.243	−343.994	−11.978	0.179
3600	110.374	644.360	545.395	356.274	−347.062	−2.449	0.036
3700	110.499	647.385	548.110	367.318	−385.476	7.363	−0.104
3800	110.618	650.334	550.762	378.373	−386.215	17.990	−0.247
3900	110.732	653.209	553.352	389.441	−386.955	28.636	−0.384
4000	110.840	656.013	555.884	400.520	−387.691	39.302	−0.513
4100	110.942	658.752	558.359	411.609	−388.420	49.986	−0.637
4200	111.039	661.426	560.782	422.708	−389.136	60.688	−0.755
4300	111.130	664.040	563.153	433.816	−389.835	71.406	−0.867
4400	111.215	666.596	565.475	444.934	−390.513	82.141	−0.975
4500	111.295	669.096	567.750	456.059	−391.165	92.890	−1.078
4600	111.370	671.543	569.980	467.193	−391.786	103.654	−1.177
4700	111.440	673.939	572.166	478.333	−392.373	114.430	−1.272
4800	111.505	676.286	574.311	489.480	−392.922	125.219	−1.363
4900	111.566	678.586	576.416	500.634	−393.430	136.020	−1.450
5000	111.622	680.840	578.482	511.793	−393.892	146.829	−1.534
5100	111.674	683.051	580.510	522.958	−394.308	157.648	−1.615
5200	111.722	685.220	582.503	534.128	−394.673	168.474	−1.692
5300	111.766	687.349	584.461	545.302	−394.985	179.307	−1.767
5400	111.807	689.438	586.386	556.481	−395.243	190.145	−1.839
5500	111.844	691.490	588.279	567.664	−395.444	200.988	−1.909
5600	111.879	693.506	590.140	578.850	−395.588	211.833	−1.976
5700	111.910	695.486	591.971	590.039	−395.672	222.681	−2.041
5800	111.939	697.433	593.772	601.232	−395.697	233.530	−2.103
5900	111.966	699.347	595.545	612.427	−395.661	244.378	−2.164
6000	111.990	701.229	597.291	623.625	−395.563	255.225	−2.222

PREVIOUS December 1966 (1 atm) CURRENT: December 1966 (1 bar)

Zirconium Chloride ($ZrCl_4$) CRYSTAL M_r = 233.032 Zirconium Chloride ($ZrCl_4$) $Cl_4Zr_1(cr)$

$S°(298.15 K) = 181.42 \pm 0.7 J\cdot K^{-1}\cdot mol^{-1}$
$T_{fus} = 710 \pm 2 J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0 K) = -981.59 \pm 1.7 kJ\cdot mol^{-1}$
$\Delta_f H°(298.15 K) = -980.52 \pm 1.7 kJ\cdot mol^{-1}$
$\Delta_{fus} H° = 50.2 \pm 12.6 kJ\cdot mol^{-1}$

Enthalpy of Formation

Gal'chenko *et al.*[1] determined enthalpy of formation of $ZrCl_4(cr)$ by the direct chlorination of highly pure Zr metal in a bomb calorimeter. Complete chlorination of the metal was accomplished as indicated by the absence of unreacted metal and of lower chlorides. They reported $\Delta_f H°(ZrCl_4$, cr, 298.15 K) = −234.17 ± 0.28 kcal·mol^{-1}.

Gal'chenko *et al.*[2] had also earlier determined the enthalpy of formation of $ZrCl_4(cr)$ by a similar technique and reported −234.35 ± 2.1 kcal·mol^{-1}. Gross *et al.*[6] measured calorimetrically the chlorination of Zr(cr) with liquid chlorine. His results led to $\Delta_f H°$(298.15 K) = −234.7 ± 0.4 kcal·mol^{-1} for $ZrCl_4(cr)$. We adopt $\Delta_f H°$(298.15 K) = −234.35 ± 0.4 kcal·mol^{-1} which is a weighted mean of these three studies. This adopted value is identical to that suggested by NBS.[4]

Less reliable studies leading to $\Delta_f H°$(298.15 K) values have been reported by Siemonsen and Siemonsen,[7] and Beck.[8] Equilibrium studies by Hildenbrand *et al.*[3] and Morozov and Korshunov[5] suggest $\Delta_f H°$(298.15 K) values 1–3 kcal·mol^{-1} less negative than our adopted value.

Heat Capacity and Entropy

Todd[9] measured the low temperature heat capacities from 52.6 to 296.7 K, and made an extrapolation to 0 K which yielded an entropy of 8.12 cal·K^{-1}·mol^{-1} at 51 K. We adopt the measured heat capacities but make our own extrapolation to 0 K, based on the ratio of the measured heat capacities of ZrF_4,[10] TiF_4[11] and $TiCl_4$[12] from 6 to 50 K. This extrapolation gives $S°$(50 K) = 6.758 ± 0.7 cal·K^{-1}·mol^{-1} which is adopted. Coughlin and King[13] measured high temperature enthalpy data from 335.9 to 566.8 K by drop calorimetry. Their data are smoothly joined with Todd's low temperature heat capacities.

Fusion Data

The melting point, T_{fus} = 710 ± 2 K, has been observed by Rahlfs and Fischer,[14] Palko *et al.*,[15] and Denisova *et al.*[16, 17] Nisel'son[18] observed a melting temperature of 708.7 K. Heat of melting data may be extracted from Palko *et al.*[15] and Denisova *et al.*[16, 17] A weighted average $\Delta_{fus}H°$ = 12 ± 3 kcal·mol^{-1} is adopted for the heat of melting.

Sublimation Data

Several sets of sublimation studies are summarized below, using a 2nd and 3rd analysis.

Source	Method	Data Points	T/K	$\Delta_{sub}H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
14	static	11	535–607	27.36 ± 0.43	26.31 ± 0.13	−1.9 ± 0.8
15	static (diaphragm)	50^a	503–575	25.75 ± 0.20	26.39 ± 0.17	1.1 ± 0.3
	static (cap. bridge)	36^b	580–689	25.87 ± 0.28	26.40 ± 0.16	0.8 ± 0.4
19	glass Bourdon gage	eqn	503–603	26.19	26.33	0.3
16	static	17^c	625–709	25.51 ± 0.34	26.42 ± 0.11	1.3 ± 0.5
20	mass spec.	eqn	373–448	27.14	26.66	−1.2
21	—	eqn	376–493	26.59	26.44	−0.4

(a)3, (b)2, (c)1 points rejected due to failure of a statistical test.

A mean of the 3rd law values, $\Delta_{sub}H°$(298.15 K) = 26.42 ± 0.12 kcal·mol^{-1}, is adopted. The sublimation temperature, T_{sub}, is obtained from the Gibbs energy crossover between the crystal and gas. Since T_{sub} is lower than T_{fus}, the liquid phase is thermodynamically unstable at normal conditions.

In analyzing the vapor pressures for the sublimation studies, corrections were made for non-ideality by means of the equation $\Delta G°/T = -R \ln p - Bp/T$. The Bertholet equation of state and the critical constants T_c = 776.65 K and p_c = 57.4 atm as determined by Nisel'son and Sokolova[22] are used to calculate B.

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Enthalpy Reference Temperature = T_r = 298.15 K						Standard State Pressure = $p°$ = 0.1 MPa	
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−24.924	−981.585	−981.585	INFINITE
100	77.990	70.509	278.997	−20.849	−984.220	−952.064	497.307
200	108.282	135.750	192.067	−11.263	−982.903	−920.258	240.347
298.15	119.788	181.418	181.418	0.	−980.520	−889.999	155.924
300	119.913	182.160	181.421	0.222	−980.471	−889.438	154.865
400	125.394	217.491	186.201	12.516	−977.676	−859.509	112.240
500	128.700	245.848	195.387	25.230	−974.729	−830.306	86.741
600	131.127	269.533	205.825	38.225	−971.690	−801.705	69.795
700	133.135	289.899	216.415	51.439	−968.586	−773.619	57.728
800	134.976	307.799	226.741	64.846	−965.428	−745.981	48.708
900	136.649	323.794	236.652	78.428	−962.235	−718.742	41.715
1000	138.239	338.274	246.101	92.173	−959.019	−691.859	36.139

PREVIOUS: December 1969 CURRENT: June 1975

Zirconium Chloride ($ZrCl_4$) IDEAL GAS $M_r = 233.032$ Zirconium Chloride ($ZrCl_4$) $Cl_4Zr_1(g)$

$S°(298.15\ K) = 367.72 \pm 0.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -868.68 \pm 2.1\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -869.98 \pm 2.1\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
377(1)	418(3)
98(2)	113(3)

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distance: 2.32 ± 0.02 Å
Bond Angle: Cl–Zr–Cl = 109.4712°
Product of the Moments of Inertia: $I_AI_BI_C = 6.03340 \times 10^{-112}\ g^3{\cdot}cm^6$

Enthalpy of Formation

The enthalpy of formation of gaseous $ZrCl_4$, $\Delta_fH°(298.15\ K) = -207.76 \pm 0.5\ kcal{\cdot}mol^{-1}$ is calculated from the enthalpies of formation and sublimation of the crystal.[1]

Hildenbrand *et al.*[14] determined the equilibrium constants by the transpiration method for the reaction: $ZrO_2(cr) + 4\ HCl(g) = ZrCl_4(g) + 2\ H_2O(g)$. 2nd and 3rd law analyses for their data are given below. The enthalpy of formation derived from this study is in fair agreement with the value adopted.

Series	Data Points	T/K	$\Delta_rH°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_fH°(298.15\ K)$ kcal·mol^{-1}
I	10	1171–1373	28.94 ± 0.44	29.16 ± 0.15	0.17 ± 0.34	−205.80
II	9	1169–1374	31.36 ± 0.60	29.65 ± 0.28	−1.19 ± 0.47	−205.11

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark *et al.*,[2,3] who recorded the Raman spectra of $ZrCl_4$ in the vapor phase (380–420 °C). These studies indicated that $ZrCl_4$ is a tetrahedral monomer in the vapor phase. Shimanouchi,[4] in his compilation of molecular vibrational frequencies, adopted the values of Clark *et al.*[2,3] for $ZrCl_4(g)$. Pontrelli[5] also observed in the Raman spectra all four fundamental vibrational frequencies (376, 99, 418, and 110 cm^{-1}). These values are in excellent agreement with those of Clark *et al.*[2,3]

Other experimental studies involving the vibrational frequencies are as follows. Wilmshurst[6] observed one fundamental vibrational frequency (421 cm^{-1}) in the infrared spectrum of $ZrCl_4$ vapor, while Buchler *et al.*[7] found the same fundamental mode at 423 cm^{-1}. Delwaulle and Francois[8] observed the symmetric stretching vibration (383 cm^{-1}) from the Raman spectra of $ZrCl_4$ in PCl_5 and $POCl_3$. Bobovich[9] reported the symmetric stretching vibration (315 cm^{-1}) from a partially polarized band in his Raman spectrometric studies.

Spiridonov *et al.*[10] measured the bond distance Zr–Cl = 2.32 ± 0.02 Å in the vapor phase by electron diffraction. The molecule was also found to be a regular tetrahedron. The same bond distance was also reported by Lister and Sutton[11] and Kimura *et al.*[12] Rabitz and Fischer,[13] through vapor density measurements, had earlier concluded that $ZrCl_4$ was monomeric in the vapor phase. The principal moments of inertia are $I_A=I_B=I_C=84.4995 \times 10^{-19}\ g{\cdot}cm^2$.

Much literature has been published on the inter–relationships between force constants and vibrational frequencies. Since the majority of these articles are based on estimated frequencies, they will not be further discussed or referenced. The same situation is true for thermodynamic tabulations of $ZrCl_4(g)$. One exception is that Clark *et al.*[2] calculated thermodynamic properties based on their experimental vibrational frequencies. Their tabulation is identical to ours in the range 100–1000 K.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−22.561	−868.681	−868.681	INFINITE
100	70.794	274.385	448.659	−17.427	−870.258	−858.489	448.429
200	89.827	330.054	376.481	−9.285	−870.384	−846.599	221.109
250	94.964	350.691	369.317	−4.656	−870.209	−840.671	175.649
298.15	98.234	367.716	367.716	0.	−869.979	−835.003	146.289
300	98.336	368.324	367.718	0.182	−869.970	−834.786	145.349
350	100.611	383.665	368.925	5.159	−869.701	−828.943	123.713
400	102.199	397.209	371.630	10.232	−869.419	−823.139	107.491
450	103.342	409.316	375.157	15.372	−869.136	−817.371	94.878
500	104.188	420.250	379.128	20.561	−868.857	−811.635	84.791
600	105.328	439.355	387.620	31.041	−868.332	−800.240	69.667
700	106.036	455.649	396.203	41.612	−867.872	−788.929	58.871
800	106.505	469.840	404.540	52.241	−867.492	−777.679	50.777
900	106.831	482.405	412.507	62.908	−867.213	−766.470	44.485
1000	107.066	493.673	420.070	73.604	−867.047	−755.286	39.452
1100	107.241	503.886	427.232	84.320	−867.003	−744.113	35.335
1200	107.374	513.224	434.015	95.051	−870.797	−732.717	31.894
1300	107.479	521.822	440.443	105.793	−870.467	−721.224	28.979
1400	107.562	529.791	446.544	116.546	−870.189	−709.755	26.481
1500	107.629	537.214	452.344	127.305	−869.975	−698.303	24.317
1600	107.684	544.162	457.868	138.071	−869.835	−686.863	22.424
1700	107.730	550.692	463.138	148.842	−869.783	−675.430	20.753
1800	107.768	556.851	468.175	159.617	−869.829	−663.996	19.269
1900	107.801	562.678	472.996	170.395	−869.985	−652.558	17.940
2000	107.829	568.208	477.620	181.177	−870.265	−641.108	16.744
2100	107.853	573.470	482.060	191.961	−870.682	−629.640	15.661
2200	107.874	578.488	486.330	202.747	−892.570	−617.403	14.659
2300	107.892	583.283	490.442	213.536	−893.714	−604.870	13.737
2400	107.908	587.876	494.407	224.326	−894.886	−592.287	12.891
2500	107.922	592.281	498.234	235.117	−896.088	−579.654	12.111
2600	107.934	596.514	501.933	245.910	−897.323	−566.972	11.391
2700	107.945	600.588	505.512	256.704	−898.593	−554.242	10.722
2800	107.955	604.513	508.978	267.499	−899.900	−541.465	10.101
2900	107.964	608.302	512.338	278.295	−901.244	−528.640	9.522
3000	107.972	611.962	515.598	289.092	−902.627	−515.768	8.980
3100	107.979	615.503	518.764	299.889	−904.048	−502.850	8.473
3200	107.986	618.931	521.841	310.688	−905.505	−489.885	7.997
3300	107.992	622.254	524.834	321.487	−906.998	−476.873	7.548
3400	107.998	625.478	527.747	332.286	−908.524	−463.817	7.126
3500	108.003	628.609	530.584	343.086	−910.079	−450.715	6.727
3600	108.007	631.651	533.349	353.887	−911.660	−437.567	6.349
3700	108.012	634.611	536.046	364.687	−913.263	−424.376	5.991
3800	108.016	637.491	538.678	375.489	−914.883	−411.142	5.652
3900	108.019	640.297	541.248	386.291	−916.517	−397.864	5.329
4000	108.023	643.032	543.759	397.093	−918.157	−384.544	5.022
4100	108.026	645.699	546.213	407.895	−919.800	−371.183	4.729
4200	108.029	648.302	548.612	418.698	−921.441	−357.783	4.450
4300	108.031	650.844	550.960	429.501	−923.073	−344.343	4.183
4400	108.034	653.328	553.259	440.304	−924.692	−330.865	3.928
4500	108.036	655.756	555.510	451.108	−926.294	−317.351	3.684
4600	108.038	658.130	557.715	461.911	−927.872	−303.801	3.450
4700	108.040	660.454	559.876	472.715	−929.423	−290.219	3.225
4800	108.042	662.728	561.995	483.519	−1491.880	−264.985	2.884
4900	108.044	664.956	564.074	494.324	−1493.016	−239.413	2.552
5000	108.046	667.139	566.113	505.128	−1494.130	−213.818	2.234
5100	108.047	669.279	568.115	515.933	−1495.217	−188.200	1.928
5200	108.049	671.377	570.081	526.738	−1496.274	−162.563	1.633
5300	108.050	673.435	572.012	537.543	−1497.295	−136.905	1.349
5400	108.052	675.455	573.909	548.348	−1498.277	−111.227	1.076
5500	108.053	677.437	575.773	559.153	−1499.217	−85.532	0.812
5600	108.054	679.384	577.606	569.958	−1500.111	−59.821	0.558
5700	108.055	681.297	579.408	580.764	−1500.958	−34.094	0.312
5800	108.056	683.176	581.181	591.569	−1501.754	−8.352	0.075
5900	108.058	685.023	582.926	602.375	−1502.497	17.402	−0.154
6000	108.058	686.839	584.643	613.181	−1503.185	43.169	−0.376

PREVIOUS. June 1975 (1 atm) CURRENT: June 1975 (1 bar)

Zirconium Chloride ($ZrCl_4$) $Cl_4Zr_1(g)$

Molybdenum Chloride ($MoCl_5$) CRYSTAL $M_r = 273.205$ Molybdenum Chloride ($MoCl_5$) $Cl_5Mo_1(cr)$

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = [238.488 \pm 12.6]\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -527.184 \pm 8.4\ kJ\cdot mol^{-1}$

$T_{fus} = 467\ K$ $\Delta_f H°[18.8 \pm 6.3]\ kJ\cdot mol^{-1}$

Heat of Formation

The heat of formation is obtained from Shchukarev *et al.*[1] The authors derived the $\Delta_f H°(MoCl_5, cr, 298.15\ K) = -126\ kcal\cdot mol^{-1}$ by measuring the heat of solution of $MoCl_5$ in NaOH(aq), which was compared with the heats of solution of MoO_3 and NaCl measured in the same solvent.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with that of WCl_5(cr). $S°(298.15\ K)$ is estimated as $57\ cal\cdot K^{-1}\cdot mol^{-1}$ the vapor pressure data for $MoCl_5(cr) \rightarrow MoCl_5(g)$ measured by Shchukarev *et al.*[2]

Melting Data

Refer to liquid table.

References

[1] S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, Zh. Neorg. Khim. 5, 1650 (1960).

[2] S. A. Shchukarev, I. V. Vasil'kova and B. N. Sharupin, *J. Gen. Chem. USSR (English Trnsl.)* **26**, 2335 (1956).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	155.645	238.488	238.488	0.	−527.184	−423.483	74.192
300	155.728	239.451	238.491	0.288	−527.097	−422.840	73.623
400	167.360	285.854	244.739	16.446	−522.070	−388.825	50.775
467.000	174.929	312.345	252.573	27.913	--- CRYSTAL <--> LIQUID ---		
500	178.657	324.413	256.920	33.747	−516.246	−356.170	37.209
600	189.954	358.022	271.026	52.198	−509.492	−324.773	28.274
700	198.740	387.996	285.634	71.654	−501.888	−294.578	21.982
800	205.016	414.962	300.143	91.855	−493.657	−265.517	17.337
900	209.618	439.388	314.279	112.598	−484.982	−237.517	13.785
1000	212.966	461.657	327.920	133.737	−475.997	−210.500	10.995

PREVIOUS: CURRENT: December 1968

Molybdenum Chloride ($MoCl_5$) LIQUID $M_r = 273.205$

$S°(298.15\ K) = [273.805]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$T_{fus} = 467\ K$

$T_{vap} = 537\ K$

$\Delta_f H°(298.15\ K) = [-510.117]\ kJ{\cdot}mol^{-1}$

$\Delta_{fus} H° = [18.828 \pm 6.3]\ kJ{\cdot}mol^{-1}$

$\Delta_{vap} H° = [50.208]\ kJ{\cdot}mol^{-1}$

Heat of Formation

The heat of formation is obtained from $\Delta_f H°(cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference between $H°(T_{fus};298.15)$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed constant and estimated as 42 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ or 7 $cal{\cdot}K^{-1}\ g{\cdot}atom^{-1}$. The entropy is obtained in a manner analogous to that of the heat of formation.

Heat of Melting Data

T_{fus} is taken from Shchukarev *et al.*[1] $\Delta_{fus} H°$ is estimated by comparison with that of $WCl_5(cr)$.

Heat of Vaporization Data

T_{vap} is the temperature at which the difference between the Gibbs energy of formation for $MoCl_5(l)$ and $MoCl_5(g)$ approaches zero. The difference between $\Delta_f H°(MoCl_5, l, 537\ K)$ and $\Delta_f H°(MoCl_5, g, 537\ K)$ is $\Delta_{vap} H°$.

Reference

[1] S. A. Shchukarev, G. I. Novikov, A. V. Suvorov and V. K. Moksimov, Russ. J. Inorg. Chem. (English Transl.) 4, 935 (1959).

Molybdenum Chloride ($MoCl_5$) $Cl_5Mo_1(l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	175.728	273.807	273.807	0.	−510.114	−416.944	73.047
300	175.728	274.894	273.811	0.325	−509.991	−416.366	72.496
400	175.728	325.448	280.703	17.898	−503.548	−386.141	50.425
467.000	175.728	352.662	289.125	29.672	--- CRYSTAL <--> LIQUID ---		
500	175.728	364.661	293.719	35.471	−497.452	−357.500	37.348
600	175.728	396.700	308.294	53.043	−491.576	−330.064	28.735
700	175.728	423.788	322.908	70.616	−485.856	−303.600	22.655
800	175.728	447.254	337.017	88.189	−480.253	−277.947	18.148
900	175.728	467.951	350.438	105.762	−474.748	−252.990	14.683
1000	175.728	486.466	363.131	123.335	−469.329	−228.642	11.943
1100	175.728	503.215	375.117	140.907	−463.995	−204.832	9.727
1200	175.728	518.505	386.438	158.480	−458.745	−181.504	7.901

PREVIOUS: CURRENT: December 1968

Molybdenum Chloride ($MoCl_5$) $Cl_5Mo_1(l)$

Molybdenum Chloride ($MoCl_5$) CRYSTAL-LIQUID

0 to 467 K crystal
above 467 K liquid

Refer to the individual tables for details.

M_r = 273.205 Molybdenum Chloride ($MoCl_5$) $Cl_5Mo_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_fH°$ (kJ·mol⁻¹)	$\Delta_fG°$ (kJ·mol⁻¹)	log K_f
0							
100							
200							
298.15	155.645	238.488	238.488	0.	−527.184	−423.483	74.192
300	155.728	239.451	238.491	0.288	−527.097	−422.840	73.623
400	167.360	285.854	244.739	16.446	−522.070	−388.825	50.775
467.000	174.929	312.345	252.573	27.913	CRYSTAL <--> LIQUID TRANSITION		
467.000	175.728	352.662	252.573	46.741			
500	175.728	364.661	259.580	52.540	−497.452	−357.500	37.348
600	175.728	396.700	279.844	70.113	−491.576	−330.064	28.735
700	175.728	423.788	298.522	87.686	−485.856	−303.600	22.655
800	175.728	447.254	315.680	105.259	−480.253	−277.947	18.148
900	175.728	467.951	331.472	122.832	−474.748	−252.990	14.683
1000	175.728	486.466	346.062	140.404	−469.329	−228.642	11.943
1100	175.728	503.215	359.599	157.977	−463.995	−204.832	9.727
1200	175.728	518.505	372.213	175.550	−458.745	−181.504	7.901

PREVIOUS: CURRENT: December 1968

Molybdenum Chloride ($MoCl_5$) $Cl_5Mo_1(cr,l)$

Molybdenum Chloride ($MoCl_5$) IDEAL GAS $M_r = 273.205$

$S°(298.15\ K) = [397.774 \pm 12.6]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -445.94 \pm 4.2\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -447.69 \pm 4.2\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[7000]	[2]
[14000]	[2]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[490](1)	[350](2)
[400](1)	[170](2)
[410](1)	[100](2)
[150](1)	[190](2)

Point Group: D_{3h} $\sigma = 6$
Bond Distance: Mo–Cl = 2.27 ± 0.02 Å
Bond Angles: Cl*–Mo–Cl* = 120°; Cl*–Mo–Cl** = 90°; Cl**–Mo–Cl** = 180°
*Equatorial **Axial
Product of the Moments of Inertia: $I_A I_B I_C = 1.02598 \times 10^{-111}\ g^3{\cdot}cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = 107.0\ kcal{\cdot}mol^{-1}$ is obtained from the vapor pressure data for $MoCl_5(cr) = MoCl_5(g)$ measured by Shchukarev *et al.*[1] and Saeki and Matsuzaki.[2]

Source	Method	Reaction	T/K	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Shchukarev *et al.*[1]	Transpiration	$MoCl_5(cr) = MoCl_5(g)$	343 – 435	19.04 ± 0.45	19.18	0.3	−106.82
Saeki and Matsuzaki	Manometric	$MoCl_5(cr) = MoCl_5(g)$	298 – 474	16.79 ± 0.06	18.94	5.6	−107.06

*Calculation based on third law $\Delta_r H°$(298.15 K)

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those of $NbCl_5$ obtained from infrared and Raman spectra by Carlson.[3] Structure, bond distance and bond angle are taken from Ewens and Lister.[4] The principal moments of inertia are: $I_A = 91.0085 \times 10^{-39}$ and $I_B = I_C = 106.1766 \times 10^{-39}\ g{\cdot}cm^2$. The electronic levels are estimated to be 0, 7000 and 14000 cm^{-1}, all doublets, by comparison with those of WCl_5(g).

References

[1] S. A. Shchukarev, I. V. Vasil'kova and B. N. Sharupin, J. Gen. Chem. USSR 26, 2335–9 (1956).
[2] Y. Saeki and R. Matsuzaki, Denki Kagaku 33, 155–8 (1965).
[3] G. L. Carlson, Spectrochim. Acta 19, 1291 (1963).
[4] R. V. G. Ewens and M. W. Lister, Trans. Faraday Soc. 34, 1358–62 (1938).

Molybdenum Chloride ($MoCl_5$) $Cl_5Mo_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−25.793	−445.945	−445.945	INFINITE
100	77.392	287.812	494.800	−20.699	−448.621	−429.448	224.321
200	107.562	352.265	408.393	−11.226	−448.584	−410.160	107.123
250	114.900	377.117	399.718	−5.650	−448.174	−400.598	83.700
298.15	119.482	397.774	397.774	0.	−447.688	−391.478	68.585
300	119.624	398.514	397.777	0.221	−447.668	−391.129	68.102
350	122.781	417.207	399.246	6.286	−447.114	−381.750	56.973
400	124.971	433.753	402.545	12.483	−446.537	−372.451	48.637
450	126.543	448.568	406.850	18.773	−445.952	−363.226	42.162
500	127.704	461.964	411.702	25.131	−445.366	−354.065	36.989
600	129.265	485.397	422.087	37.986	−444.208	−335.914	29.244
700	130.234	505.402	432.595	50.964	−443.082	−317.955	23.726
800	130.878	522.837	442.809	64.022	−441.994	−300.154	19.598
900	131.332	538.279	452.575	77.134	−440.950	−282.487	16.395
1000	131.674	552.135	461.850	90.285	−439.953	−264.934	13.839
1100	131.950	564.698	470.638	103.466	−439.010	−247.479	11.752
1200	132.192	576.190	478.962	116.674	−438.125	−230.106	10.016
1300	132.417	586.780	486.854	129.904	−437.307	−212.805	8.551
1400	132.639	596.601	494.346	143.157	−436.558	−195.564	7.297
1500	132.862	605.760	501.472	156.432	−435.886	−178.374	6.212
1600	133.092	614.342	508.261	169.730	−435.294	−161.227	5.264
1700	133.328	622.418	514.741	183.051	−434.790	−144.113	4.428
1800	133.570	630.045	520.937	196.395	−434.381	−127.027	3.686
1900	133.817	637.274	526.871	209.765	−434.074	−109.961	3.023
2000	134.067	644.144	532.565	223.159	−433.880	−92.908	2.427
2100	134.317	650.691	538.035	236.578	−433.808	−75.861	1.887
2200	134.566	656.945	543.299	250.022	−433.872	−58.815	1.396
2300	134.811	662.933	548.371	263.491	−434.083	−41.763	0.948
2400	135.053	668.675	553.265	276.984	−434.455	−24.699	0.538
2500	135.288	674.193	557.992	290.501	−435.003	−7.615	0.159
2600	135.516	679.504	562.565	304.042	−435.753	9.495	−0.191
2700	135.736	684.622	566.991	317.604	−436.748	26.638	−0.515
2800	135.947	689.562	571.281	331.189	−438.052	43.823	−0.818
2900	136.150	694.337	575.442	344.794	−475.633	61.111	−1.101
3000	136.342	698.956	579.483	358.418	−475.769	79.622	−1.386
3100	136.525	703.429	583.409	372.062	−475.934	98.137	−1.654
3200	136.697	707.766	587.228	385.723	−476.128	116.659	−1.904
3300	136.860	711.975	590.945	399.401	−476.350	135.187	−2.140
3400	137.012	716.063	594.565	413.094	−476.598	153.722	−2.362
3500	137.155	720.037	598.093	426.803	−476.870	172.265	−2.571
3600	137.287	723.903	601.535	440.525	−477.160	190.816	−2.769
3700	137.410	727.666	604.893	454.260	−477.466	209.375	−2.956
3800	137.523	731.332	608.172	468.007	−477.782	227.942	−3.133
3900	137.627	734.905	611.376	481.764	−478.104	246.518	−3.302
4000	137.722	738.391	614.508	495.532	−478.425	265.102	−3.462
4100	137.808	741.793	617.571	509.308	−478.741	283.694	−3.614
4200	137.885	745.115	620.569	523.093	−479.046	302.294	−3.760
4300	137.955	748.360	623.503	536.885	−479.333	320.901	−3.898
4400	138.017	751.532	626.377	550.684	−479.599	339.514	−4.031
4500	138.071	754.634	629.193	564.488	−479.836	358.132	−4.157
4600	138.118	757.670	631.953	578.298	−480.040	376.757	−4.278
4700	138.159	760.641	634.659	592.112	−480.205	395.384	−4.394
4800	138.193	763.550	637.314	605.929	−480.328	414.015	−4.505
4900	138.221	766.399	639.920	619.750	−480.404	432.649	−4.612
5000	138.243	769.192	642.477	633.573	−1071.814	457.013	−4.774
5100	138.259	771.930	644.989	647.398	−1073.463	487.607	−4.994
5200	138.271	774.615	647.456	661.225	−1075.201	518.232	−5.206
5300	138.278	777.248	649.880	675.052	−1077.021	548.892	−5.410
5400	138.280	779.833	652.263	688.880	−1078.922	579.588	−5.606
5500	138.277	782.371	654.605	702.708	−1080.896	610.319	−5.796
5600	138.271	784.862	656.909	716.536	−1082.941	641.087	−5.980
5700	138.261	787.309	659.176	730.362	−1085.051	671.891	−6.157
5800	138.248	789.714	661.406	744.188	−1087.224	702.734	−6.329
5900	138.231	792.077	663.600	758 012	−1089.452	733.614	−6.495
6000	138.212	794.400	665.761	771.834	−1091.738	764.532	−6.656

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

Niobium Chloride ($NbCl_5$) CRYSTAL $M_r = 270.1714$ Niobium Chloride ($NbCl_5$) $Cl_5Nb_1(cr)$

$S°(298.15\ K) = [214.05 \pm 4.2]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 478.9 \pm 1.5\ K$
$\Delta_{fus}H° = 33.878 \pm 0.96\ kJ{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = Unknown$
$\Delta_fH°(298.15\ K) = -797.47 \pm 4.2\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The adopted value for the enthalpy of formation of $NbCl_5(cr)$ is $\Delta_fH°(298.15\ K) = -190.6 \pm 1.0\ kcal{\cdot}mol^{-1}$ and is based on the study by Gross *et al.*[2] This value was determined from measurements of the enthalpy evolved in the reaction $Nb(cr) + 5/2\ Cl_2(l) = NbCl_5(cr)$. Schafer and Kahlenberg[1] also determined the enthalpy formation of $NbCl_5(cr)$ via calorimetric measurement of the heats of solution of Nb(cr) and $NbCl_5(cr)$ in hydrofluoric acid. Their procedure consisted of five steps; four were determined experimentally and one was based on literature data. Using their data and auxiliary results,[7] we calculate $\Delta_fH°(298.15\ K) = -190.0 \pm 1.0\ kcal{\cdot}mol^{-1}$ for $NbCl_5(cr)$. This value is in good agreement with our adopted value. Shchukarev *et al.*[3] determined a $\Delta_fH°(298.15\ K)$ value from a heat of hydrolysis for $NbCl_5(cr)$. A recalculation of this data, using current auxiliary $\Delta_fH°(298.15\ K)$ data for $Nb_2O_5(cr)$,[10] $H_2O(l)$,[7] and HCl(g),[10] yields $\Delta_fH°(298.15\ K) = -192.8 \pm 0.7\ kcal{\cdot}mol^{-1}$.

Three compilations on Nb species suggested a similar or closely related $\Delta_fH°(298.15\ K)$ value for $NbCl_5(cr)$:[6,8,9] in particular, the NBS Technical Note 270 Series suggested $-190.6\ kcal{\cdot}mol^{-1}$.[9]

Heat Capacity and Entropy

Keneshea *et al.*[5] measured the saturation enthalpy increments above 298.15 K for the condensed phases of $NbCl_5$ in a drop calorimeter up to the critical point (804 ± 3 K). A figure presented by Keneshea *et al.*[5] indicated roughly 30 data points, the lowest occurring at approximately 360 K. The differences between the saturation and standard enthalpy increments for the crystal phase are negligible, so that the heat capacity values which we adopt are those which are derived from the reported enthalpy equation, $H°(T)-H°(298.15\ K) = [-10.53 + 3.535 \times 10^{-2}T] \pm 0.07\ kcal{\cdot}mol^{-1}$. This equation is reported to apply to the temerature region 298.15–478.9 K.

Schafer and Kahlenberg[1] estimated the heat capacity of $NbCl_5(cr)$ to be given by $C_p° = 38.0–3 \times 10^5T^{-2}\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. For the crystal range 298.15–478.9 K, these estimated $C_p°$ values vary from 34.63 to 36.69 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$. These values are in fair agreement with the adopted values and were estimated by comparison with $ZrCl_4(cr)$ and $HfCl_4(cr)$. Amosov[4] also estimated the heat capacity of $NbCl_5$ based on Neumann and Koppe's rule, $C_p° = 26.71 + 35.2 \times 10^{-3}T\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. These latter values vary between 37.20 and 43.57 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ over the region 298.15–478.9 K and differ significantly from those $C_p°$ values derived from the experimental data of Keneshea *et al.*[5]

As there is no low temperature heat capacity data reported in the literature, the entropy of $NbCl_5(cr)$ at 298.15 K is calculated from the equation $\Delta_{sub}S°(298.15\ K) = S°(g, 298.15\ K) - S°(cr, 298.15\ K)$; $S°(g, 298.15\ K) = 96.56\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ as given in the $NbCl_5(g)$ table[10] and $\Delta_{sub}S°(298.15\ K) = 45.40\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ as obtained Keneshea *et al.*[5] based on their evaluation of the available vapor pressure data by a modified Σ approach.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K)$ is the difference between the $\Delta_fH°(298.15\ K)$ values for $NbCl_5(g)$ and $NbCl_5(cr)$. For sublimation studies are summarized in the $NbCl_5(l)$ table.

References

[1] H. Schafer and F. kahlenberg, Z. anorg. allg. Chem. **305**, 291 (1960).
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[5] F. J. Keneshea, D. Cubicciotti, G. Withers and H. Eding, J. Phys. Chem. **72**, 1272 (1968).
[6] V. I. Lavrentev and Ya. I. Gerassimov, At. Energy Rev. **1968**, 7 (1968).
[7] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[8] J. O. Hill, I. G. Worsley and L. G. Hepler, Chem. Rev. **71**, 127 (1971).
[9] U. S. Nat. Bur. Stand. Tech. Note 270–5, (1971).
[10] JANAF Thermochemical Tables: $Nb_2O_5(cr)$, 12–31–72; HCl(g), 9–3–64' $NbCl_5(g)$, 12–31–74.

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	$\log K_f$
0							
100							
200							
298.15	147.904	214.053	214.053	0.	−797.470	−684.141	119.859
300	147.904	214.968	214.056	0.274	−797.400	−683.438	118.997
400	147.904	257.518	219.858	15.064	−793.792	−646.006	84.360
478.900	147.904	284.145	228.321	26.734	--- CRYSTAL <--> LIQUID ---		
500	147.904	290.522	230.813	29.854	−790.494	−609.446	63.668
600	147.904	317.488	243.080	44.645	−787.397	−573.530	49.930
700	147.904	340.287	255.380	59.435	−784.442	−538.121	40.155

PREVIOUS: CURRENT: December 1974

Niobium Chloride ($NbCl_5$) LIQUID $M_r = 270.1714$ Niobium Chloride ($NbCl_5$) $Cl_5Nb_1(l)$

$S°(298.15\ K) = [260.970 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-773.354]\ kJ \cdot mol^{-1}$

$T_{fus} = 478.9 \pm 1.5\ K$ $\Delta_{fus}H° = 33.878 \pm 0.96\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(NbCl_5, l, 298.15\ K)$ is calculated from that of $NbCl_5(cr)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(478.9\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The liquid phase heat capacity values are derived from the enthalpy equation reported by Keneshea *et al.*[5] The equation is used for the region 478.9–600 K, i.e. that region in which the saturation heat capacity and the heat capacity at constant pressure are essentially the same in value. This equation is used also to extrapolate to 700 K and to an assumed glass transition temperature at $T_{gls} = 350$ K. Below T_{gls} the heat capacity values are those of the crystal. $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_f H°(298.15\ K)$.

Fusion Data

The adopted value of T_{fus} is that reported by Keneshea *et al.*[5] This value, 205.7°C or 478.9 K, was obtained by visual observation on four different samples in evacuated capsules. Other values for T_{fus} reported in the literature are: 205.3 ± 1.5C°,[6] 204.8°C,[4] 206.8 ± 0.3°C,[3] 204.5°C,[2] and 204.7°C.[1] Earlier determinations of melting point have been summarized by Schafer and Pietruck[1] and Meyer *et al.*[3]

The adopted heat of fusion, $\Delta_{fus}H° = 8.097 \pm 0.23\ kcal \cdot mol^{-1}$, is calculated as the difference at 478.9 K in the enthalpy equations for $NbCl_5(l)$ and $NbCl_5(cr)$ as reported by Keneshea *et al.*[5] Meyer *et al.*,[3] from an examination of the $NbCl_5$–$NbOCl_3$ system, reported a value of $8.30 \pm 0.4\ kcal\ mol^{-1}$ for $\Delta_{fus}H°$. Voitovich *et al.*[4] studied the $NbCl_5$–S_2Cl_2 system and calculated $\Delta_{fus}H° = 8.15\ kcal \cdot mol^{-1}$. These two latter values are in excellent agreement with our adopted value.

Johnson and Cubicciotti,[6] in their study of the orthobaric densities of $NbCl_5$, discussed the possible molecular behavior of $NbCl_5$. The explanation served to explain the large entropy of melting, $\Delta_{fus}S° = 16.91\ kcal \cdot mol^{-1}$. Based on currently available information, they suggested that between the melting point and about 650 K the substance changes from a dimeric solid to a monomeric liquid. This change was suggested to manifest itself in the unusually large volume change[6] (27 ± 2%) and entropy of fusion and in the inverse curvature of the liquid density curve just above the melting point. For additional references, refer to the $NbCl_5(g)$ table.

Vaporization Data

T_{vap} is calculated as that temperature for which $\Delta_r G° = 0$ for the process $NbCl_5(l) = NbCl_5(g)$. $\Delta_{vap}H°$ is calculated as the difference between the $\Delta_f H°$ values for $NbCl_5(g)$ and $NbCl_5(l)$ at T_{vap}. Seven vaporization studies are summarized in the $NbCl_5(g)$ table. Sheka *et al.*[2] studied the vapor-liquid equilibrium in the $NbCl_5$–$POCl_3$ system and measured a boiling point (at 760 mm) of 521.7 K for pure $NbCl_5$. The vaporization studies discussed in the $NbCl_5(g)$ table which included the boiling point yielded normal boiling points (p = 760 mm) in the range 519.2–520.6 K.

References

[1] H. Schafer and C. Pietruck, Z. Anorg. Allg. Chem. 267, 174 (1951).
[2] I. A. Sheka, B. A. Voitovich and L. A. Nisel-son, Russ. J. Inorg. Chem. 4, 813 (1959).
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[5] F. J. Keneshea, D. Cubicciotti, G. Withers and H. Eding, J. Phys. Chem. 72, 1272 (1968).
[6] J. W. Johnson and D. Cubicciotti, Hig Temp. Sci. 2, 9 (1970).

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	147.904	260.970	260.970	0.	−773.354	−674.012	118.084
300	147.904	261.885	260.973	0.274	−773.283	−673.396	117.249
350	147.904	284.684	262.773	7.669	−771.430	−656.897	98.036
350.000	147.904	284.684	262.773	7.669	---- GLASS <--> LIQUID ----		
350.000	228.292	284.684	262.773	7.669	TRANSITION		
400	224.848	314.949	267.451	18.999	−765.740	−640.926	83.696
478.900	218.448	354.886	278.680	36.495	--- CRYSTAL <--> LIQUID ---		
500	216.564	364.264	282.096	41.084	−755.148	−610.971	63.828
600	206.397	402.878	299.132	62.248	−745.678	−583.044	50.759
700	194.430	433.819	316.241	82.304	−737.456	−556.607	41.535
800	180.611	458.900	332.560	101.072	−730.635	−531.254	34.687

PREVIOUS: CURRENT: December 1974

Niobium Chloride ($NbCl_5$) $Cl_5Nb_1(l)$

Niobium Chloride ($NbCl_5$) CRYSTAL-LIQUID

0 to 478.9 K crystal
above 478.9 K liquid

Refer to the individual tables for details.

M_r = 270.1714 Niobium Chloride ($NbCl_5$) $Cl_5Nb_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	147.904	214.053	214.053	0.	−797.470	−684.141	119.859
300	147.904	214.968	214.056	0.274	−797.400	−683.438	118.997
400	147.904	257.518	219.858	15.064	−793.792	−646.006	84.360
478.900	147.904	284.145	228.321	26.734	CRYSTAL <--> LIQUID TRANSITION		
478.900	218.448	354.886	228.321	60.612			
500	216.564	364.264	233.862	65.201	−755.148	−610.971	63.828
600	206.397	402.878	258.937	86.364	−745.678	−583.044	50.759
700	194.430	433.819	281.789	106.421	−737.456	−556.607	41.535
800	180.611	458.900	302.414	125.189	−730.635	−531.254	34.687

PREVIOUS: CURRENT: December 1974

Niobium Chloride ($NbCl_5$) IDEAL GAS $M_r = 270.1714$ Niobium Chloride ($NbCl_5$) $Cl_5Nb_1(g)$

$S°(298.15\ K) = 404.111 \pm 3.14\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -701.48 \pm 8.4\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -703.33 \pm 8.4\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
394.0 (1)	[492.4](2)
317.0 (1)	179.9 (2)
[414.1](1)	54.1 (2)
[143.5](1)	148.0 (2)

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: D_{3h}
Bond Distance: Nb–Cl = 2.28 ± 0.02 Å
Bond Angles: Cl*–Nb–Cl* = 120°; Cl*–Nb–Cl** = 90°; Cl**–Nb–Cl** = 180°
(* = equatorial ** = axial)
Product of the Moments of Inertia: $I_AI_BI_C = 1.05340 \times 10^{-111}\ g^3{\cdot}cm^6$

Enthalpy of Formation

The vapor pressures over $NbCl_5(cr)$ and $NbCl_5(l)$ have been measured by seven investigators. The reported vapor pressures are corrected for vapor non–ideality by means of the equation $\Delta G°/T = -R\ln p - Bp/T$. The Berthelot equation of state and critical constants $T_c = 803.5 \pm 2$ K and $p_c = 48.2$ atm. reported by Johnson *et al.*[9] [10] are used to calculate B. The corrected vapor pressures are used to calculate $\Delta_fH°(298.15\ K)$ by both 2nd and 3rd law methods. By means of comparison, Nisel'son *et al.*[6] measured the orthobaric densities of $NbCl_5(l)$, as did Johnson *et al.*,[9] and reported $T_c = 807$ K and $p_c = 46$ atm.

Source	Method	T/K	Data Points	$\Delta_fH°(298.15\ K)$ kcal·mol⁻¹ 2nd law	 3rd law	Drift cal·K⁻¹·mol⁻¹
$NbCl_5(cr) = NbCl_5(g)$						
Opykhtina and Fleischer[1]	transpiration	373–Tm	Eqn	20.74	22.28	3.6
Tarasenkov and Komandin[2]	static	446–Tm	Eqn	19.20	22.41	7.0
Alexander and Fairbrother[3]	static	402–Tm	7*	22.02 ± 0.30	22.69 ± 0.09	1.5 ± 0.7
Schafer and Polert[7]	flow	351–384	25	22.71 ± 0.10	22.52 ± 0.03	−0.5 ± 0.3
$NbCl\ (l_5) = NbCl\ (g_5)$						
Opykhtina and Fleisher[1]	transpiration	Tm–503	Eqn	16.42	16.55	0.3
Tarasenkov and Komandin[2]	static	Tm–506	Eqn	18.41	16.73	−3.4
	boiling	504–520	Eqn	15.08	16.70	3.2
Alexander and Fairbrother[3]	static	Tm–528	13	16.98 ± 0.05	16.91 ± 0.01	−0.2 ± 0.1
Ainscough *et al.*[4]	boiling	516–530	Eqn	16.65	16.76	0.2
Hart and Meyer[5]	static	544–594	32*	16.45 ± 0.08	16.79 ± 0.03	0.6 ± 0.1
Johnson *et al.*[10]	boiling	503–594	10	16.42 ± 0.04	16.76 ± 0.04	0.6 ± 0.1

*One point is rejected due to statistical test.

The adopted value for $\Delta_fH°(298.15\ K)$ of $NbCl_5(g)$ is $-168.1 \pm 2.0\ kcal{\cdot}mol^{-1}$ ($-703.330 \pm 8.4\ kJ{\cdot}mol^{-1}$). This value is based on a rounded mean of the 3rd law results for both the sublimation and vaporization studies and the appropriate $\Delta_fH°(298.15\ K)$ value for the crystal or liquid.

Reznitskii[8] measured the enthalpy of chlorination for Nb(cr) and reported $\Delta_rH°(680\ K) = -169.1 \pm 1\ kcal{\cdot}mol^{-1}$ for the reaction $Nb(cr) + 5/2\ Cl_2(g) = NbCl_5(g)$. Using auxiliary data for Nb(cr) and $Cl_2(g)$,[11] we calculated $\Delta_fH°(298.15\ K) = -170.1 \pm 1.0\ kcal{\cdot}mol^{-1}$ for $NbCl_5(g)$.

Heat Capacity and Entropy

Monomeric $NbCl_5(g)$ was shown by Spiridonov and Romanov,[19] [20] using electron diffraction techniques, to have a trigonal bipyramidal structure of D_{3h} symmetry: all the Nb–Cl bond lengths being equal within experimental uncertainty, 2.28 ± 0.2 Å. Skinner and Sutton[12] earlier used electron diffraction techniques and had suggested the same structure although a square pyramidal structure was consistent with the experimental results. We adopt the results of Spiridonov and Romanov.[19,20] The principal moments of inertia are: $I_A = 91.8121 \times 10^{-39}$ and $I_B = I_C = 107.1141 \times 10^{-39}\ g{\cdot}cm^2$.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−26.343	−701.481	−701.481	INFINITE
100	80.548	293 472	501.092	−20.762	−703.961	−684.800	357.703
200	107.409	358.746	414.693	−11.189	−704.080	−665.472	173.803
250	114.494	383.531	406 048	−5.629	−703.751	−655.855	137.033
298.15	119.040	404.111	404.111	0.	−703.330	−646.667	113.293
300	119.183	404.848	404 114	0.220	−703.313	−646.315	112.534
350	122.372	423.475	405.577	6.264	−702.811	−636.855	95.045
400	124.611	439.970	408.865	12.442	−702.274	−627.469	81.939
450	126.230	454.745	413.157	18.715	−701.717	−618.152	71.753
500	127.434	468.110	417.994	25.058	−701.151	−608.897	63.611
600	129.061	491.501	428.351	37.890	−700.012	−590.553	51.412
700	130.076	511.477	438.834	50.850	−698.887	−572.399	42.713
800	130.749	528.893	449.027	63.893	−697.791	−554.404	36.199
900	131.217	544.322	458.774	76.993	−696.731	−536.545	31.140
1000	131.556	558.166	468.033	90.133	−695.713	−518.802	27.099
1100	131.808	570.716	476.806	103.301	−694.740	−501.158	23.798
1200	132.001	582.194	485.117	116.492	−693.814	−483.601	21.051
1300	132.151	592.766	492.996	129.700	−692.935	−466.119	18.729
1400	132.271	602.564	500.477	142.921	−692.106	−448.703	16.741
1500	132.368	611.693	507.591	156.154	−691.333	−431.345	15.021
1600	132.448	620.238	514.367	169.395	−690.624	−414.036	13.517
1700	132.514	628.270	520.833	182.643	−689.989	−396.769	12.191
1800	132.570	635.846	527.014	195.897	−689.434	−379.537	11.014
1900	132.617	643.015	532.933	209.156	−688.969	−362.334	9.961
2000	132.657	649.818	538.608	222.420	−688.602	−345.152	9.014
2100	132.691	656.292	544.059	235.688	−688.341	−327.987	8.158
2200	132.721	662.465	549.302	248.958	−688.194	−310.831	7.380
2300	132.748	668.365	554.352	262.232	−688.174	−293.679	6.670
2400	132.771	674.016	559.221	275.508	−688.294	−276.525	6.018
2500	132.791	679.436	563.922	288.786	−688.573	−259.363	5.419
2600	132.809	684.645	568.465	302.066	−689.038	−242.186	4.866
2700	132.825	689.657	572.862	315.347	−689.729	−224.986	4.353
2800	132.839	694.488	577.120	328.631	−717.062	−207.273	3.867
2900	132.852	699.150	581.248	341.915	−717.071	−189.066	3.405
3000	132.864	703.654	585.253	355.201	−717.126	−170.858	2.975
3100	132.875	708.010	589.143	368.488	−717.230	−152.648	2.572
3200	132.884	712.229	592.924	381.776	−717.379	−134.434	2.194
3300	132.893	716.318	596.602	395.065	−717.572	−116.213	1.839
3400	132.901	720.286	600.182	408.355	−717.805	−97.987	1.505
3500	132.908	724.138	603.668	421.645	−718.076	−79.753	1.190
3600	132.915	727.883	607.067	434.936	−718.379	−61.511	0.892
3700	132.921	731.524	610.382	448.228	−718.710	−43.260	0.611
3800	132.927	735.069	613.617	461.520	−719.062	−25.000	0.344
3900	132.932	738.522	616.775	474.813	−719.430	−6.731	0.090
4000	132.937	741.888	619.861	488.107	−719.807	11.549	−0.151
4100	132.941	745.170	622.878	501.401	−720.187	29.837	−0.380
4200	132.946	748.374	625.828	514.695	−720.564	48.135	−0.599
4300	132.949	751.502	628.714	527.990	−720.930	66.442	−0.807
4400	132.953	754.559	631.540	541.285	−721.280	84.757	−1.006
4500	132.956	757.547	634.307	554.580	−721.608	103.079	−1.197
4600	132.960	760.469	637.018	567.876	−721.907	121.410	−1.379
4700	132.963	763.328	639.675	581.172	−722.173	139.745	−1.553
4800	132.965	766.128	642.280	594 469	−722.398	158.086	−1.720
4900	132.968	768.869	644.836	607.765	−722.580	176.432	−1.881
5000	132.971	771.556	647.343	621.062	−722.712	194.780	−2.035
5100	132.973	774.189	649.805	634.359	−722.792	213.131	−2.183
5200	132.975	776.771	652.222	647.657	−1413.486	240.792	−2.419
5300	132.977	779.304	654.596	660.954	−1413.781	272.608	−2.687
5400	132.979	781.790	656.928	674.252	−1413.986	304.425	−2.945
5500	132.981	784.230	659.221	687.550	−1414.198	336.250	−3.193
5600	132.983	786.626	661.474	700.848	−1414.370	368.077	−3.433
5700	132.984	788.980	663.691	714.147	−1414.501	399.908	−3.665
5800	132.986	791.292	665.871	727.445	−1414.589	431.741	−3.888
5900	132.987	793.566	668.016	740.744	−1414.633	463.574	−4.104
6000	132.989	795.801	670.127	754.043	−1414.633	495.408	−4.313

PREVIOUS: December 1974 (1 atm) CURRENT· December 1974 (1 bar)

Continued on page 941

Phosphorus Chloride (PCl_5) IDEAL GAS $M_r = 208.23876$ Phosphorus Chloride (PCl_5) $Cl_5P_1(g)$

$S°(298.15\ K) = 364.288\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -354.72 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -360.18 \pm 4.2\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm⁻¹	ν, cm⁻¹	ν, cm⁻¹
394 (1)	394 (1)	465 (1)
[176] (2)	592 (2)	335 (2)
100 (2)	280 (2)	

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: D_{3h}
Bond Distance: P–Cl* = 2.04 Å; P–Cl** = 2.19 Å
Bond Angle: Cl–P–Cl* = 120°; Cl**–P–Cl** = 180°; Cl*–P–Cl** = 90
(* = equatorial ** = axial)
Product of the Moments of Inertia: $I_A I_B I_C = 6.3873 \times 10^{-112}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was calculated from the $\Delta_r H°(298.15\ K)$ for the reaction: $PCl_3(g) + Cl_2(g) \leftarrow PCl_5(g)$. A third law calculation using experimental equilibrium constants, and free energy functions from JANAF Tables gave a $\Delta_r H°(298.15\ K) = -20.884\ kcal \cdot mol^{-1}$. This $\Delta_r H°$ is the average of C. Holland[1] $\Delta_r H°(298.15\ K) = -20.766 \pm 0.26\ kcal \cdot mol^{-1}$ and W. Nernst[2] $\Delta_r H(298.15\ K) = -21.001 \pm 0.24\ kcal \cdot mol^{-1}$. The first, $\Delta_r H°$ C. Holland,[1] was obtained from eleven experimental equillibrium constants measured by Holland[1] as corrected by Nernst.[2] The second, $\Delta_r H°$ W. Nernst,[2] was obtained from thirteen experimental equillibrium constants measured by Fischer and Jubermann.[3]

For the same reaction, $PCl_3(g) + Cl_2(g) = PCl_5(g)$, a 3rd law calculation by Stevenson and Yost[4] gave a $\Delta H°(0\ K) = -21.320 \pm 0.107\ kcal \cdot mol^{-1}$. With a new assignment of fundamental frequencies Wilmshurst and Bernstein[5] reported a $\Delta E°(0\ K) = -20.525 \pm 0.16\ kcal \cdot mol^{-1}$.

The $\Delta_f H°(298.15\ K)$ values corresponding to these heats of reaction are:

$\Delta_f H°(298.15\ K)$	Source
−82.9 kcal·mol⁻¹	4
−82.1 kcal·mol⁻¹	5
−81.9 kcal·mol⁻¹	Calculated using Gibbs energy function from JANAF Tables

Heat Capacity and Entropy

The fundamental vibrational frequencies were assigned by Wilmshurst and Bernstein[5] from their infrared and Raman spectral data, except the frequency, 176 cm⁻¹, which they calculated. Electron diffraction data of Rouault[6] and Sargent and Schomaker,[7] show the free PCl^5 molecule to be a trigonal bipyramid of D_{3h} symmerty. The bond lengths were calculated from force constants and Badger's rule by Wilmshurst and Bernstein.[5] Their values are in good agreement with the electron diffraction bond lengths of Rouault.[6] The principal moments of inertia are $I_A = 73.5006 \times 10^{-39}$ and $I_B = I_C = 93.2215 \times 10^{-39}\ g \cdot cm^2$.

References

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[2] W. Nernst, Z. Electrochem. 22, 37 (1916).
[3] W. Fischer and O. Jubermann, Z. Anorg. Allg. Chim. 235, 337 (1938)
[4] D. P. Stevenson and D. M. Yost, J. Chem. Phys. 9, 403 (1941).
[5] J. K. Wilmshurst and H. J. Bernstein, J. Chem. Phys. 27, 661 (1957).
[6] M. Rouault, Ann. Phys. 14, 78 (1940).
[7] Sargen and Schomaker, quoted by Stevenson and Yost.[4]

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−22.852	−354.723	−354.723	INFINITE
100	63.002	267.936	451.647	−18.371	−358.410	−336.183	175.604
200	95.704	322.664	374.087	−10.285	−360.181	−313.307	81.827
250	105.426	345.132	366.097	−5.241	−360.276	−301.572	63.010
298.15	111.890	364.288	364.288	0.	−360.184	−290.271	50.854
300	112.096	364.981	364.290	0.207	−360.178	−289.838	50.465
350	116.747	382.631	365.673	5.935	−360.682	−278.059	41.498
400	120.070	398.449	368.799	11.860	−360.452	−266.270	34.771
450	122.505	412.739	372.900	17.927	−360.141	−254.515	29.543
500	124.332	425.745	377.544	24.100	−359.772	−242.799	25.365
600	126.825	448.652	387.538	36.668	−358.917	−219.482	19.108
700	128.396	468.329	397.708	49.435	−357.963	−196.317	14.649
800	129.443	485.547	407.634	62.330	−356.949	−173.293	11.315
900	130.175	500.838	417.156	75.313	−355.900	−150.399	8.729
1000	130.705	514.582	426.223	88.359	−354.829	−127.623	6.666
1100	131.101	527.059	434.832	101.450	−353.745	−104.955	4.984
1200	131.404	538.480	443.000	114.576	−416.229	−81.307	3.539
1300	131.641	549.007	450.755	127.728	−414.364	−53.473	2.149
1400	131.830	558.770	458.126	140.902	−412.508	−25.781	0.962
1500	131.983	567.871	465.142	154.093	−410.661	1.777	−0.062
1600	132.109	576.393	471.832	167.298	−408.826	29.213	−0.954
1700	132.213	584.405	478.220	180.514	−407.005	56.535	−1.737
1800	132.301	591.965	484.332	193.740	−405.199	83.750	−2.430
1900	132.375	599.120	490.186	206.974	−403.412	110.865	−3.048
2000	132.439	605.912	495.804	220.215	−401.646	137.886	−3.601
2100	132.494	612.375	501.203	233.462	−399.904	164.820	−4.100
2200	132.541	618.540	506.397	246.713	−398.190	191.671	−4.551
2300	132.583	624.432	511.402	259.970	−396.506	218.445	−4.961
2400	132.619	630.076	516.230	273.230	−394.857	245.146	−5.335
2500	132.651	635.490	520.893	286.493	−393.247	271.780	−5.679
2600	132.680	640.693	525.401	299.760	−391.677	298.350	−5.994
2700	132.705	645.701	529.764	313.029	−390.152	324.861	−6.285
2800	132.728	650.528	533.992	326.301	−388.674	351.315	−6.554
2900	132.748	655.186	538.091	339.575	−387.243	377.718	−6.803
3000	132.767	659.686	542.070	352.850	−385.860	404.072	−7.036
3100	132.783	664.040	545.934	366.128	−384.526	430.381	−7.252
3200	132.799	668.256	549.691	379.407	−383.238	456.648	−7.454
3300	132.812	672.343	553.346	392.688	−381.995	482.875	−7.643
3400	132.825	676.308	556.905	405.969	−380.793	509.065	−7.821
3500	132.837	680.158	560.372	419.253	−379.630	535.220	−7.988
3600	132.847	683.900	563.751	432.537	−378.500	561.343	−8.145
3700	132.857	687.540	567.048	445.822	−377.398	587.435	−8.293
3800	132.866	691.084	570.266	459.108	−376.319	613.496	−8.433
3900	132.874	694.535	573.408	472.395	−375.256	639.530	−8.566
4000	132.882	697.899	576.478	485.683	−374.204	665.537	−8.691
4100	132.889	701.180	579.480	498.972	−373.155	691.518	−8.810
4200	132.896	704.383	582.416	512.261	−372.104	717.473	−8.923
4300	132.902	707.510	585.289	525.551	−371.045	743.403	−9.031
4400	132.908	710.565	588.102	538.841	−369.969	769.308	−9.133
4500	132.913	713.552	590.856	552.132	−368.872	795.188	−9.230
4600	132.918	716.474	593.555	565.424	−367.748	821.044	−9.323
4700	132.923	719.332	596.201	578.716	−366.591	846.874	−9.412
4800	132.927	722.131	598.796	592.008	−365.395	872.680	−9.497
4900	132.931	724.872	601.341	605.301	−364.156	898.461	−9.578
5000	132.935	727.557	603.838	618.595	−362.869	924.215	−9.655
5100	132.939	730.190	606.290	631.888	−361.531	949.944	−9.729
5200	132.943	732.771	608.698	645.182	−360.136	975.645	−9.800
5300	132.946	735.304	611.063	658.477	−358.682	1001.320	−9.869
5400	132.949	737.789	613.387	671.772	−357.167	1026.966	−9.934
5500	132.952	740.228	615.671	685.067	−355.586	1052.584	−9.997
5600	132.955	742.624	617.916	698.362	−353.939	1078.172	−10.057
5700	132.957	744.977	620.125	711.658	−352.223	1103.730	−10.115
5800	132.960	747.290	622.298	724.953	−350.437	1129.259	−10.170
5900	132.962	749.562	624.435	738.250	−348.579	1154.754	−10.223
6000	132.964	751.797	626.540	751.546	−346.648	1180.218	−10.275

PREVIOUS: September 1962 (1 atm) CURRENT: September 1962 (1 bar)

Phosphorus Chloride (PCl_5) $Cl_5P_1(g)$

Tantalum Chloride ($TaCl_5$) CRYSTAL $M_r = 358.2129$ Tantalum Chloride ($TaCl_5$) $Cl_5Ta_1(cr)$

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = [221.75 \pm 6.3]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -858.98 \pm 4.2\ kJ \cdot mol^{-1}$

$T_{fus} = 489.7 \pm 1.5\ K$ $\Delta_{fus} H° = 35.146 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Gross *et al.*[3] measured the heat evolved in the reaction $Ta(cr) + 5/2\ Cl_2(l) = TaCl_5(cr)$. Using their data for 6 runs we calculate $\Delta_f H°(298.15\ K) = -205.6\ kcal \cdot mol^{-1}$ for $TaCl_5(cr)$. Gal'chenko *et al.*[4,5] also determined the heat of reaction for the direct chlorination of Ta(15 runs involving 2 samples). They reported $\Delta_f H°(298.15\ K) = -205.05 \pm 0.18\ kcal \cdot mol^{-1}$. We adopt an intermediate value, $\Delta_f H°(298.15\ K) = -205.3 \pm 1.0\ kcal \cdot mol^{-1}$ ($-858.975 \pm 4.2\ kJ \cdot mol^{-1}$), based on these two studies.[3-5]

Schafer and Kahlenberg[1] determined the heat of formation of $TaCl_5(cr)$ via calorimetric measurements of the heats of solution of Ta(cr) and $TaCl_5(cr)$ in hydrofluoric acid. Their procedure involved eight steps and resulted in $\Delta_f H°(298.15\ K) = -205.0 \pm 0.3\ kcal \cdot mol^{-1}$. This is in good agreement with our adopted value. In the case of $NbCl_5(cr)$ [$TaCl_5(cr)$] the $\Delta_f H°(298.15\ K)$ value derived from the data of Schafer and Kahlenberg[1,2] is $0.6\ kcal \cdot mol^{-1}$ [$0.3\ kcal \cdot mol^{-1}$] more positive than that derived from the data of Gross *et al.*[3]

Heat Capacity and Entropy

The heat capacity for $TaCl_5(cr)$ is assumed to be the same as that for $NbCl_5(cr)$.[6] We adopt $S°(298.15\ K) = 53.0 \pm 1.5\ cal \cdot K^{-1} \cdot mol^{-1}$ in order to reproduce the sublimation and vaporization data. Schafer and Kahlenberg[1,2] assumed a similar relationship based on a comparison with the corresponding values for the halides of Zr, Hf, and U.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The enthalpy of sublimation is discussed in the $TaCl_5(g)$ table.[6] Seven sublimation studies are analyzed and lead to a 3rd law result of $\Delta_{sub} H°(298.15\ K) = 22.5\ kcal \cdot mol^{-1}$.

References

[1] H. Schafer and F. Kahlenberg, Z. Anorg. Allg. Chem. 294, 243 (1958).
[2] H. Schafer and F. Kahlenberg, Z. Anorg. Allg. Chem. 305, 291 (1960).
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[4] G. L. Gal'chenko, D. A. Gedakyan, B. I. Timofiev, S. M. Skuratov, T. I. Serebryakova, and G. V. Samsonov, Dokl. Akad. Nauk. SSSR 170, 132 (1966).
[5] G. L. Gal'chenko, D. A. Gedakyan, B. I. Timofiev, Russ. J. Inorg. Chem. 13, 159 (1968).
[6] JANAF Thermochemical Tables: $NbCl_5(cr)$ and $TaCl_5(g)$, 12–31–74.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	147.904	221.752	221.752	0.	−858.975	−746.448	130.775
300	147.904	222.667	221.755	0.274	−858.905	−745.750	129.847
400	147.904	265.216	227.556	15.064	−855.349	−708.578	92.531
489.700	147.904	295.142	237.288	28.331	--- CRYSTAL <--> LIQUID ---		
500	147.904	298.220	238.511	29.854	−852.096	−672.267	70.231
600	147.904	325.186	250.778	44.645	−849.046	−636.591	55.420
700	147.904	347.986	263.078	59.435	−846.139	−601.413	44.878

PREVIOUS: CURRENT: December 1974

Tantalum Chloride ($TaCl_5$) $Cl_5Ta_1(cr)$

Tantalum Chloride ($TaCl_5$) LIQUID $M_r = 358.2129$ Tantalum Chloride ($TaCl_5$) $Cl_5Ta_1(l)$

$S°(298.15\ K) = [268.135]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 489.7 \pm 1.5\ K$

$\Delta_f H°(298.15\ K) = [-834.347]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 35.146 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(TaCl_5, l, 298.15K)$ is calculated from that of $TaCl_5(cr)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(489.7\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The liquid phase heat capacity is assumed to be identical to that for $NbCl_5(l)$.[4] As in the case of $NbCl_5(l)$, there is a glass transition assumed at 350 K. $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_f H°(298.15\ K)$.

Fusion Data

We adopt $T_{fus} = 478.9 \pm 1.5$ K (216.5°C) based on the work by Schafer and Pietruck (216.5°C),[1] Sheka *et al.* (216.5°C),[2] and Voitovich *et al.* (216.7°C).[3] Earlier reported melting points range between 204°C and 221°C and have been summarized by Schafer and Pietruck.[1]

The adopted heat of fusion, $\Delta_{fus}H° = 8.4 \pm 0.5\ kcal \cdot mol^{-1}$, is based on the analysis of the S_2Cl_2–$TaCl_5$ system by Voitovich *et al.*[3] A similar study on the S_2Cl_2–$NbCl_5$ system[3] yielded a heat of melting for $NbCl_5$ which was within $0.063\ kcal \cdot mol^{-1}$ of the result determined by drop calorimetry.[4] The discussion of the molecular behavior of $NbCl_5(l)$[4] is assumed to also apply to $TaCl_5$: that is, between the melting point and ~650 K, the substance changes from a dimeric solid to a monomeric liquid.

Vaporization Data

T_{vap} is calculated as that temperature for which $\Delta_r G° = 0$ for the process $TaCl_5(l) = TaCl_5(g)$. $\Delta_{vap}H°$ is calculated as the difference between the $\Delta_f H°$ values for $TaCl_5(g)$ and $TaCl_5(l)$ at T_{vap}. Three vaporization studies are summarized in the $TaCl_5(g)$ table.[4] Sheka *et al.*[2] studied the vapor–liquid equilibrium in the $TaCl_5$–$POCl_3$ system and measured a boiling point (at 760 mm) of 507.3 K for pure $TaCl_5$. The vaporization studies discussed in the $TaCl_5(g)$ table which included the boiling point yielded normal boiling points (p = 760 mm) in the range 506.0–506.9 K.

References

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[2] I. A. Sheka, B. A. Voitovich, and L. A. Nisel'son, Russ. J. Inorg. Chem. 4, 813 (1959).
[3] B. A. Voitovich, A. S. Barabanova, and N. Kh. Tumanova, Russ. J. Inorg. Chem. 6, 1286 (1961).
[4] JANAF Thermochemical Tables: $NbCl_5(\ell)$, $NbCl_5(g)$ and $TaCl_5(g)$, 12–31–74.

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	147.904	268.135	268.135	0.	−834.347	−735.649	128.883
300	147.904	269.050	268.138	0.274	−834.277	−735.037	127.981
350	147.904	291.849	269.938	7.669	−832.452	−718.643	107.252
350.000	147.904	291.849	269.938	7.669	---- GLASS <--> LIQUID ----		
350.000	228.280	291.849	269.938	7.669	TRANSITION		
400	224.848	322.113	274.616	18.999	−826.786	−702.774	91.773
489.700	217.482	366.911	287.580	38.849	--- CRYSTAL <--> LIQUID ---		
500	216.564	371.429	289.261	41.084	−816.238	−673.014	70.309
600	206.397	410.042	306.297	62.247	−806.816	−645.274	56.176
700	194.430	440.983	323.406	82.304	−798.643	−619.014	46.191
800	180.611	466.064	339.725	101.072	−791.858	−593.834	38.773

PREVIOUS: CURRENT: December 1974

Tantalum Chloride ($TaCl_5$) CRYSTAL-LIQUID

0 to 489.7 K crystal
above 489.7 K liquid

Refer to the individual tables for details.

M_r = 358.2129 Tantalum Chloride ($TaCl_5$) $Cl_5Ta_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0							
100							
200							
298.15	147.904	221.752	221.752	0.	−858.975	−746.448	130.775
300	147.904	222.667	221.755	0.274	−858.905	−745.750	129.847
400	147.904	265.216	227.556	15.064	−855.349	−708.578	92.531
489.700	147.904	295.142	237.288	28.331	CRYSTAL <--> LIQUID TRANSITION		
489.700	217.482	366.911	237.288	63.477			
500	216.564	371.429	240.005	65.712	−816.238	−673.014	70.309
600	206.397	410.042	265.250	86.875	−806.816	−645.274	56.176
700	194.430	440.983	288.223	106.932	−798.643	−619.014	46.191
800	180.611	466.064	308.940	125.700	−791.858	−593.834	38.773

PREVIOUS: CURRENT: December 1974

Tantalum Chloride ($TaCl_5$) $Cl_5Ta_1(cr,l)$

$S°(298.15\ K) = 412.973 \pm 3.14\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -763.07 \pm 8.4\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -764.84 \pm 8.4\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
406.0 (1)	[458.0](2)
324.0 (1)	180.9 (2)
[377.2](1)	53.9 (2)
[112.1](1)	127.0 (2)

Ground State Quantum Weight: [1]
Point Group: D_{3h}
$\sigma = 6$
Bond Distance: Ta–Cl = 2.27 ± 0.02 Å
Bond Angles: Cl*–Ta–Cl* = 120°; Cl*–Ta–Cl** = 90°; Cl**–Ta–Cl* = 180°
(* = equatorial ** = axial)
Product of the Moments of Inertia: $I_A I_B I_C = 1.02598 \times 10^{-111}\ g^3{\cdot}cm^6$

Enthalpy of Formation

The vapor pressures over $TaCl_5$(cr) and $TaCl_5$(l) have been measured by eight investigators. The reported vapor pressures are corrected for vapor non-ideality by means of the equation $\Delta G°/T = R\ln p - Bp/T$. The Berthelot equation of state and critical constants $T_c = 767$ K and $P_c = 43$ atm. reported by Nisel'son *et al.*[6] are used to calculate B. The corrected vapor pressures are used to calculate $\Delta_f H°(298.15\ K)$ by both 2nd and 3rd law methods.

Source	Method	T/K	Data Points	$\Delta_f H°(298.15\ K)$ kcal·mol⁻¹ 2nd law	3rd law	Drift cal·K⁻¹·mol⁻¹
$TaCl_5(cr) = TaCl_5(g)$						
Opykhtina and Fleischer[1]	transpiration	393–Tm	Eqn	23.12	22.46	−1.5
Tarasenkov and Komandin[2]	static	301–475	Eqn	20.63	22.26	4.3
Alexander and Fairbrother[3]	static	412–Tm	10*	22.94 ± 0.09	22.76 ± 0.03	−0.4 ± 0.2
Shchukarev and Kurbanov[5]	membrane	425–Tm	Eqn	23.46	22.67	−1.7
Schafer and Polert[7]	flow	350–385	17	22.75 ± 0.06	22.53 ± 0.02	−0.6 ± 0.2
Saeki *et al.*[8]	static	363–Tm	Eqn	22.31	22.53	0.6
Brink and Stevenson[9]	transpiration	431–473	28	21.80 ± 0.20	22.59 ± 0.08	1.8 ± 0.4
$TaCl_5(l) = TaCl_5(g)$						
Alexander and Fairbrother[3]	static	Tm–511	6*	17.17 ± 0.13	16.79 ± 0.01	−0.8 ± 0.3
Ainscough *et al.*[4]	boiling point	502–513	Eqn	16.73	16.62	−0.2
Saeki *et al.*[8]	static	490–505	Eqn	17.17	16.66	−1.0

*One point rejected due to a statistical test.

The adopted value for $\Delta_f H°(298.15\ K)$ of $TaCl_5(g)$ is −182.8 ± 2.0 kcal·mol⁻¹. This value is calculated using the rounded mean 3rd law result for the seven sublimation studies, $\Delta_{sub}H°(298.15\ K) = 22.5$ kcal·mol⁻¹. The rounded mean 3rd law result for the three vaporization studies leads to a $\Delta_f H°(298.15\ K)$ value for the gas which is 0.1 kcal·mol⁻¹ more positive.

Heat Capacity and Entropy

$TaCl_5(g)$ was shown by Spiridonov and Romanov,[15,16] using electron diffraction techniques, to have a trigonal bipyramidal structure of D_{3h} symmetry: all the Ta–Cl bond lengths being equal within experimental uncertainty, Ta–Cl = 2.27 ± 0.02 Å. Skinner and Sutton[10] earlier used electron diffraction techniques and had suggested the same structure although a square pyramidal structure was consistent with their experimental results. We adopt the results of Spiridonov and Romanov.[15,16] The principal moments of inertia are: $I_A = 91.0085 \times 10^{-39}$ and $I_B = I_C = 106.1766 \times 10^{-39}\ g{\cdot}cm^2$. A normal coordinate treatment of $TaCl_5(g)$ in the Urey-Bradley force fields was performed by So[18] using the reported vibrational frequencies of Beattie and Ozin.[17] This work by So[18] was intended to check the correctness of the reported fundamental frequencies and predict those frequencies which had not been observed (ν_3, ν_4, ν_5). Beattie and Ozin[17] had recorded the gas phase Raman spectra of $NbCl_5$, $NbBr_5$, $TaCl_5$, and $TaBr_5$. We adopt the results of So[18] which support the work of Beattie and Ozin.[17]

There are many references in the literature to spectroscopic observations (IR and Raman) of $TaCl_5$ in the solid state and in organic solvents. Many problems arise in any attempt in relating the observed spectra. Tantalum pentachloride was shown to be dimeric in the solid phase,[11] while there are indications that it is also dimeric in solution.[12-14]

Continued on page 941

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K⁻¹mol⁻¹	$S°$ J·K⁻¹mol⁻¹	$-[G°-H°(T_r)]/T$ J·K⁻¹mol⁻¹	$H°-H°(T_r)$ kJ·mol⁻¹	$\Delta_f H°$ kJ·mol⁻¹	$\Delta_f G°$ kJ·mol⁻¹	log K_f
0	0.	0.	INFINITE	−26.869	−763.071	−763.071	INFINITE
100	82.867	300.387	511.324	−21.094	−765.570	−746.743	390.059
200	109.077	367.054	423.672	−11.324	−765.647	−727.758	190.071
250	115.849	392.176	414.929	−5.688	−765.283	−718.325	150.086
298.15	120.137	412.973	412.973	0.	−764.835	−709.321	124.270
300	120.271	413.716	412.975	0.222	−764.817	−708.976	123.444
350	123.250	432.494	414.451	6.315	−764.294	−699.710	104.426
400	125.326	449.095	417.764	12.532	−763.741	−690.522	90.173
450	126.821	463.948	422.085	18.838	−763.173	−681.403	79.095
500	127.928	477.370	426.953	25.208	−762.602	−672.348	70.240
600	129.419	500.837	437.367	38.082	−761.469	−654 404	56.971
700	130.346	520.862	447.900	51.073	−760.361	−636.648	47.507
800	130.960	538.310	458.134	64.141	−759.277	−619.049	40.420
900	131.386	553.761	467.917	77.259	−758.215	−601.584	34.915
1000	131.693	567.620	477.206	90.414	−757.182	−584.237	30.517
1100	131.922	580.183	486.006	103.595	−756.186	−566.991	26.924
1200	132.097	591.670	494.339	116.796	−755.237	−549.834	23.934
1300	132.234	602.249	502.239	130.013	−754.334	−532.753	21.406
1400	132.343	612.052	509.737	143.242	−753.470	−515.741	19.243
1500	132.431	621.186	516.866	156.481	−752.635	−498.790	17.369
1600	132.503	629.736	523.656	169.728	−751.825	−481.894	15.732
1700	132.563	637.770	530.134	182.981	−751.048	−465.047	14.289
1800	132.613	645.349	536.327	196.240	−750.323	−448.245	13.008
1900	132.656	652.520	542.255	209.504	−749.666	−431.481	11.862
2000	132.692	659.325	547.940	222.771	−749.085	−414.750	10.832
2100	132.723	665.800	553.399	236.042	−748.581	−398.045	9.901
2200	132.751	671.975	558.650	249.316	−748.157	−381.363	9.055
2300	132.774	677.877	563.706	262.592	−747.820	−364.699	8.283
2400	132.795	683.528	568.582	275.870	−747.577	−348.047	7.575
2500	132.814	688.949	573.289	289.151	−747.439	−331.403	6.924
2600	132.830	694.159	577.838	302.433	−747.418	−314.763	6.324
2700	132.845	699.172	582.240	315.717	−747.526	−298.120	5.767
2800	132.858	704.004	586.503	329.002	−747.779	−281.472	5.251
2900	132.869	708.666	590.635	342.288	−748.192	−264.811	4.770
3000	132.880	713.171	594.645	355.576	−748.782	−248.133	4.320
3100	132.889	717.528	598.539	368.864	−749.569	−231.432	3.900
3200	132.898	721.747	602.324	382.154	−750.570	−214.703	3.505
3300	132.906	725.837	606.005	395.444	−788.263	−197.468	3.126
3400	132.913	729.804	609.588	408.735	−789.332	−179.549	2.758
3500	132.920	733.657	613.078	422.026	−790.439	−161.598	2.412
3600	132.926	737.402	616.480	435.319	−791.578	−143.615	2.084
3700	132.931	741.044	619.798	448.612	−792.744	−125.600	1.773
3800	132.937	744.589	623.035	461.905	−793.932	−107.554	1.478
3900	132.941	748.042	626.196	475.199	−795.135	−89.476	1.198
4000	132.946	751.408	629.285	488.493	−796.349	−71.366	0.932
4100	132.950	754.691	632.304	501.788	−797.565	−53.226	0.678
4200	132.954	757.895	635.256	515.083	−798.777	−35.057	0.436
4300	132.957	761.023	638.144	528.379	−799.980	−16.859	0.205
4400	132.960	764.080	640.972	541.675	−801.166	1.367	−0.016
4500	132.963	767.068	643.741	554.971	−802.330	19.619	−0.228
4600	132.966	769.990	646.454	568.267	−803.465	37.898	−0.430
4700	132.969	772.850	649.113	581.564	−804.566	56.199	−0.625
4800	132.972	775.649	651.720	594.861	−805.628	74.525	−0.811
4900	132.974	778.391	654.277	608.158	−806.646	92.873	−0.990
5000	132.976	781.078	656.786	621.456	−807.615	111.239	−1.162
5100	132.978	783.711	659.249	634.754	−808.531	129.626	−1.328
5200	132.980	786.293	661.668	648.052	−809.390	148.029	−1.487
5300	132.982	788.826	664.043	661.350	−810.188	166.449	−1.640
5400	132.984	791.312	666.377	674.648	−810.924	184.883	−1.788
5500	132.986	793.752	668.671	687.946	−811.594	203.331	−1.931
5600	132.987	796.148	670.926	701.245	−812.196	221.789	−2.069
5700	132.989	798.502	673.144	714.544	−812.729	240.258	−2.202
5800	132.990	800.815	675.325	727.843	−1551.944	261.537	−2.355
5900	132.992	803.088	677.471	741.142	−1552.546	292.809	−2.592
6000	132.993	805.324	679.584	754.441	−1553.118	324.091	−2.821

PREVIOUS: December 1974 (1 atm) CURRENT December 1974 (1 bar)

Tungsten Chloride (WCl$_5$) CRYSTAL $M_r = 361.115$

$S°(298.15 \text{ K}) = [217.56] \text{ J·K}^{-1}\text{·mol}^{-1}$
$T_{fus} = 526 \text{ K}$

$\Delta_f H°(0 \text{ K}) = \text{Unknown}$
$\Delta_f H°(298.15 \text{ K}) = -512.95 \pm 41.8 \text{ kJ·mol}^{-1}$
$\Delta_{fus} H° = 20.573 \pm 4.2 \text{ kJ·mol}^{-1}$
$\Delta_{sub} H°(298.15 \text{ K}) = 10.416 \text{ kJ·mol}^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(\text{WCl}_5, \text{cr}, 298.15 \text{ K}) = -122.6 \text{ kcal·mol}^{-1}$, is calculated from that of the gas less the enthalpy of sublimation, $\Delta_{sub} H°(298.15 \text{ K}) = 24.0 \text{ kcal·mol}^{-1}$. The latter is calculated by the third law method from partial pressures of WCl$_5$(g) derived from the total pressure data* of Shchukarev *et al.*[1] Dimer pressures, calculated from the same authors dimer–monomer dissociation data, are subtracted from the total pressures in order to obtain the monomer pressures. Analyses of the monomer pressures over both crystal and liquid give similar results and the average values for $\Delta_{sub} H°(298.15 \text{ K})$ are 20.6 (second law) and 24.0 kcal·mol^{-1} (third law) with a drift of about 7 cal·K^{-1}·mol^{-1}.

*Earlier data reported by Schukarev *et al.*,[2] have been revised and are not used here.

Heat Capacity and Entropy

$C_p° = 6.2 \text{ cal·K}^{-1}\text{·mol}^{-1}$ and $C_p°(526) = 7.25 \text{ cal·K}^{-1}\text{·mol}^{-1}$ are estimated using the method described by Kubaschewski and Evans.[3] Between 298.15 and 528, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, $S°(298.15 \text{ K}) = 52 \text{ cal·K}^{-1}\text{·mol}^{-1}$, is listed by comparison with those of WCl$_2$(cr), WCl$_4$(cr) and WCl$_6$(cr).

Fusion Data

The melting point was determined from vapor pressure data by Shchukarev *et al.*[1] The heat of melting is the difference at the melting point between the second law enthalpies of vaporization and sublimation derived from total vapor pressure data of Schchukarev *et al.*[1]

Sublimation Data

Refer to the ideal gas table for details.

References

[1] S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4 Ser. Fiz I Khim., No. 1, 120 (1959).
[2] Shchukarev *et al.*, Zhur. Neorg. Khim. 1, 357 (1956); 3, 2650 (1958).
[3] O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).

Tungsten Chloride (WCl$_5$) Cl$_5$W$_1$(cr)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0							
100							
200							
298.15	155.645	217.568	217.568	0.	−512.958	−401.811	70.396
300	155.875	218.531	217.571	0.288	−512.872	−401.122	69.842
400	167.435	264.957	223.823	16.454	−507.845	−364.608	47.613
500	178.996	303.562	236.011	33.775	−501.966	−329.460	34.418
526.000	182.004	312.711	239.577	38.468	--- CRYSTAL <--> LIQUID ---		
600	189.954	337.194	250.129	52.239	−495.140	−295.585	25.733
700	198.531	367.151	264.746	71.684	−487.476	−262.921	19.619
800	205.016	394.106	279.260	91.877	−479.177	−231.402	15.109
900	209.618	418.534	293.399	112.621	−470.422	−200.952	11.663
1000	212.966	440.806	307.043	133.763	−461.356	−171.494	8.958
1100	215.811	461.240	320.145	155.205	−452.069	−142.956	6.788
1200	217.903	480.113	332.699	176.896	−442.606	−115.271	5.018
1300	219.325	497.614	344.720	198.762	−433.042	−88.381	3.551
1400	220.288	513.905	356.230	220.745	−423.429	−62.229	2.322
1500	220.915	529.126	367.254	242.808	−413.806	−36.765	1.280

PREVIOUS: December 1962 CURRENT: December 1966

Tungsten Chloride (WCl$_5$) Cl$_5$W$_1$(cr)

Tungsten Chloride (WCl$_5$) LIQUID $M_r = 361.115$ Tungsten Chloride (WCl$_5$) Cl$_5$W$_1$(l)

$S°(298.15\ K) = [248.500]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$T_{fus} = 526\ K$

$\Delta_f H°(298.15\ K) = -495.386\ kJ{\cdot}mol^{-1}$

$\Delta_{fus} H° = 20.573 \pm 4.2\ kJ{\cdot}mol^{-1}$

Heat of Formation

The heat of formation $\Delta_f H°(WCl_5, l, 298.15\ K) = -118.4\ kcal{\cdot}mol^{-1}$, is calculated from that of WCl$_5$(cr) by adding the heat of melting and the difference between $H°(526;298.15)$ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be constant at 7.25 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

The entropy of WCl$_5$(l), $S°(298.15\ K) = 59.393\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ is calculated in a manner analogous to that of the heat of formation.

Melting Data

Refer to the crystal table for details.

Vaporization Data

The boiling point (f = 1 atm), 561.4 K, is calculated as the temperature at which the Gibbs energy of formation for both WCl$_5$(l) and WCl$_5$(g) are equal. The difference in the enthalpies of formation of WCl$_5$(l) and WCl$_5$(g) at the boiling point is the enthalpy of vaporization. Shchukarev *et al.*[1] revised their previous data[2] and derived the boiling point as 561.2 K from their vapor pressure measurements.

References

[1] S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz I Khim., No. 1, 120 (1959).

[2] S. A. Shchukarev and G. I. Novikov, Zhur. Neorg. Khim. 1, 357 (1956).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	182.004	248.498	248.498	0.	−495.387	−393.462	68.933
300	182.004	249.624	248.502	0.337	−495.252	−392.830	68.398
400	182.004	301.983	255.641	18.537	−488.190	−359.764	46.980
500	182.004	342.596	269.121	36.738	−481.432	−328.444	34.312
526.000	182.004	351.823	272.983	41.470	--- CRYSTAL <--> LIQUID ---		
600	182.004	375.780	284.216	54.938	−474.870	−298.465	25.984
700	182.004	403.836	299.352	73.138	−468.450	−269.574	20.116
800	182.004	428.139	313.966	91.339	−462.144	−241.595	15.775
900	182.004	449.576	327.866	109.539	−455.933	−214.400	12.443
1000	182.004	468.752	341.012	127.740	−449.808	−187.892	9.814
1100	182.004	486.099	353.426	145.940	−443.762	−161.994	7.692
1200	182.004	501.935	365.152	164.140	−437.791	−136.643	5.948
1300	182.004	516.503	376.241	182.341	−431.891	−111.787	4.492
1400	182.004	529.991	386.748	200.541	−426.061	−87.382	3.260
1500	182.004	542.548	396.721	218.742	−420.301	−63.392	2.208

PREVIOUS: December 1962 CURRENT: December 1966

Tungsten Chloride (WCl_5) CRYSTAL-LIQUID

0 to 526 K crystal
above 526 K liquid

Refer to the individual tables for details.

$M_r = 361.115$ Tungsten Chloride (WCl_5) $Cl_5W_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K						Standard State Pressure = $p°$ = 0.1 MPa	
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	155.645	217.568	217.568	0.	−512.958	−401.811	70.396
300	155.875	218.531	217.571	0.288	−512.872	−401.122	69.842
400	167.435	264.957	223.823	16.454	−507.845	−364.608	47.613
500	178.996	303.562	236.011	33.775	−501.966	−329.460	34.418
526.000	182.004	312.711	239.577	38.468	CRYSTAL <--> LIQUID		
526.000	182.004	351.823	239.577	59.041		TRANSITION	
600	182.004	375.780	254.931	72.509	−474.870	−298.465	25.984
700	182.004	403.836	274.250	90.710	−468.450	−269.574	20.116
800	182.004	428.139	292.001	108.910	−462.144	−241.595	15.775
900	182.004	449.576	308.342	127.111	−455.933	−214.400	12.443
1000	182.004	468.752	323.441	145.311	−449.808	−187.892	9.814
1100	182.004	486.099	337.452	163.511	−443.762	−161.994	7.692
1200	182.004	501.935	350.509	181.712	−437.791	−136.643	5.948
1300	182.004	516.503	362.725	199.912	−431.891	−111.787	4.492
1400	182.004	529.991	374.197	218.113	−426.061	−87.382	3.260
1500	182.004	542.548	385.006	236.313	−420.301	−63.392	2.208

PREVIOUS: CURRENT December 1966

Tungsten Chloride (WCl$_5$) IDEAL GAS $M_r = 361.115$ Tungsten Chloride (WCl$_5$) Cl$_5$W$_1$(g)

$\Delta_f H°(0\ \mathrm{K}) = 410.9 \pm 33\ \mathrm{kJ \cdot mol^{-1}}$

$S°(298.15\ \mathrm{K}) = [405.693]\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ $\Delta_f H°(298.15\ \mathrm{K}) = -412.5 \pm 33\ \mathrm{kJ \cdot mol^{-1}}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[7000]	[2]
[14000]	[2]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[480](1)	[350](2)
[400](1)	[150](2)
[380](1)	[100](2)
[130](1)	[180](2)

Ground State Quantum Weight: [2] $\sigma = [6]$
Point Group: [D$_{3h}$]
Bond Distance: W–Cl = [2.26] Å
Bond Angles: Cl*–W–Cl* = [120]°; Cl*–W–Cl** = [90]°; Cl**–W–Cl** = [180]°
Product of the Moments of Inertia: $I_A I_B I_C = [9.98 \times 10^{-112}]\ \mathrm{g^3 \cdot cm^6}$

Enthalpy of Formation

The heat of formation, $\Delta_f H°(\mathrm{WCl_5, g}, 298.15\ \mathrm{K}) = -98.6\ \mathrm{kcal \cdot mol^{-1}}$, is calculated from $\Delta_r H°(298.15\ \mathrm{K}) = 19.4\ \mathrm{kcal \cdot mol^{-1}}$ for $\mathrm{WCl_6(g) \rightarrow WCl_5(g) + 1/2\ Cl_2(g)}$. The value of $\Delta_r H°(298.15\ \mathrm{K})$ is calculated by the third law method from the equation for log K_p given by Shchukarev.[1] The second law $\Delta_r H°(298.15\ \mathrm{K})$ is 24.6 kcal·mol^{-1} and the third law drift is −8.5 cal·K^{-1}·mol^{-1}.

Heat Capacity and Entropy

The molecular configuration is assumed to be a trigonal bipyramid similar to that of MoCl$_5$ determined by electron diffraction by Ewens and Lister.[2] The bond distance is estimated to be the same as that in WCl$_6$(g). The three principal moments of inertia are: $I_A = 90.2084 \times 10^{-39}$ and $I_B = I_C = 105.2432 \times 10^{-39}\ \mathrm{g \cdot cm^2}$.

All vibrational frequencies are estimated from those of SbCl$_5$, PCl$_5$, NbCl$_5$ and TaCl$_5$ obtained from infrared and Raman spectra by Carlson.[3]

If it is considered that the metal atoms are effectively ionized, then the W^{5+} will have a single d electron *in a field of chloride ions*. The electronic splitting would be roughly the inverse of that in CuCl$_2$(g) as given by DeKock and Gruen,[4] where Cu has a d^9 configuration. By analogy with the splitting in CuCl$_2$, the low lying electronic levels are estimated to be 7000 cm^{-1}, both doublets.

References

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[3] G. L. Carlson, Spectrochim. Acta 19, 1291 (1963).
[4] C. W. DeDock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−26.248	−410.866	−410.866	INFINITE
100	79.886	293.996	503.816	−20.982	−413.531	−394.718	206.179
200	108.885	359.776	416.397	−11.324	−413.475	−375.794	98.147
250	115.882	384.884	407.651	−5.692	−413.047	−366.420	76.559
298.15	120.235	405.693	405.693	0.	−412.542	−357.485	62.630
300	120.370	406.438	405.696	0.223	−412.522	−357.143	62.184
350	123.362	425.232	407.173	6.321	−411.945	−347.959	51.930
400	125.434	441.848	410.489	12.544	−411.340	−338.859	44.250
450	126.918	456.712	414.814	18.854	−410.721	−329.836	38.286
500	128.014	470.144	419.686	25.229	−410.097	−320.882	33.522
600	129.486	493.625	430.108	38.110	−408.853	−303.156	26.392
700	130.400	513.659	440.648	51.108	−407.636	−285.637	21.314
800	131.006	531.114	450.889	64.180	−406.458	−268.289	17.517
900	131.434	546.570	460.678	77.303	−405.325	−251.086	14.573
1000	131.757	560.436	469.972	90.463	−404.240	−234.008	12.223
1100	132.019	573.006	478.777	103.652	−403.205	−217.035	10.306
1200	132.250	584.503	487.115	116.866	−402.221	−200.154	8.712
1300	132.467	595.098	495.019	130.102	−401.285	−183.353	7.367
1400	132.681	604.922	502.523	143.359	−400.399	−166.623	6.217
1500	132.900	614.084	509.658	156.638	−399.560	−149.954	5.222
1600	133.125	622.668	516.456	169.940	−398.768	−133.340	4.353
1700	133.357	630.746	522.944	183.264	−398.022	−116.774	3.588
1800	133.596	638.375	529.146	196.611	−397.323	−100.250	2.909
1900	133.841	645.605	535.087	209.983	−396.671	−83.764	2.303
2000	134.088	652.476	540.786	223.380	−396.070	−67.311	1.758
2100	134.336	659.024	546.262	236.801	−395.520	−50.887	1.266
2200	134.583	665.279	551.531	250.247	−395.024	−34.488	0.819
2300	134.827	671.267	556.607	263.717	−394.588	−18.110	0.411
2400	135.067	677.010	561.505	277.212	−394.214	−1.750	0.038
2500	135.301	682.529	566.237	290.730	−393.906	14.596	−0.305
2600	135.528	687.840	570.812	304.272	−393.664	30.932	−0.621
2700	135.748	692.959	575.242	317.836	−393.520	47.260	−0.914
2800	135.958	697.900	579.535	331.421	−393.510	63.584	−1.186
2900	136.160	702.674	583.699	345.027	−393.676	79.911	−1.439
3000	136.352	707.293	587.742	358.653	−394.047	96.247	−1.676
3100	136.534	711.767	591.671	372.297	−394.666	112.600	−1.897
3200	136.706	716.105	595.493	385.959	−395.563	128.976	−2.105
3300	136.868	720.314	599.212	399.638	−396.764	145.387	−2.301
3400	137.020	724.402	602.834	413.332	−398.302	161.837	−2.486
3500	137.162	728.376	606.364	427.042	−400.237	178.339	−2.662
3600	137.294	732.242	609.807	440.764	−402.663	194.903	−2.828
3700	137.416	736.005	613.167	454.500	−440.440	211.733	−2.989
3800	137.529	739.671	616.448	468.247	−440.547	229.360	−3.153
3900	137.632	743.245	619.654	482.005	−440.658	246.991	−3.308
4000	137.727	746.731	622.788	495.774	−440.770	264.624	−3.456
4100	137.813	750.133	625.852	509.551	−440.876	282.261	−3.596
4200	137.890	753.455	628.851	523.336	−440.971	299.899	−3.730
4300	137.960	756.700	631.787	537.128	−441.049	317.540	−3.857
4400	138.021	759.873	634.662	550.927	−441.105	335.182	−3.979
4500	138.075	762.975	637.479	564.732	−441.132	352.825	−4.095
4600	138.122	766.010	640.240	578.542	−441.127	370.469	−4.207
4700	138.163	768.981	642.948	592.357	−441.083	388.112	−4.313
4800	138.196	771.890	645.604	606.175	−440.996	405.753	−4.415
4900	138.224	774.740	648.210	619.996	−440.862	423.393	−4.513
5000	138.246	777.533	650.769	633.819	−440.677	441.028	−4.607
5100	138.263	780.271	653.281	647.645	−440.438	458.661	−4.698
5200	138.274	782.956	655.749	661.472	−440.140	476.287	−4.784
5300	138.281	785.590	658.175	675.299	−439.782	493.907	−4.868
5400	138.283	788.174	660.558	689.128	−439.360	511.520	−4.948
5500	138.280	790.712	662.902	702.956	−438.873	529.126	−5.025
5600	138.274	793.203	665.206	716.783	−438.318	546.720	−5.100
5700	138.264	795.650	667.473	730.610	−437.695	564.305	−5.171
5800	138.251	798.055	669.704	744.436	−437.001	581.878	−5.240
5900	138.234	800.418	671.899	758.260	−436.237	599.438	−5.307
6000	138.214	802.741	674.061	772.083	−435.401	616.984	−5.371

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

Iron Chloride (Fe_2Cl_6) IDEAL GAS $M_r = 324.412$ Iron Chloride ($(FeCl_3)_2$) $Cl_6Fe_2(g)$

$S°(298.15 K) = [537.016] J·K^{-1}·mol^{-1}$

$\Delta_f H°(0 K) = -658.290 \pm 8.4 kJ·mol^{-1}$
$\Delta_f H°(298.15 K) = -654.378 \pm 8.4 kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[300](1)	[110](1)	[230](1)
[200](1)	[350](1)	[85](1)
[120](1)	[100](1)	[70](1)
[95](1)	[18](1)	[260](1)
[35](1)	[310](1)	[110](1)
[250](1)	[110](1)	[90](1)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: D_{2h}
Bond Distances: Fe–Cl = 2.11 ± 0.03 Å; $Fe–Cl_{bridge} = 2.28 \pm 0.03$ Å
Bond Angles: Cl–Fe–Cl = 128 ± 3°; $Cl_{bridge}–Fe–Cl_{bridge} = 92 \pm 3°$
Product of the Moments of Inertia: $I_A I_B I_C = 7.35910 \times 10^{-111} g^3·cm^6$

Enthalpy of Formation

The vaporization of $FeCl_3(cr)$ is complex. It involves three possible chemical reactions, i.e. (1) $2FeCl_3(cr) = Fe_2Cl_6(g)$; (2) $FeCl_3(cr) = FeCl_3(g)$; and (3) $2FeCl_3(cr) = 2FeCl_2(cr) + Cl_2(g)$. Although these equilibria have been studied previously by many investigators, a review of their reported data reveals inconsistencies and errors. At room temperature the main vapor species present above $FeCl_3(cr)$ is $Fe_2Cl_6(g)$, a dimer of $FeCl_3(g)$. As temperature increases, the dimer gradually decomposes into monomers ($FeCl_3$, g). Simultaneously, part of $FeCl_3(cr)$ also decomposes into $FeCl_2(cr)$ and $Cl_2(g)$. Therefore in order to obtain the partial pressure of $Fe_2Cl(g)$, the partial pressures of other vapor species, e.g. $Cl_2(g)$ and $FeCl_3(g)$, must be known and deducted from the observed total pressures. However, only few investigators made such corrections. The total pressures above $FeCl_3(cr)$, at 500–600 K, have been determined by Maier[1] and Johnstone *et al.*,[2] respectively. The partial pressures of $Fe_2Cl_6(g)$ were evaluated by the subtraction of the calculated equilibrium pressures of $Cl_2(g)$, obtained from reaction,[3] from the reported total pressures. The partial pressures of $FeCl_3(g)$ were found to be insignificant at these temperatures. Using the partial pressures obtained for $Fe_2Cl_6(g)$, the enthalpy change $\Delta_r H°(298.15 K)$ of reaction[1] was derived by both the second and third law methods. Then the value of $\Delta_f H°(Fe_2Cl_6$, g, 298.15 K) was calculated. The results are given in this table.

Wilson and Gregory[3] have investigated the vaporization and thermal decomposition equilibria of $FeCl_3(cr)$ by gas saturation flow and diaphragm gage techniques. Using the partial pressures for $Fe_2Cl_6(g)$, calculated from an equation, the values of $\Delta_r H°(298.15 K)$ and $\Delta_f H°(298.15 K)$ were also evaluated and listed in the table. Based on the total pressures measured by Stirnemann[4] and Sano,[5] the equations for the pressures of $Fe_2Cl_6(g)$ and $Cl_2(g)$ in equilibrium with $FeCl_3(cr)$ and $FeCl_2(cr)$ as a function of temperature were reported by Wilson and Gregory.[3] The corresponding values of $\Delta_r H°(298.15 K)$ and $\Delta_f H°(298.15 K)$ were hence calculated. A brief summary and discussion of results of some other previous investigators were also given in the same report.

Source	T/K	$\Delta_r H°(298.15 K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15 K)$* kcal·mol^{-1}
Maier[1]	489.6–591.5	32.18 ± 0.40	34.67	−156.25 ± 0.50
Johnstone *et al.*[2]	505.2–562.2	34.8 ± 0.49	34.50	−156.42 ± 0.50
Wilson and Gregory[3]	463.4–577.2	34.46	34.45	−156.47 ± 0.40
Stirnemann[4]	526.2–574.2	35.04	34.49	−156.42 ± 0.50
Sano[5]	513.2–569.2	30.67	34.76	−156.16 ± 0.50

*Based on the third law values for $\Delta_r H°(298.15 K)$.

The value of $\Delta_f H°(298.15 K)$ for $Fe_2Cl_6(g)$ is selected as −156.4 ± 2.0 kcal·mol^{-1}.

Heat Capacity and Entropy

The molecular structure, bond distances and angles were obtained from Zasorin *et al.*[6] The vibrational frequencies were estimated by comparison with those for $Al_2Cl_6(g)$ such that the values of $\Delta H°$ derived from the equilibrium data by the second and third law methods are in reasonable agreement. The three principal moments of inertia are: $I_A = 2.79395 \times 10^{-37}$, $I_B = 1.16349 \times 10^{-37}$ and $I_C = 2.26383 \times 10^{-37}$ g·cm^2.

References

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[5] K. Sano, J. Chem. Soc. Japan, 59, 1073 (1938).
[6] E. Z. Zasorin, N. G. Rambidi and P. A. Akishin, Zh. Strukt. Khim., 4, 910 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−40.447	−658.269	−658.269	INFINITE
100	132.329	365.442	683.671	−31.823	−659.226	−637.855	333.181
200	164.177	469.299	552.585	−16.657	−656.711	−617.413	161.252
250	170.184	506.640	539.778	−8.285	−655.470	−607.734	126.979
298.15	173.663	536.937	536.937	0.	−654.378	−598.641	104.879
300	173.768	538.011	536.940	0.321	−654.338	−598.295	104.172
350	176.052	564.982	539.065	9.071	−653.317	−589.037	87.909
400	177.587	588.597	543.811	17.914	−652.411	−579.917	75.729
450	178.665	609.579	549.975	26.822	−651.626	−570.904	66.269
500	179.449	628.446	556.894	35.776	−650.968	−561.971	58.709
600	180.486	661.263	571.635	53.777	−650.035	−544.268	47.383
700	181.121	689.137	586.480	71.860	−649.620	−526.680	39.301
800	181.537	713.351	600.858	89.994	−649.813	−509.113	33.242
900	181.824	734.751	614.569	108.163	−650.863	−491.473	28.524
1000	182.030	753.919	627.563	126.356	−653.374	−473.648	24.741
1100	182.183	771.276	639.851	144.567	−657.699	−455.437	21.627
1200	182.300	787.133	651.473	162.792	−660.940	−436.946	19.020
1300	182.391	801.729	662.477	181.026	−660.909	−418.282	16.807
1400	182.463	815.248	672.913	199.269	−661.066	−399.613	14.910
1500	182.521	827.839	682.826	217.519	−661.411	−380.927	13.265
1600	182.569	839.620	692.262	235.773	−661.945	−362.212	11.825
1700	182.609	850.689	701.259	254.032	−664.568	−343.420	10.552
1800	182.642	861.128	709.853	272.295	−666.151	−324.484	9.416
1900	182.670	871.003	718.077	290.560	−696.123	−304.051	8.359
2000	182.694	880.374	725.960	308.828	−698.572	−283.353	7.400
2100	182.715	889.288	733.527	327.099	−701.052	−262.531	6.530
2200	182.733	897.788	740.801	345.371	−703.566	−241.590	5.736
2300	182.748	905.911	747.805	363.645	−706.120	−220.534	5.008
2400	182.762	913.689	754.556	381.921	−708.715	−199.367	4.339
2500	182.774	921.150	761.071	400.198	−711.358	−178.090	3.721
2600	182.785	928.319	767.367	418.476	−714.050	−156.706	3.148
2700	182.795	935.218	773.457	436.755	−716.796	−135.217	2.616
2800	182.803	941.866	779.353	455.035	−719.598	−113.626	2.120
2900	182.811	948.281	785.068	473.315	−722.457	−91.934	1.656
3000	182.818	954.478	790.613	491.597	−725.373	−70.143	1.221
3100	182.824	960.473	795.996	509.879	−728.347	−48.253	0.813
3200	182.830	966.278	801.227	528.162	−1427.977	−11.418	0.186
3300	182.835	971.904	806.314	546.445	−1427.259	32.838	−0.520
3400	182.840	977.362	811.265	564.729	−1426.656	77.074	−1.184
3500	182.844	982.662	816.087	583.013	−1426.164	121.294	−1.810
3600	182.848	987.813	820.786	601.297	−1425.780	165.501	−2.401
3700	182.852	992.823	825.368	619.582	−1425.499	209.700	−2.960
3800	182.855	997.699	829.839	637.868	−1425.315	253.891	−3.490
3900	182.858	1002.449	834.205	656.153	−1425.223	298.079	−3.992
4000	182.861	1007.079	838.469	674.439	−1425.218	342.267	−4.470
4100	182.864	1011.594	842.636	692.726	−1425.293	386.455	−4.923
4200	182.866	1016.001	846.712	711.012	−1425.444	430.645	−5.356
4300	182.869	1020.303	850.699	729.299	−1425.663	474.840	−5.768
4400	182.871	1024.508	854.602	747.586	−1425.946	519.041	−6.162
4500	182.873	1028.617	858.423	765.873	−1426.287	563.249	−6.538
4600	182.875	1032.637	862.167	784.160	−1426.681	607.466	−6.898
4700	182.877	1036.570	865.836	802.448	−1427.123	651.690	−7.243
4800	182.878	1040.420	869.433	820.736	−1427.610	695.926	−7.573
4900	182.880	1044.191	872.961	839.024	−1428.138	740.172	−7.890
5000	182.881	1047.885	876.423	857.312	−1428.704	784.428	−8.195
5100	182.883	1051.507	879.821	875.600	−1429.306	828.697	−8.488
5200	182.884	1055.058	883.156	893.888	−1429.941	872.977	−8.769
5300	182.885	1058.542	886.433	912.177	−1430.609	917.270	−9.040
5400	182.886	1061.960	889.652	930.465	−1431.310	961.577	−9.301
5500	182.887	1065.316	892.815	948.754	−1432.043	1005.897	−9.553
5600	182.889	1068.611	895.925	967.043	−1432.810	1050.229	−9.796
5700	182.890	1071.848	898.983	985.332	−1433.613	1094.576	−10.031
5800	182.890	1075.029	901.991	1003.621	−1434.454	1138.938	−10.257
5900	182.891	1078.156	904.951	1021.910	−1435.337	1183.314	−10.476
6000	182.892	1081.230	907.863	1040.199	−1436.265	1227.705	−10.688

PREVIOUS: June 1965 (1 atm) CURRENT: June 1965 (1 bar)

Molybdenum Chloride ($MoCl_6$) CRYSTAL $M_r = 308.658$ Molybdenum Chloride ($MoCl_6$) $Cl_6Mo_1(cr)$

$S°(298.15\ K) = [255.224 \pm 16.7]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K)$ = Unknown

$\Delta_fH°(298.15\ K) = [-523.000 \pm 41.8]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Novikov and Galitskii,[1] assumed that the equilibrium $MoCl_6(cr) = MoCl_5(g) + 1/2\ Cl_2(g)$ exists. They then calculated values for the constant of the above equilibrium and estimated the thermodynamic characteristics, $\Delta_rH°(T) = 4\ kcal\ mol^{-1}$ and $\Delta_rS(T) = 8\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, of the equilibrium $MoCl_6(cr) = MoCl_5(cr) + 1/2\ Cl_2(g)$, from which they obtained the $\Delta_fH°(MoCl_6, cr, 298.15\ K) = -125\ kcal{\cdot}mol^{-1}$.

Heat Capacity and Entropy

The adopted heat capacity is the same as that of $WCl_6(\alpha, cr)$, since the heat capacities of W and Mo are almost the same. The entropy is estimated from that of $MoCl_5(cr)$ by the addition of $4\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ due to one extra chlorine atom in the molecule.

Vaporization Data

The sublimation point is calculated from the free energy crossover between crystal and gas. However, it should be noted that $MoCl_6(cr)$ is unstable with respect to $MoCl_5(cr)$ at all temperatures and thus sublimation could occur only under an atmosphere of Cl_2.

References

[1] G. I. Novikov and N. V. Galitskii, Zh. Neorg. Khim. 10, 576–8 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	$\log K_f$
0							
100							
200							
298.15	175.310	255.224	255.224	0.	−523.000	−391.033	68.507
300	175.728	256.310	255.227	0.325	−522.908	−390.215	67.942
400	192.464	309.156	262.320	18.734	−517.364	−346.787	45.286
500	209.200	353.955	276.271	38.842	−510.519	−304.907	31.853
600	223.007	393.425	292.572	60.512	−502.362	−264.531	23.029
700	229.702	428.347	309.526	83.175	−493.387	−225.594	16.834
800	233.049	459.266	326.350	106.333	−484.049	−187.973	12.273
900	233.886	486.768	342.675	129.684	−474.626	−151.529	8.795
1000	234.304	511.432	358.339	153.093	−465.239	−116.133	6.066
1100	234.722	533.783	373.288	176.544	−455.901	−81.675	3.878
1200	235.141	554.224	387.526	200.037	−446.612	−48.065	2.092
1300	235.559	573.063	401.083	223.574	−437.373	−15.228	0 612
1400	235.840	590.531	413.999	247.145	−428.198	16.900	−0.631
1500	235.978	606.808	426.317	270.737	−419.104	48.375	−1.685

PREVIOUS: CURRENT December 1968

Molybdenum Chloride (MoCl$_6$) IDEAL GAS M_r = 308.658 Molybdenum Chloride (MoCl$_6$) Cl$_6$Mo$_1$(g)

$\Delta_f H°(0\ K) = [-438.253 \pm 83.7]\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = [419.538 \pm 16.7]\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-439.320 \pm 83.7]\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}
[347](1)	[144](3)
[326](2)	[171](3)
[390](3)	[106](3)

Ground State Quantum Weights = [1]
Point Group = O_h
Bond Distance: Mo–Cl = [2.26] Å
Bond Angle: Cl–Mo–Cl = [90°]; $\sigma = 24$
Product of the Moments of Inertia: $I_A I_B I_C = [1.7396 \times 10^{-111}]\ g^3\cdot cm^6$

Enthalpy of Formation

Novikov and Galitskii,[1] assumed that the equilibrium $MoCl_6(cr) = MoCl_5(g) + 1/2\ Cl_2(g)$ exists. They then calculated values for the constant of the above equilibrium and estimated the thermodynamic characteristics, $\Delta_T H° = 2.5\ kcal\cdot mol^{-1}$ and $\Delta_T S° = 10\ cal\cdot K^{-1}\cdot mol^{-1}$ of the equilibrium $MoCl_6(g) = MoCl_5(g) + 1/2\ Cl_2(g)$, from which they obtained the $\Delta_f H°(MoCl_6, g, 298.15\ K) = -105\ kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those of MoF_6 and WF_6, given by Nakamoto[2], and WCl_6 given by Evans and Lo.[3]

Structure, bond distance and bond angle are estimated to be the same as those of WCl_6. The three principal moments of inertia are $I_A = I_B = I_C = 120.2684 \times 10^{-39}\ g\cdot cm^2$.

References

[1] G. I. Novikov and N. V. Galitskii, Zh. Neorg. Khim. 10, 576–82 (1965).
[2] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York–London, (1963).
[3] J. C. Evans and G. Y. S. Lo, J. Mol. Spectrosc. 26, 147 (1968).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−31.060	−438.253	−438.253	INFINITE
100	94.690	285.524	537.586	−25.206	−441.626	−412.774	215.611
200	131.116	364.480	432.505	−13.605	−440.980	−384.002	100.291
250	139.219	394.683	422.003	−6.830	−440.179	−369.847	77.275
298.15	144.125	419.654	419.654	0.	−439.320	−356.378	62.436
300	144.276	420.546	419.657	0.267	−439.286	−355.864	61.961
350	147.587	443.052	421.427	7.569	−438.354	−342.033	51.046
400	149.853	462.917	425.396	15.008	−437.410	−328.338	42.876
450	151.463	480.665	430.569	22.543	−436.468	−314.760	36.536
500	152.644	496.687	436.393	30.147	−435.533	−301.287	31.475
600	154.221	524.669	448.840	45.497	−433.696	−274.611	23.907
700	155.193	548.521	461.419	60.972	−431.910	−248.239	18.524
800	155.833	569.289	473.633	76.525	−430.177	−222.119	14.503
900	156.276	587.670	485.302	92.132	−428.498	−196.213	11.388
1000	156.595	604.153	496.377	107.776	−426.876	−170.492	8.906
1100	156.832	619.090	506.864	123.448	−425.317	−144.929	6.882
1200	157.013	632.744	516.794	139.141	−423.829	−119.506	5.202
1300	157.154	645.318	526.203	154.849	−422.418	−94.203	3.785
1400	157.266	656.968	535.132	170.570	−421.092	−69.006	2.575
1500	157.357	667.822	543.620	186.302	−419.859	−43.901	1.529
1600	157.431	677.980	551.704	202.041	−418.726	−18.874	0.616
1700	157.493	687.526	559.415	217.788	−417.700	6.084	−0.187
1800	157.545	696.529	566.785	233.539	−416.793	30.986	−0.899
1900	157.588	705.048	573.840	249.296	−416.012	55.841	−1.535
2000	157.626	713.133	580.604	265.057	−415.370	80.658	−2.107
2100	157.658	720.824	587.100	280.821	−414.878	105.446	−2.623
2200	157.686	728.159	593.346	296.588	−414.549	130.216	−3.092
2300	157.711	735.169	599.361	312.358	−414.396	154.973	−3.520
2400	157.732	741.882	605.161	328.130	−414.433	179.728	−3.912
2500	157.751	748.321	610.759	343.905	−414.677	204.489	−4.273
2600	157.768	754.508	616.170	359.681	−415.152	229.265	−4.606
2700	157 783	760.463	621.404	375.458	−415.902	254.064	−4.915
2800	157.796	766.201	626.474	391.237	−416.991	278.896	−5.203
2900	157.808	771.739	631.388	407.017	−454.386	303.823	−5.472
3000	157.819	777.089	636.156	422.799	−454.363	329.968	−5.745
3100	157.829	782.264	640.786	438.581	−454.398	356.113	−6.000
3200	157.838	787.275	645.286	454.364	−454.488	382.259	−6.240
3300	157.846	792.132	649.663	470.149	−454.631	408.410	−6.465
3400	157.853	796.844	653.923	485.934	−454.823	434.565	−6.676
3500	157.860	801.420	658.072	501.719	−455.060	460.727	−6.876
3600	157.866	805.867	662.116	517.505	−455.336	486.897	−7.065
3700	157.872	810.193	666.060	533.292	−455.645	513.074	−7.243
3800	157.877	814.403	669.908	549.080	−455.979	539.259	−7.413
3900	157.882	818.504	673.666	564.868	−456.333	565.455	−7.573
4000	157.887	822.501	677.337	580.656	−456.699	591.659	−7.726
4100	157.891	826.400	680.925	596.445	−457.068	617.873	−7.872
4200	157.895	830.205	684.435	612.234	−457.432	644.095	−8.010
4300	157.898	833.920	687.868	628.024	−457.785	670.326	−8.143
4400	157.902	837.550	691.229	643.814	−458.119	696.566	−8.269
4500	157.905	841.099	694.520	659.604	−458.425	722.811	−8.390
4600	157.908	844.569	697.744	675.395	−458.698	749.065	−8.506
4700	157.911	847.965	700.904	691.186	−458.929	775.322	−8.617
4800	157.913	851.290	704.003	706.977	−459.113	801.585	−8.723
4900	157.916	854.546	707.042	722.769	−459.245	827.852	−8.825
5000	157.918	857.736	710.024	738.560	−1050.702	859.850	−8.983
5100	157.920	860.864	712.951	754.352	−1052.391	898.079	−9.198
5200	157.922	863.930	715.825	770.144	−1054.158	936.340	−9.406
5300	157.924	866.938	718.648	785.937	−1055.996	974.636	−9.606
5400	157.926	869.890	721.422	801.729	−1057.901	1012.968	−9.799
5500	157.928	872.788	724.148	817.522	−1059.868	1051.336	−9.985
5600	157.929	875.634	726.827	833.315	−1061.891	1089.739	−10.165
5700	157.931	878.429	729.463	849.108	−1063.964	1128.179	−10.339
5800	157.932	881.176	732.055	864.901	−1066.084	1166.657	−10.507
5900	157.934	883.875	734.605	880.694	−1068.244	1205.170	−10.670
6000	157.935	886.530	737.115	896.488	−1070.444	1243.720	−10.828

PREVIOUS: December 1968 (1 atm) CURRENT· December 1968 (1 bar)

Tungsten Chloride, alpha (WCl_6) CRYSTAL(α_1–α_2) $M_r = 96.568$ Tungsten Chloride, Alpha (α–WCl_6) $Cl_6W_1(cr)$

$S°(298.15 K) = [238.488] J·K^{-1}·mol^{-1}$
T_{trs} ($\alpha_1 \rightarrow \alpha_2$) = 450 ± 10 K
T_{trs} ($\alpha_2 \rightarrow \beta$) = 503 ± 3 K

$\Delta_f H°(0 K)$ = Unknown
$\Delta_f H°(298.15 K) = -593.71 \pm 25.1 kJ·mol^{-1}$
$\Delta_{trs}H°(\alpha_1 \rightarrow \alpha_2) = [4.2] kJ·mol^{-1}$
$\Delta_{trs}H°(\alpha_2 \rightarrow \beta) = 15.774 kJ·mol^{-1}$

Enthalpy of Formation

Shchukarev *et al.*[1] have measured calorimetrically the heat of solution of $WCl_6(cr)$ and also of $H_2WO_4(cr)$ in a 12% solution of NaOH as −188.0 ± 0.3 and −13.6 ± 0.11 $kcal·mol^{-1}$, respectively. Based on these data and a heat of dilution value for Na_2WO_4 which is essentially zero, we obtain $\Delta_r H°(298.15 K) = -174.4 \pm 0.3 kcal·mol^{-1}$ for $WCl_6(cr) + 6 NaOH(aq, 16.3 H_2O) \rightarrow H_2WO_4(cr) + 6 NaCl(aq, 22000 H_2O) + 2 H_2O(l)$. This reaction gives $\Delta_f H°(WCl_6, cr, 298.15 K) = -141.9 \pm 6 kcal·mol^{-1}$, using a revised $\Delta_f H°(H_2WO_4, cr, 298.15 K) = 270.5 kcal·mol^{-1}$, and other auxiliary data from JANAF Tables and from Parker.[2] The authors have suggested a possible uncertainty of the order of 5 $kcal·mol^{-1}$ due to the slowness of the dissolution of $WCl_6(cr)$.

Heat Capacity and Entropy

Welty[5] has measured the enthalpy changes for $WCl_6(\alpha, cr)$ in the temperature range from 406 to 502.4 K by drop calorimetry. Few points were measured in the region of the $\alpha_1 \rightarrow \alpha_2$ transition and no attempt was made to investigate the phase present at the conclusion of the drop. Thus, these data appear to be inadequate to define the heat capacities of the α_1 and α_2 phase. The adopted heat capacities are estimated so that they are reasonably consistent with the enthalpy data.

The entropy, $S°(298.15 K) = 57.0 cal·K^{-1}·mol^{-1}$, is calculated from that of the gas using $\Delta S°(298.15 K) = 43.155 cal·K^{-1}·mol^{-1}$ from the vaporization and sublimation data given in the $WCl_6(g)$ table (December 31, 1966).

Transition Data

Transition temperatures and heats of transition have been reported by the following investigators, and their results are summarized as follows:

Source	Method	$\alpha_1 \rightarrow \alpha_2$ Transition T/K	$\alpha_1 \rightarrow \alpha_2$ Transition $\Delta_{trs}H°$ $kcal·mol^{-1}$	$\alpha_2 \rightarrow \beta$ Transition T/K	$\alpha_2 \rightarrow \beta$ Transition $\Delta_{trs}H°$ $kcal·mol^{-1}$
Ketelaar *et. al*[3]	Vapor pressure	441	—	500	3.4
Stevenson[4]	Cooling curve	458	—	503	—
	Vapor pressure	—	—	503	1.9
Welty[5]	Drop calorimetric	—	—	504	3.4
Shchukarev *et al.*[6]	Vapor pressure	—	—	504	3.4
Dobrotin *et al.*[7]	Approximate calorimetric	—	—	493 ± 10	5.5

The adopted $\Delta_f H°(450 K)$ ($\alpha_1 \rightarrow \alpha_2$) and $\Delta_f H°(503 K)$ ($\alpha_2 \rightarrow \beta$) are calculated as 1.0 and 3.77 $kcal·mol^{-1}$, respectively, based on the adopted heat capacities and the enthalpy data. The enthalpies are assumed to refer to α_1 phase as the final state, although no experimental evidence for this is given.

Fusion Data

Refer to the β–crystal table for details.

Sublimation Data

Refer to the ideal gas table for details.

References

[1] S. A. Shchukarev, I. V. Vasilkova and G. I. Novikov, Zh. Neorg. Khim. 3, 2642 (1958).
[2] V. B. Parker, NSRDS-NBS 2, (1965).
[3] J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. 62, 597 (1943).
[4] F. D. Stevenson, Ph.D. Thesis, Oregon State University (1962); U.S. Bur. Mines RI 6367, (1964).
[5] J. R. Welty, Ph.D. Thesis, Oregon State University (1962).
[6] S. A Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. I Khim., No. 1, 87 (1961).
[7] R. B. Dobrotin, A. V. Suvorov and Y. V. Kondrat'ev Vestnik Leningrad. Univ. 19, No. 4 Fiz. I Khim. No. 1, 95 (1964).

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	175.418	238.488	238.488	0.	−593.710	−455.544	79.809
300	175.728	239.574	238.491	0.325	−593.618	−454.687	79.168
400	192.464	292.420	245.584	18.734	−588.082	−409.178	53.433
450	200.832	315.572	252.090	28.567	−584.830	−387.006	44.923
450.000	200.832	324.870	252.090	32.751	-------- I <--> II	--------	
500	209.200	346.463	260.459	43.002	−577.043	−365.681	38.202
503.000	209.702	347.716	260.976	43.630	------- II <--> III	--------	
600	222.170	385.865	278.144	64.633	−568.866	−324.158	28.220
700	229.367	420.706	296.072	87.244	−559.872	−284.076	21.198
800	232.840	451.598	313.620	110.383	−550.476	−245.315	16.017
900	234.095	479.108	330.508	133.740	−540.969	−207.741	12.057
1000	234.304	503.792	346.624	157.168	−531.485	−171.225	8.944

PREVIOUS: December 1962   CURRENT: December 1966

Tungsten Chloride, Alpha (α–WCl_6) $Cl_6W_1(cr)$

Tungsten Chloride, beta (WCl_6) CRYSTAL(β) $M_r = 396.568$

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = [280.604]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(298.15\ K) = [-572.877]\ kJ{\cdot}mol^{-1}$

$T_{trs}\ (\alpha_2 \to \beta) = 503 \pm 3\ K$

$\Delta_{trs} H°(\alpha_2 \to \beta) = [15.774]\ kJ{\cdot}mol^{-1}$

$T_{fus} = 555 \pm 2\ K$

$\Delta_{fus} H° = [6.694]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(WCl_6, \beta, cr, 298.15\ K) = -136.921\ kcal{\cdot}mol^{-1}$, is calculated from that of $WCl_6(\alpha,cr)$ by adding the heat of $\alpha_2 \to \beta$ transition and the difference between $H°(593;298.15)$ for $WCl_6(\alpha,cr)$ and $WCl_6(\beta, cr)$.

Heat Capacity and Entropy

Welty[1] has measured the enthalpy changes for $WCl_6(\beta,cr)$ in the temperature range from 508 to 553 K by drop calorimetry. Because of the short temperature range, poor distribution of pints and lack of identification of the phase present at the conclusion of each drop, we feel that the enthalpy data are insufficient to define the heat capacity accurately. The adopted heat capacities are estimated so that they are consistent with the enthalpy data within their probable uncertainty.

The entropy of $WCl_6(\beta,cr)$, $S°(298.15\ K) = 67.066\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ is calculated in a manner analogous to that of the heat of formation.

Transition Data

Refer to the α–crystal table for details.

Fusion Data

Melting point and heat of melting have been reported by the following investigators, and their results are summarized as follows:

Source	Method	T_{fus}/K	$\Delta H°(kcal{\cdot}mol^{-1})$
Ketelaar *et al.*[2]	Vapor pressure	557	2.3
Stevenson[3]	Cooling curve	555	-
	Vapor Pressure	555	1.5
Welty[1]	Drop calorimetric	556	1.6
Shchukarev *et al.*[4]	Vapor pressure	564	2.0
Dobrotin *et al.*[5]	Approximate calorimetric	545 ± 12	4.2

The adopted heat of melting, $\Delta_f H°(555\ K) = 1.6\ kcal{\cdot}mol^{-1}$, is calculated from the adopted heat capacities and the enthalpy data. The enthalpies are assumed to refer to α_1 phase as the final state, although no experimental evidence for this is available.

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is calculated as the difference between $\Delta_f H°(298.15\ K)$ for $WCl_6(\beta, cr)$ and $WCl_6(g)$.

References

[1] J. R. Welty, Ph.D. Thesis, Oregon State University (1962).

[2] J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. 62, 597 (1943).

[3] T. D. Stevenson, Ph.D. Thesis, Oregon State University (1962); U. S. Bur. Mines RI 6367, (1964).

[4] S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. I Khim., No. 1, 87 (1961).

[5] R. B. Dobrotin, A. V. Suvorov and Y. V. Kondrat'ev, Vestnik Leningrad. Univ. 19, No. 4, Ser. Fiz. I Khim., No. 1, 95 (1964).

Tungsten Chloride, Beta (β–WCl_6) $Cl_6W_1(cr)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	188.280	280.604	280.604	0.	−572.877	−447.269	78.360
300	188.280	281.769	280.608	0.348	−572.763	−446.490	77.741
400	188.280	335.934	287.993	19.176	−566.808	−405.309	52.928
500	188.280	377.947	301.938	38.004	−561.208	−365.588	38.193
503.000	188.280	379.075	302.397	38.569	−−−−−− II <−−> III −−−−−−−		
555.000	188.280	397.597	310.463	48.360	−−−−− III <−−> LIQUID −−−−		
600	188.280	412.275	317.554	56.832	−555.834	−326.972	28.465
700	188.280	441.298	333.212	75.660	−550.623	−289.242	21.584
800	188.280	466.439	348.329	94.488	−545.539	−252.250	16.470
900	188.280	488.616	362.708	113.316	−540.561	−215.889	12.530
1000	188.280	508.453	376.308	132.144	−535.676	−180.077	9.406
1100	188.280	526.398	389.150	150.972	−530.878	−144.750	6.874
1200	188.280	542.780	401.280	169.800	−526.160	−109.857	4.782
1300	188.280	557.851	412.752	188.628	−521.518	−75.354	3.028
1400	188.280	571.804	423.621	207.456	−516.952	−41.205	1.537
1500	188.280	584.794	433.938	226.284	−512.460	−7.380	0.257

PREVIOUS: CURRENT: December 1966

Tungsten Chloride (WCl_6) LIQUID $M_r = 396.568$ Tungsten Chloride (WCl_6) $Cl_6W_1(l)$

$S°(298.15\text{ K}) = [284.868]\text{ J·K}^{-1}\text{·mol}^{-1}$ $\Delta_fH°(298.15\text{ K}) = [-569.405]\text{ kJ·mol}^{-1}$

$T_{fus} = 555 \pm 2\text{ K}$ $\Delta_{fus}H° = 6.694\text{ kJ·mol}^{-1}$

Enthalpy of Formation

$\Delta_fH°(WCl_6, l, 298.15\text{ K})$ is calculated from that of $WCl_6(\beta, cr)$ by adding the enthalpy of fusion and the difference in enthalpy, $H°(555\text{ K})-H°(298.15\text{ K})$, between the β–crystal and liquid.

Heat Capacity and Entropy

Welty,[1] has measured the enthalpy changes for $WCl_6(l)$ in the temperature range from 560 to 603 K by drop calorimetry. Since the temperature range was very short and no attempt was made to investigate the phase present at the conclusion of the drop, we feel that the enthalpy data are insufficient to define the heat capacity accurately. The adopted heat capacities are estimated so that they are reasonably consistent with the enthalpy data.

$S°(298.15\text{ K})$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the β–crystal table for details.

Vaporization Data

T_{vap} is calculated as the temperature at which the Gibbs energies of formation for both $WCl_6(l)$ and $WCl_6(g)$ are equal. The difference in the enthalpies of formation of $WCl_6(l)$ and $WCl_6(g)$ at T_{vap} is the enthalpy of vaporization.

Ketelaar *et al.*,[2] have determined the boiling point and the heat of vaporization as 609.7 K and 15.24 kcal·mol^{-1}, respectively, from vapor pressure measurements. Shchukarev *et al.*[3-5] revised their previous data and gave the boiling point and the heat of vaporization as 616.2 K and 14.7 kcal·mol^{-1}, respectively, from their vapor pressure measurements.

Refer to the ideal gas table for additional information.

References

[1] J. R. Welty, Ph.D. Thesis, Oregon State University (1962).
[2] J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. **62**, 597 (1943).
[3] S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. **16**, No. 4, Ser. Fiz. I Khim., No. 1, 87 (1961).
[4] S. A. Shchukarev and G. I. Novikov, Zh. Neorg. Khim. **1**, 357 (1956).
[5] S. A. Shchukarev, G. I. Novikov, A. V. Suvorov and A K. Baev, Zh. Neorg. Khim. **3**, 2630 (1958).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	200.832	284.868	284.868	0.	−569.405	−445.068	77.974
300	200.832	286.110	284.872	0.372	−569.267	−444.296	77.359
400	200.832	343.886	292.749	20.455	−562.057	−403.739	52.723
500	200.832	388.701	307.625	40.538	−555.202	−364.958	38.127
555.000	200.832	409.659	316.716	51.584	------ III <--> LIQUID ----		
600	200.832	425.317	324.281	60.621	−548.573	−327.535	28.514
700	200.832	456.275	340.983	80.704	−542.106	−291.209	21.730
800	200.832	483.092	357.108	100.788	−535.767	−255.801	16.702
900	200.832	506.747	372.446	120.871	−529.533	−221.180	12.837
1000	200.832	527.907	386.953	140.954	−523.394	−187.249	9.781
1100	200.832	547.048	400.651	161.037	−517.340	−153.928	7.309
1200	200.832	564.523	413.589	181.120	−511.367	−121.155	5.274
1300	200.832	580.598	425.826	201.204	−505.470	−88.877	3.571
1400	200.832	595.481	437.419	221.287	−499.649	−57.050	2.129
1500	200.832	609.337	448.424	241.370	−493.901	−25.637	0.893

PREVIOUS: December 1962 CURRENT: December 1966

Tungsten Chloride (WCl_6) **LIQUID(α_1–α_2–β)**

0 to 450 K crystal, alpha$_1$
450 to 503 K crystal, alpha$_2$
503 to 555 K crystal, beta
above 555 K liquid

Refer to the individual tables for details.

M_r = 396.568 Tungsten Chloride (WCl_6) **Cl W (cr,l)**

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	175.418	238.488	238.488	0.	−593.710	−455.544	79.809
300	175.728	239.574	238.491	0.325	−593.618	−454.687	79.168
400	192.464	292.420	245.584	18.734	−588.082	−409.178	53.433
450	200.832	315.572	252.090	28.567	−584.830	−387.006	44.923
450.000	200.832	324.870	252.090	32.751	- - - - - - - -	I <- - > II	- - - - - - -
500	209.200	346.463	260.459	43.002	−577.043	−365.681	38.202
503.000	209.702	347.716	260.976	43.630		II <- - > III	
503.000	188.280	379.075	260.976	59.404		TRANSITION	
555.000	188.280	397.597	272.923	69.194		III <- - > LIQUID	
555.000	200.832	409.659	272.923	75.889		TRANSITION	
600	200.832	425.317	283.773	84.926	−548.573	−327.535	28.514
700	200.832	456.275	306.262	105.009	−542.106	−291.209	21.730
800	200.832	483.092	326.727	125.092	−535.767	−255.801	16.702
900	200.832	506.747	345.441	145.176	−529.533	−221.180	12.837
1000	200.832	527.907	362.648	165.259	−523.394	−187.249	9.781
1100	200.832	547.048	378.555	185.342	−517.340	−153.928	7.309
1200	200.832	564.523	393.335	205.425	−511.367	−121.155	5.274
1300	200.832	580.598	407.130	225.508	−505.470	−88.877	3.571
1400	200.832	595.481	420.058	245.592	−499.649	−57.050	2.129
1500	200.832	609.337	432.221	265.675	−493.901	−25.637	0.893

PREVIOUS: CURRENT: December 1966

Tungsten Chloride (WCl_6) **Cl_6W_1(cr,l)**

Tungsten Chloride (WCl_6) IDEAL GAS $M_r = 396.568$ Tungsten Chloride (WCl_6) $Cl_6W_1(g)$

$S°(298.15 \text{ K}) = [419.166] \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_fH°(0 \text{ K}) = -491.99 \pm 25.1 \text{ kJ·mol}^{-1}$

$\Delta_fH°(298.15 \text{ K}) = -493.71 \pm 25.1 \text{ kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
[360](1)	[140](3)
[340](2)	[180](3)
375 (3)	[120](3)

Ground State Quantum Weight = 1 $\sigma = 24$

Point Group: O_h

Bond Distance: W–Cl = 2.26 Å

Bond Angle: Cl–W–Cl = 90°

Product of the Moments of Inertia: $I_AI_BI_C = 1.74003 \times 10^{-111} \text{ g}^3\text{·cm}^6$

Enthalpy of Formation

The enthalpy of formation of $WCl_6(g)$, $\Delta_fH°(298.15 \text{ K}) = -118.0 \text{ kcal·mol}^{-1}$, is calculated from that of the crystal plus the adopted heat of sublimation, $\Delta_{sub}H°(298.15 \text{ K}) = 23.9 \text{ kcal·mol}^{-1}$ for $WCl_6(\alpha, cr) \rightarrow WCl_6(g)$. The latter was obtained from third law analysis of the vapor pressure data,[1-4] using all JANAF functions (December 31, 1966).

Source	Phase Studied	T/K	Data Points	$\Delta_{sub}H°$(298.15 K), kcal mol 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_fH°$(298.15 K) kcal·mol^{-1}
Stevenson[1]	α, cr	462 – 502	38	20.9 ± 0.5	23.74	6.2 ± 1.0	−118.16
	β*, cr	503 – 551	15	23.1 ± 0.2	23.89	1.5 ± 0.3	−118.01
	l*	557 – 598	13	24.2 ± 0.1	23.89	−0.6 ± 0.1	−118.01
Shchukarev *et al.*[2]	α, cr	**	--	22.0	23.80	4.0	−118.10
	β*, cr		--	23.8	23.98	0.4	−117.92
	l*		--	24.1	23.98	−0.2	−117.92
Ketelaar *et al.*[3]	α, cr	425 – 500	21	23.1 ± 0.1	23.94	1.7 ± 0.4	−117.96
	β*, cr	504 – 554	21	24.4 ± 0.1	23.91	−0.8 ± 0.1	−117.99
	l*	523 – 635	21	24.4 ± 0.1	23.85	−1.0 ± 0.1	−118.05
Vernon[4]	α, cr	298 – 423	4	16.1 ± 4.1	21.02	10.8 ± 12.8	−120.88

Vernon[4] has also determined the equilibrium constants in the temperature range from 1360 to 1600 K for the decomposition of $WCl_6(g)$ to W(cr) and $Cl_2(g)$ by reaction of the sample with a hot tungsten filament in a vacuum bulb. Using the reported equilibrium constants, the heat of formation of $WCl_6(g)$ at 298 K is calculated by the second and third law method as $-131.8 \pm 2.9 \text{ kcal·mol}^{-1}$ and $-135.2 \text{ kcal·mol}^{-1}$, respectively. The third law drift is $2.4 \pm 1.9 \text{ cal·K}^{-1}\text{·mol}^{-1}$. Unfortunately the reported equilibrium constants may be seriously in error since atomic chlorine is the main species at the pressure and temperature studied.

* Enthalpy changes are converted to $\Delta_{sub}H°(298.15 \text{ K})$ for $WCl_6(\alpha, cr) \rightarrow WCl_6(g)$.

** Vapor presssure equations for the crystal (α, β) and the liquid to gas are given.

Heat Capacity and Entropy

Ewens and Lister[5] have determined the octahedral structure for $WCl_6(g)$ by electron diffraction and found the bond length to be 2.26 Å.

The vibrational frequency of ν_3, 375 cm^{-1}, was observed in the infrared spectra by Evans.[6] The values of ν_1, ν_2, and ν_5 (360, 340 and 180 cm^{-1}, respectively) are estimated based on those of the aqueous ion $PtCl_6^{2}$– reported by Woodward and Creighton.[7] The values of ν_4 and ν_6 (140 and 120 cm^{-1}, respectively) are estimated by comparison with those of WF (g_6).

The principal moments of inertia are: $I_A = I_B = I_C = 120.2779 \times 10^{-39} \text{ g·cm}^2$.

References

[1] F. D. Stevenson, Ph.D. Thesis, Oregon State University (1962); U.S. Bur. Mines RI. 6367, (1964).

[2] S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Previous vapor pressure measurements, cited in Zh. Neorg. Khim. 1, 357 (1956) and 3, 2630 (1958), have been revised and are not used as reference here.

[3] J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. 62, 597 (1943).

[4] A. A. Vernon, J. Amer. Chem. Soc. 59, 1832 (1937).

[5] R. V. G. Ewens and M. W. Lister, Trans. Faraday Soc. 34, 1358 (1938).

[6] J. C. Evans, The Dow Chemical Company, private communication, (December 1, 1966).

[7] L. A. Woodward and J. A. Creighton, Spectrochim. Acta 17, 594 (1961)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$ (kJ·mol^{-1})	$\Delta_fG°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−30.790	−491.987	−491.987	INFINITE
100	93.109	285.822	536.701	−25.088	−495.672	−466.591	243.722
200	130.658	364.112	431.993	−13.576	−495.281	−437.471	114.256
250	138.942	394.234	421.510	−6.819	−494.537	−423.101	88.402
298.15	143.941	419.166	419.166	0.	−493.712	−409.416	71.728
300	144.093	420.057	419.169	0.266	−493.679	−408.893	71.195
350	147.459	442.539	420.936	7.561	−492.765	−394.833	58.926
400	149.758	462.389	424.902	14.995	−491.824	−380.907	49.741
450	151.390	480.127	430.070	22.526	−490.873	−367.100	42.612
500	152.586	496.143	435.889	30.127	−489.921	−353.398	36.919
600	154.182	524.116	448.330	45.472	−488.029	−326.272	28.404
700	155.165	547.963	460.901	60.943	−486.175	−299.459	22.346
800	155.812	568.727	473.110	76.494	−484.368	−272.910	17.819
900	156.259	587.106	484.775	92.099	−482.613	−246.583	14.311
1000	156.581	603.587	495.846	107.741	−480.914	−220.449	11.515
1100	156.821	618.523	506.330	123.412	−479.273	−194.483	9.235
1200	157.003	632.176	516.257	139.104	−477.691	−168.663	7.342
1300	157.146	644.749	525.663	154.811	−476.170	−142.973	5.745
1400	157.259	656.399	534.591	170.532	−474.711	−117.398	4.380
1500	157.351	667.252	543.077	186.263	−473.316	−91.924	3.201
1600	157.426	677.410	551.159	202.002	−471.986	−66.542	2.172
1700	157.488	686.956	558.869	217.747	−470.723	−41.241	1.267
1800	157.541	695.959	566.237	233.499	−469.529	−16.012	0.465
1900	157.585	704.478	573.291	249.255	−468.406	9.152	−0.252
2000	157.623	712.562	580.054	265.016	−467.359	34.260	−0.895
2100	157.655	720.253	586.549	280.780	−466.391	59.317	−1.475
2200	157.683	727.588	592.794	296.547	−465.505	84.329	−2.002
2300	157.708	734.598	598.808	312.316	−464.706	109.303	−2.482
2400	157.730	741.311	604.607	328.088	−463.999	134.245	−2.922
2500	157.749	747.750	610.205	343.862	−463.388	159.159	−3.325
2600	157.766	753.937	615.615	359.638	−462.874	184.050	−3.698
2700	157.781	759.892	620.849	375.415	−462.486	208.924	−4.042
2800	157.794	765.630	625.918	391.194	−462.262	233.787	−4.361
2900	157.807	771.167	630.831	406.974	−462.243	258.644	−4.659
3000	157.818	776.517	635.599	422.755	−462.457	283.505	−4.936
3100	157.827	781.692	640.229	438.537	−462.947	308.378	−5.196
3200	157.836	786.703	644.728	454.321	−463.741	333.271	−5.440
3300	157.845	791.560	649.104	470.105	−464.864	358.195	−5.670
3400	157.852	796.273	653.364	485.890	−466.346	383.157	−5.886
3500	157.859	800.848	657.513	501.675	−468.248	408.169	−6.092
3600	157.865	805.296	661.556	517.461	−470.659	433.242	−6.286
3700	157.871	809.621	665.500	533.248	−508.441	458.581	−6.474
3800	157.876	813.831	669.348	549.036	−508.567	484.718	−6.663
3900	157.881	817.932	673.106	564.823	−508.711	510.859	−6.842
4000	157.886	821.929	676.776	580.612	−508.868	537.004	−7.013
4100	157.890	825.828	680.365	596.401	−509.027	563.153	−7.175
4200	157.894	829.633	683.873	612.190	−509.183	589.306	−7.329
4300	157.898	833.348	687.307	627.979	−509.327	615.462	−7.476
4400	157.901	836.978	690.667	643.769	−509.451	641.622	−7.617
4500	157.904	840.527	693.958	659.560	−509.548	667.783	−7.751
4600	157.907	843.997	697.182	675.350	−509.612	693.948	−7.880
4700	157.910	847.393	700.342	691.141	−509.634	720.111	−8.003
4800	157.913	850.718	703.440	706.932	−509.609	746.276	−8.121
4900	157.915	853.974	706.479	722.724	−509.531	772.440	−8.234
5000	157.917	857.164	709.461	738.515	−509.395	798.601	−8.343
5100	157.920	860.292	712.388	754.307	−509.195	824.759	−8.447
5200	157.922	863.358	715.262	770.099	−508.927	850.912	−8.548
5300	157.924	866.366	718.085	785.891	−508.586	877.060	−8.644
5400	157.926	869.318	720.858	801.684	−508.170	903.201	−8.737
5500	157.927	872.216	723.584	817.476	−507.676	929.333	−8.826
5600	157.929	875.062	726.264	833.269	−507.099	955.455	−8.912
5700	157.930	877.857	728.899	849.062	−506.439	981.567	−8.995
5800	157.932	880.604	731.491	864.855	−505.693	1007.666	−9.075
5900	157.933	883.303	734.041	880.649	−504.860	1033.751	−9.152
6000	157.935	885.958	736.551	896.442	−503.939	1059.821	−9.227

PREVIOUS: December 1966 (1 atm) CURRENT. December 1966 (1 bar)

Tungsten Chloride ($(WCl_5)_2$) IDEAL GAS $M_r = 722.230$ Tungsten Chloride ($(WCl_5)_2$) $Cl_{10}W_2(g)$

$S°(298.15\ K) = [713.581]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -873.16 \pm 41.8\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(2981.5\ K) = -868.60 \pm 41.8\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[500](2)	[150](2)	[90](2)
[400](2)	[125](4)	[80](2)
[350](2)	[100](6)	[60](4)
[250](2)		[40](2)

Ground State Quantum Weight: [3] $\sigma = [4]$
Point Group: [D_{2h}]
Bond Distance: W–Cl = [2.26] Å
Bond Angles: Cl*–W–Cl* = [90]°; W–Cl*$_{bridge}$–W = [90]°
Cl**–W–Cl** = [180]°; Cl*–W–Cl** = [90]°
* = Equatorial ** = Axial
Product of the Moments of Inertia: $I_AI_BI_C = [6.64026 \times 10^{-110}]\ g^3{\cdot}cm^6$

Heat of Formation

The heat of formation, $\Delta_fH°(W_2Cl_{10}$, g, 298.15 K) = −207.6 kcal·mol^{-1}, is calculated from $\Delta_rH°$(298.15 K) = 10.4 kcal·mol^{-1} for $W_2Cl_{10}(g) = 2\ WCl_5(g)$, using all JANAF functions (December 31, 1966). The value of $\Delta_rH°$(2981.5 K) is obtained from third law analysis of the partial pressures of $WCl_5(g)$ and $W_2Cl_{10}(g)$ derived from *PVT* data determined by Shchukarev *et al.*[1] The second law $\Delta_rH°$(298.15 K) is 10.4 ± 0.3 kcal·mol^{-1}.

Heat Capacity and Entropy

The molecular configuration is estimated by analogy with that of Mo_2Cl_{10} reported by Sands and Zalkin.[2] Chlorine atoms are placed octahedrally around two tungsten atoms and these two octahedra share one common edge with six chlorine and two tungsten atoms in a plane. The bond length is estimated to be the same as that in $WCl_6(g)$. The three principal moments of inertia re $I_A = 210.4863 \times 10^{-39}$ $I_B = 546.8356 \times 10^{-39}$, and $I_C = 576.9051 \times 10^{-39}\ g{\cdot}cm^2$.

All vibrational frequencies are estimated based on those of WCl_5, $(AlCl_3)_2$ and Cs_2Cl_2, such that $S°(W_2Cl_{10}$, g, 607 K) = 216.65 cal·K^{-1}·mol^{-1}. This entropy is derived from $\Delta S°$(607 K) = 19.92 ± 0.5 cal·K^{-1}·mol^{-1} for $W_2Cl_{10}(g) = 2WCl_5(g)$, obtained by second law analysis of the data of Shchukarev *et al.*[1] The frequencies are not in point group order.

References

[1] S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim, No. 1, 120 (1959).
[2] D. Z. Sands and A. Zalkin, Acta Cryst. 12, 723 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$ (kJ·mol^{-1})	$\Delta_fG°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−60.408	−873.157	−873.157	INFINITE
100	200.630	455.551	934.652	−47.910	−876.522	−825.651	431.276
200	246.532	611.501	737.242	−25.148	−872.964	−775.991	202.668
250	256.975	667.725	717.886	−12.540	−870.764	−752.000	157.122
298.15	263.467	713.581	713.581	0.	−868.598	−729.322	127.774
300	263.668	715.212	713.586	0.488	−868.515	−728.459	126.836
350	268.139	756.214	716.814	13.790	−866.254	−705.295	105.259
400	271.243	792.234	724.036	27.279	−864.001	−682.454	89.119
450	273.470	824.317	733.429	40.900	−861.764	−659.895	76.599
500	275.117	853.219	743.987	54.616	−859.548	−637.585	66.608
600	277.333	903.592	766.512	82.248	−855.192	−593.603	51.678
700	278.710	946.454	789.232	110.055	−850.946	−550.342	41.067
800	279.620	983.734	811.266	137.975	−846.815	−507.682	33.148
900	280.252	1016.707	832.296	165.970	−842.799	−465.532	27.019
1000	280.708	1046.260	852.240	194.019	−838.901	−423.824	22.138
1100	281.047	1073.031	871.114	222.108	−835.121	−382.500	18.163
1200	281.307	1097.497	888.975	250.226	−831.461	−341.516	14.866
1300	281.509	1120.021	905.893	278.367	−827.921	−300.831	12.088
1400	281.671	1140.890	921.942	306.527	−824.503	−260.415	9.716
1500	281.801	1160.327	937.194	334.701	−821.209	−220.239	7.669
1600	281.908	1178.518	951.714	362.886	−818.042	−180.278	5.885
1700	281.997	1195.611	965.563	391.082	−815.003	−140.511	4.317
1800	282.071	1211.732	978.796	419.285	−812.097	−100.920	2.929
1900	282.135	1226.985	991.461	447.495	−809.327	−61.486	1.690
2000	282.188	1241.458	1003.602	475.712	−806.700	−22.195	0.580
2100	282.235	1255.227	1015.259	503.933	−804.221	16.969	−0.422
2200	282.275	1268.357	1026.467	532.158	−801.897	56.018	−1.330
2300	282.310	1280.906	1037.259	560.388	−799.736	94.965	−2.157
2400	282.341	1292.921	1047.663	588.620	−797.745	133.822	−2.913
2500	282.369	1304.448	1057.705	616.856	−795.930	172.599	−3.606
2600	282.393	1315.523	1067.410	645.094	−794.292	211.308	−4.245
2700	282.414	1326.181	1076.798	673.334	−792.890	249.958	−4.836
2800	282.434	1336.452	1085.889	701.577	−791.799	288.560	−5.383
2900	282.451	1346.363	1094.701	729.821	−791.100	327.131	−5.892
3000	282.467	1355.939	1103.250	758.067	−790.846	365.685	−6.367
3100	282.481	1365.201	1111.552	786.314	−791.125	404.239	−6.811
3200	282.494	1374.170	1119.619	814.563	−791.996	442.810	−7.228
3300	282.505	1382.863	1127.465	842.813	−793.506	481.421	−7.620
3400	282.516	1391.297	1135.101	871.064	−795.718	520.086	−7.990
3500	282.526	1399.486	1142.539	899.316	−798.755	558.828	−8.340
3600	282.535	1407.445	1149.787	927.569	−802.799	597.671	−8.672
3700	282.543	1415.187	1156.856	955.823	−877.571	637.023	−8.993
3800	282.551	1422.722	1163.754	984.078	−877.024	677.950	−9.319
3900	282.558	1430 061	1170.489	1012.333	−876.508	718.864	−9.628
4000	282.564	1437.215	1177.068	1040.589	−876.012	759.765	−9.922
4100	282.570	1444.192	1183.498	1068.846	−875.522	800.654	−10.200
4200	282.576	1451.002	1189.787	1097.103	−875.025	841.530	−10.466
4300	282.581	1457.651	1195.939	1125.361	−874.508	882.394	−10.719
4400	282.586	1464.147	1201.961	1153.619	−873.959	923.246	−10.960
4500	282.591	1470.498	1207.858	1181.878	−873.365	964.085	−11.191
4600	282.595	1476.709	1213.636	1210.138	−872.714	1004.911	−11.411
4700	282.599	1482.787	1219.298	1238.397	−871.995	1045.720	−11.622
4800	282.603	1488.736	1224.849	1266.657	−871.198	1086.514	−11.824
4900	282.606	1494.563	1230.294	1294.918	−870.312	1127.292	−12.017
5000	282.609	1500.273	1235.637	1323.179	−869.328	1168.048	−12.203
5100	282.613	1505.869	1240.881	1351.440	−868.239	1208.786	−12.380
5200	282.615	1511.357	1246.030	1379.701	−867.037	1249.500	−12.551
5300	282.618	1516.740	1251.087	1407.963	−865.714	1290.190	−12.716
5400	282.621	1522.023	1256.056	1436.225	−864.265	1330.854	−12.873
5500	282.623	1527.209	1260.939	1464.487	−862.684	1371.491	−13.025
5600	282.626	1532.302	1265.739	1492.749	−860.968	1412.096	−13.171
5700	282.628	1537.304	1270.460	1521.012	−859.112	1452.670	−13.312
5800	282.630	1542.219	1275.103	1549.275	−857.114	1493.212	−13.448
5900	282.632	1547 051	1279.671	1577.538	−854.970	1533.716	−13.578
6000	282.634	1551.801	1284.167	1605.801	−852.679	1574.181	−13.704

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

Continuation of discussions of selected Cl species

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to SCl and S$_3$. In addition, Donovan *et al.*[11] observed during flash photolysis of S$_2$Cl$_2$ a number of transient bands in the region 30221–34200 cm^{-1} which may be due to S$_2$Cl. By analogy with the known electronic levels for the isoelectronic radical cations SCl$_2^+$, OCl$_2^+$, and OF$_2^+$,[12] we predict the existence of three excited states for S$_2$Cl which should give rise to transitions from the ground state in the 20000–30000 cm^{-1} region. No attempt is made here to make definite assignments for the observed absorption spectra[7 10, and 11] assigned to S$_2$Cl since this will require the results of higher resolution experiments. We prefer to predict the electronic configurations for the ground and excited states from the Walsh correlation diagram[5] and to estimate their relative term values based on the vertical ionization potentials[8,12] observed in the photoelectron spectra of SCl$_2$, OCl$_2$, and OF$_2$. A detailed description of the factors considered in making these estimates can be found on the SF$_2^+$ gas table.[2]

Additional support for the existence of the S$_2$Cl radical is provided by the matrix photolysis work of Herring *et al.*[6]

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Tremmel *et al.*[13] The antisymmetric stretching frequency (ν_3) is that observed in the infrared absorption spectra of gaseous CoC$_2$ by Leroi *et al.*[7] This value has been confirmed from results of two infrared matrix isolation studies.[8,9] The doubly degenerate bending frequency (ν_2) was observed by Thompson and Carlson[8] in the infrared spectra of CoCl$_2$ isolated in an argon matrix. The infrared–inactive symmetric stretching frequency (ν_1) is estimated by comparison with similar data for FeCl$_2$ [1] and NiCl$_2$.[14] Some additional support for this value is provided by calculations of DeKock and Gruen.[11] Assuming linear model, they calculated $\nu_1 = 332$ cm^{-1} from $\nu_3 = 493$ cm^{-1}. Also, Clifton and Gruen[15] observed a vibrational spacing of 332 cm^{-1} in the fluorescence spectrum of argon matrix–isolated CoCl$_2$ which may be ν_1. A similar assignment for NiCl$_2$ was recently proposed[14] based on observations of vibrational spacings in its fluorescence spectrum.

Chlorine

The electronic spectra of $CoCl_2$ have been extensively investigated both in the gas phase[10, 11 16] and in various matrices.[9 12, 15, 17] Unfortunately, most of the results are conflicting and difficult to interpret. It is not certain whether the ground state configuration is $^4\phi$ or $^4\Sigma$. Theroretical arguments based on a ligand–field model[12, 18] favor the former, but recently Lever and Hollebone[19] interpreted the electronic spectra of $CoCl_2$ in terms of an "orbital angular over–lap" model and preferred the latter ground state configuration. Other problems associated with band assignments in the $CoCl_2$ spectra have been dealt with by Smith.[18] The adopted states and levels comprise one of two sets of assignments proposed by Lever and Hollebone.[19] The alternate functions derived from their second set of assignments[19] suggest that the adopted entropies may be biased by as much as +2 $cal\cdot K^{-1}\cdot mol^{-1}$ at 298 K and +0.2 $cal\cdot K^{-1}\cdot mol^{-1}$ at 4000 K. Functions based on the assignments of Smith[18] agree with those adopted to better than 1 $cal\cdot K^{-1}\cdot mol^{-1}$ at all temperatures.

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The drift indicated that the entropy of $FeCl_2$(g) is made more consistent by introducing two low lying electronic levels and a relatively low bending frequency. The enthalpies derived by 2nd and 3rd law analyses are in good agreement.

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The ground state of the linear $NiCl_2$ molecule is established as $^3\Pi g$ from numerous studies on the Laporte–forbidden d–d transitions[14–16] as well as a study of the Laporte–allowed charge–transfer transitions.[17] The very complex electronic spectra for both the gas phase and matrix isolated $NiCl_2$ have been studied by numerous investigators and interpreted using crystal field or ligand field theory. Our adopted values for the excited states are from Lever and Hollebone[14] who used an "orbital angular overlap" model to fit the spin–allowed and spin–forbidden d–d transition spectra. These assignments are in good agreement with those of DeKock and Gruen[16,18] and Smith[15] but differ from those of Hougen *et al*.[19]

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Sublimation Data

Refer to the ideal gas table for details.

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The vibrational frequencies are from the matrix infrared studies of Hastie *et al.*[19] Both of the stretching frequencies (ν_1 and ν_3)were observed in matrices of N_2, Ar, and Ne. The adopted values are gas–phase frequencies which were estimated by Hastie *et al.*[19] from their matrix data. Other matrix infrared[20] and matrix Raman[21] studies have led to stretching frequencies which deviate by less than 30 cm^{-1} from our adopted values. Also, ν_1 is in agreement with the value of 314 cm^{-1} which was observed by Beattie and Perry[22] in a gas–phase Raman study at 1000°C. The bending frequency (ν_2) is somewhat more uncertain that the stretching frequencies. Hastie *et al.*[19] observed a relatively weak band at 80 cm^{-1} when $PbCl_2$ was trapped in a neon matrix and assigned this band to ν_2. Gas–phase[22] and matrix[21] Raman studies have indicated that ν_2 lies much closer to 100 cm^{-1}. The gas–phase Raman spectrum[22] was obtained in the presence of an excess of chlorine to suppress decomposition and subsequent resonance fluorescence. We prefer the lower value (80 cm^{-1}) but assign an uncertainty of ±20 cm^{-1} which corresponds to 0.5 $cal \cdot K^{-1} \cdot mol^{-1}$ in $S°$(298.15 K).

The ground state is assumed to be $^1A_1$ based on an analogy with those for other Group IV A dichlorides.[23] The upper $^1B_1$ level at 31000 cm^{-1} was observed by Hastie *et al.*[23] Also included is a triplet level ($^3B_1$) at 22000 cm^{-1}. The energy separation for the $^1B_1$–$^3B_1$ states (9000 cm^{-1}) is assumed to be similar to that observed for other Group IV A dichlorides.[23]

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A normal coordinate treatment of $NbCl_5(g)$ in the Urey–Bradley force fields was performed by So[22] using the reported vibrational frequencies of Beattie and Ozin.[21] This work by So[22] was intended to check the correctness of the reported fundamental frequencies and predict those frequencies which had not been observed (ω_3, ω_4, ω_5). The calculations of So[22] suggested that the ω_5 value reported for $NbCl_5(g)$ was incorrect. Beattie and Ozin[21] had recorded the gas phase Raman spectra of $NbCl_5$, $NbBr_5$, $TaCl_5$ and $TaBr_5$ and has assigned ω_5 only in the case of $NbCl_5$. It was noted that this appeared only very weakly in the spectra. We adopt the results of So[22] which support the work of Beattie and Ozin[21] except for the ω_5 assignment.

There are many references in the literature to spectroscopic observations (IR and Raman) of $NbCl_5$ in the solid state, in organic solvents, and in matrices. Many problems arise in any attempt in relating the observed spectra. Niobium pentachloride was shown to be dimeric in the solid phase.[13] There are also indications that $NbCl_5$ is dimeric in solution.[15-17]

On the basis of these frequencies and the adopted structure, we calculate $S°(298.15\ K) = 96.56 \pm 0.75$ $cal \cdot K^{-1} \cdot mol^{-1}$, as was also calculated by So.[22] This compares to a value of 90.29 $cal \cdot K^{-1} \cdot mol^{-1}$ calculated by Gaunt and Ainscough[14] and 95.52 $cal \cdot K^{-1} \cdot mol^{-1}$ by Werder *et al.*[18]

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Cobalt (Co)

REFERENCE STATE

0	to	700.1	K	crystal, alpha
700.1	to	1768	K	crystal, beta
1768	to	3184.943	K	liquid
above		3184.943	K	ideal monatomic gas

Refer to the individual tables for details.

A_r = 58.9332 Cobalt (Co) Co$_1$(ref)

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = p° = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	0.	0.	INFINITE	−4.771	0.	0.	0.
100	13.909	7.681	50.176	−4.249	0.	0.	0.
200	22.226	20.588	32.287	−2.340	0.	0.	0.
298.15	24.802	30.067	30.067	0.	0.	0.	0.
300	24.833	30.221	30.068	0.046	0.	0.	0.
400	26.527	37.597	31.062	2.614	0.	0.	0.
500	28.200	43.700	32.996	5.352	0.	0.	0.
600	29.665	48.973	35.229	8.246	0.	0.	0.
700	31.045	53.650	37.533	11.282	0.	0.	0.
700.100	31.047	53.655	37.535	11.285	ALPHA <--> BETA TRANSITION		
700.100	30.583	54.300	37.535	11.737			
800	32.426	58.497	39.894	14.883	0.	0.	0.
900	34.518	62.433	42.181	18.227	0.	0.	0.
1000	36.987	66.194	44.396	21.799	0.	0.	0.
1100	39.832	69.849	46.544	25.635	0.	0.	0.
1200	43.221	73.445	48.636	29.771	0.	0.	0.
1300	48.660	77.110	50.685	34.354	0.	0.	0.
1394.000	54.978	80.719	52.587	39.215	C_p LAMBDA MAXIMUM TRANSITION		
1394.000	54.999	80.719	52.587	39.215			
1400	44.225	80.930	52.708	39.511	0.	0.	0.
1500	39.748	83.794	54.688	43.659	0.	0.	0.
1600	38.284	86.307	56.587	47.552	0.	0.	0.
1700	37.782	88.608	58.404	51.347	0.	0.	0.
1768.000	37.990	90.092	59.594	53.921	BETA <--> LIQUID TRANSITION		
1768.000	40.501	99.251	59.594	70.113			
1800	40.501	99.977	60.305	71.409	0.	0.	0.
1900	40.501	102.167	62.452	75.459	0.	0.	0.
2000	40.501	104.245	64.490	79.509	0.	0.	0.
2100	40.501	106.221	66.430	83.560	0.	0.	0.
2200	40.501	108.105	68.282	87.610	0.	0.	0.
2300	40.501	109.905	70.053	91.660	0.	0.	0.
2400	40.501	111.629	71.750	95.710	0.	0.	0.
2500	40.501	113.282	73.378	99.760	0.	0.	0.
2600	40.501	114.871	74.944	103.810	0.	0.	0.
2700	40.501	116.399	76.451	107.860	0.	0.	0.
2800	40.501	117.872	77.904	111.910	0.	0.	0.
2900	40.501	119.293	79.307	115.961	0.	0.	0.
3000	40.501	120.666	80.663	120.011	0.	0.	0.
3100	40.501	121.994	81.975	124.061	0.	0.	0.
3184.943	40.501	123.089	83.057	127.501	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
3184.943	26.233	240.840	83.057	502.529			
3200	26.233	240.963	83.800	502.924	0.	0.	0.
3300	26.245	241.771	88.574	505.548	0.	0.	0.
3400	26.269	242.555	93.092	508.174	0.	0.	0.
3500	26.305	243.317	97.373	510.802	0.	0.	0.
3600	26.354	244.058	101.437	513.435	0.	0.	0.
3700	26.416	244.781	105.302	516.073	0.	0.	0.
3800	26.491	245.487	108.982	518.719	0.	0.	0.
3900	26.579	246.176	112.491	521.372	0.	0.	0.
4000	26.679	246.850	115.841	524.035	0.	0.	0.
4200	26.919	248.157	122.111	529.394	0.	0.	0.
4400	27.209	249.416	127.869	534.806	0.	0.	0.
4600	27.546	250.633	133.180	540.281	0.	0.	0.
4800	27.930	251.813	138.099	545.827	0.	0.	0.
5000	28.358	252.962	142.671	551.456	0.	0.	0.
5200	28.829	254.083	146.934	557.174	0.	0.	0.
5400	29.342	255.181	150.923	562.990	0.	0.	0.
5600	29.896	256.258	154.666	568.913	0.	0.	0.
5800	30.492	257.317	158.187	574.951	0.	0.	0.
6000	31.003	258.351	161.508	581.056	0.	0.	0.

PREVIOUS: September 1967 (1 atm) — CURRENT: September 1967 (1 bar)

$S°(298.15\ K) = 30.067 \pm 0.10\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta) = 700\ K$
$T_{fus} = 923 \pm 1\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.452\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°(923\ K) = 16.192 \pm 0.25\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity of Co(cr) is adopted from Hultgren *et al.*[1] Their selected values are based on the data from nineteen investigations. The entropy values are based on $S°(1\ K) = 0.0011\ cal \cdot K^{-1} \cdot mol^{-1}$ The heat capacity has a maximum value of $13.14\ cal \cdot K^{-1} \cdot mol^{-1}$ at the Curie point (1394 K).

Transition Data

The exact nature of the α(hcp)–β(fcc) transition is yet to be clearly elucidated. Three investigations[2-4] indicate that it is not a simple time– and temperature–dependent phenomenon. Crystalline cobalt exists as pure β–phase above 700 K whereas mixtures of alpha and beta cobalt commonly coexist in varying proportions below this temperature. The values of T_{trs} and $\Delta_{trs}H°$ are those selected by Hultgren *et al.*[1]

Fusion Data

The temperature and enthalpy of melting are those selected by Hultgren *et al.*[1]

Sublimation Data

The enthalpy of sublimation is calculated from the data of Edwards *et al.*[5] See the ideal gas table for details.

References

[1] R. Hultgen, R. L. Orr and K. K. Kelley, Supplement to Selected Values of Thermodynamic Properties of Metal and Alloys, University of California, Berkeley, Calif., (1966).
[2] O. S. Edwards and H. Lipson, J. Inst. Metals 69, 177 (1943).
[3] A. R. Rtoiano and J. L. Tokich, Trans. Am. Inst. Mining Met. Engrs. 175, 728 (1948).
[4] P. R. Rao, Proc. Indian Acad. Sci. Sect. A, 61, 230 (1965).
[5] J. W Edwards, H. L. Johnston and W. E. Ditmars, J. Am. Chem. Soc. 73, 4729 (1951).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.771	0.	0.	0.
100	13.909	7.681	50.176	−4.249	0.	0.	0.
200	22.226	20.588	32.287	−2.340	0.	0.	0.
250	23.984	25.738	30.475	−1.184	0.	0.	0.
298.15	24.802	30.067	30.067	0.	0.	0.	0.
300	24.833	30.221	30.068	0.046	0.	0.	0.
350	25.682	34 113	30.373	1.309	0.	0.	0.
400	26.527	37.597	31.062	2.614	0.	0.	0.
450	27.390	40.772	31.967	3.962	0.	0.	0.
500	28.200	43.700	32.996	5.352	0.	0.	0.
600	29.665	48.973	35.229	8.246	0.	0.	0.
700	31.045	53.650	37.533	11.282	0.	0.	0.
700.100	31.047	53.655	37.535	11.285	ALPHA <−−> BETA		
700.100	30.583	54.300	37.535	11.737	TRANSITION		
800	32.426	58.497	39.894	14.883	0.	0.	0.
900	34.518	62.433	42.181	18.227	0.	0.	0.
1000	36.987	66.194	44.396	21.799	0.	0.	0.
1100	39.832	69.849	46.544	25.635	0.	0.	0.
1200	43.221	73.445	48.636	29.771	0.	0.	0.
1300	48.660	77.110	50.685	34.354	0.	0.	0.
1394.000	54.978	80.719	52.587	39.215	C_p LAMBDA MAXIMUM		
1394.000	54.999	80.719	52.587	39.215	TRANSITION		
1400	44.225	80.930	52.708	39.511	0.	0.	0.
1500	39.748	83.794	54.688	43.659	0.	0.	0.
1600	38.284	86.307	56.587	47.552	0.	0.	0.
1700	37.782	88.608	58.404	51.347	0.	0.	0.
1768.000	37.990	90.092	59.594	53.921	−−−− BETA <−−> LIQUID −−−−		
1800	37.656	90.776	60.142	55.141	−16.269	0.293	−0.009
1900	37.656	92.812	61.809	58.906	−16.553	1.221	−0 034
2000	37.656	94.744	63.408	62.672	−16.838	2.164	−0.057
2100	37.656	96.581	64.944	66.437	−17.122	3.121	−0.078
2200	37.656	98.333	66.422	70.203	−17.407	4.092	−0 097
2300	37.656	100.006	67.846	73.969	−17.691	5.076	−0.115
2400	37.656	101.609	69.220	77.734	−17.976	6.071	−0.132
2500	37.656	103.146	70.546	81.500	−18.260	7.079	−0.148

PREVIOUS: CURRENT: September 1967

$S°(298.15\ K) = [41.000]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = [18.004]\ kJ{\cdot}mol^{-1}$
$T_{fus} = 1768\ K$ $\Delta_{fus}H° = 16.192 \pm 0.25\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in $H°(1768\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of Co(l) selected by Hultgren *et al.*[1] is used at temperatures above 1768 K. The capacities at temperatures below the melting point are estimated by assuming a glass transition at 1100 K and heat capacities similar to those of the crystal below 1100 K.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

The boiling point is calculated from the adopted thermodynamic functions and the chosen enthalpy of sublimation at 298.15 K so that the Gibbs energy functions calculated by integration of the crystal liquid data and by statistical methods from the gas phase are equal at the boiling point.

Reference

[1] R. Hultgren, R. L. Orr and K. K. Kelley, Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, University of California, Berkeley, Calif. (1966).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	24.811	41.000	41.000	0.	18.004	14.745	−2.583
300	24.842	41.153	41.000	0.046	18.004	14.724	−2.564
350	25.686	45.046	41.306	1.309	18.004	14.178	−2.116
400	26.527	48.531	41.995	2.614	18.005	13.631	−1.780
450	27.390	51.706	42.900	3.963	18.005	13.084	−1.519
500	28.200	54.634	43.929	5.353	18.005	12.538	−1.310
600	29.665	59.909	46.162	8.248	18.006	11.444	−0.996
700	30.878	64.568	48.465	11.272	17.994	10.351	−0.772
800	32.426	68.786	50.745	14.433	17.555	9.323	−0.609
900	34.518	72.723	52.971	17.777	17.555	8.294	−0.481
1000	36.987	76.484	55.135	21.349	17.555	7.265	−0.379
1100	39.832	80.140	57.243	25.187	17.556	6.236	−0.296
1100.000	39.832	80.140	57.243	25.187	____ GLASS <--> LIQUID ____		
1100.000	39.832	80.140	57.243	25.187	TRANSITION		
1200	39.999	83.613	59.297	29.178	17.412	5.211	−0.227
1300	40.166	86.821	61.293	33.187	16.837	4.214	−0.169
1400	40.334	89.804	63.224	37.212	15.705	3.282	−0.122
1500	40.501	92.593	65.090	41.255	15.600	2.401	−0.084
1600	40.501	95.207	66.891	45.305	15.757	1.517	−0.050
1700	40.501	97.662	68.630	49.355	16.012	0.619	−0.019
1768.000	40.501	99.251	69.777	52.109	---- BETA <--> LIQUID ----		
1800	40.501	99.977	70.308	53.405	0.	0.	0.
1900	40.501	102.167	71.928	57.455	0.	0.	0.
2000	40.501	104.245	73.492	61.505	0.	0.	0.
2100	40.501	106.221	75.004	65.555	0.	0.	0.
2200	40.501	108.105	76.466	69.606	0.	0.	0.
2300	40.501	109.905	77.881	73.656	0.	0.	0.
2400	40.501	111.629	79.251	77.706	0.	0.	0.
2500	40.501	113.282	80.580	81.756	0.	0.	0.
2600	40.501	114.871	81.868	85.806	0.	0.	0.
2700	40.501	116.399	83.119	89.856	0.	0.	0.
2800	40.501	117.872	84.334	93.906	0.	0.	0.
2900	40.501	119.293	85.515	97.956	0.	0.	0.
3000	40.501	120.666	86.664	102.006	0.	0.	0.
3100	40.501	121.994	87.783	106.057	0.	0.	0.
3184.943	40.501	123.089	88.710	109.497	---- FUGACITY = 1 bar -----		
3200	40.501	123.280	88.872	110.107	−374.813	1.773	−0.029
3300	40.501	124.526	89.934	114.157	−373.387	13.519	−0.214
3400	40.501	125.736	90.969	118.207	−371.962	25.222	−0.387
3500	40.501	126.910	91.979	122.257	−370.541	36.883	−0.550
3600	40.501	128.051	92.965	126.307	−369.124	48.504	−0.704
3700	40.501	129.160	93.929	130.357	−367.712	60.085	−0.848
3800	40.501	130.240	94.870	134.407	−366.307	71.628	−0.985
3900	40.501	131.292	95.790	138.457	−364.910	83.135	−1.113
4000	40.501	132.318	96.691	142.508	−363.523	94.605	−1.235

PREVIOUS: CURRENT: September 1967

Cobalt (Co) **CRYSTAL(α–β)–LIQUID**

0 to 700.1 K crystal, alpha
700.1 to 1768 K crystal, beta
above 1768 K liquid

Refer to the individual tables for details.

A_r = 58.9332 Cobalt (Co) **$Co_1(cr,l)$**

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.771	0.	0.	0.
100	13.909	7.681	50.176	−4.249	0.	0.	0.
200	22.226	20.588	32.287	−2.340	0.	0.	0.
250	23.984	25.738	30.475	−1.184	0.	0.	0.
298.15	24.802	30.067	30.067	0.	0.	0.	0.
300	24.833	30.221	30.068	0.046	0.	0.	0.
350	25.682	34.113	30.373	1.309	0.	0.	0.
400	26.527	37.597	31.062	2.614	0.	0.	0.
450	27.390	40.772	31.967	3.962	0.	0.	0.
500	28.200	43.700	32.996	5.352	0.	0.	0.
600	29.665	48.973	35.229	8.246	0.	0.	0.
700	31.045	53.650	37.533	11.282	0.	0.	0.
700.100	31.047	53.655	37.535	11.285		ALPHA <--> BETA	
700.100	30.583	54.300	37.535	11.737		TRANSITION	
800	32.426	58.497	39.894	14.883	0.	0.	0.
900	34.518	62.433	42.181	18.227	0.	0.	0.
1000	36.987	66.194	44.396	21.799	0.	0.	0.
1100	39.832	69.849	46.544	25.635	0.	0.	0.
1200	43.221	73.445	48.636	29.771	0.	0.	0.
1300	48.660	77.111	50.685	34.354	0.	0.	0.
1394.000	54.978	80.719	52.587	39.215		C_p LAMBDA MAXIMUM	
1394.000	54.978	80.719	52.587	39.215		TRANSITION	
1400	44.225	80.930	52.708	39.511	0.	0.	0.
1500	39.748	83.794	54.688	43.659	0.	0.	0.
1600	38.284	86.307	56.587	47.552	0.	0.	0.
1700	37.782	88.608	58.404	51.347	0.	0.	0.
1768.000	37.990	90.092	59.594	53.921		BETA <--> LIQUID	
1768.000	40.501	99.251	59.594	70.113		TRANSITION	
1800	40.501	99.977	60.305	71.409	0.	0.	0.
1900	40.501	102.167	62.452	75.459	0.	0.	0.
2000	40.501	104.244	64.490	79.509	0.	0.	0.
2100	40.501	106.221	66.430	83.560	0.	0.	0.
2200	40.501	108.105	68.282	87.610	0.	0.	0.
2300	40.501	109.905	70.053	91.660	0.	0.	0.
2400	40.501	111.629	71.750	95.710	0.	0.	0.
2500	40.501	113.282	73.378	99.760	0.	0.	0.
2600	40.501	114.871	74.944	103.810	0.	0.	0.
2700	40.501	116.399	76.451	107.860	0.	0.	0.
2800	40.501	117.872	77.904	111.910	0.	0.	0.
2900	40.501	119.293	79.307	115.960	0.	0.	0.
3000	40.501	120.666	80.663	120.011	0.	0.	0.
3100	40.501	121.994	81.975	124.061	0.	0.	0.
3184.943	40.501	123.089	83.057	127.501		----- FUGACITY = 1 bar -----	
3200	40.501	123.280	83.246	128.111	−374.813	1.773	−0.029
3300	40.501	124.526	84.478	132.161	−373.387	13.519	−0.214
3400	40.501	125.735	85.673	136.211	−371.963	25.222	−0.387
3500	40.501	126.910	86.835	140.261	−370.541	36.883	−0.550
3600	40.501	128.050	87.964	144.311	−369.124	48.504	−0.704
3700	40.501	129.160	89.063	148.361	−367.712	60.085	−0.848
3800	40.501	130.240	90.132	152.411	−366.307	71.629	−0.985
3900	40.501	131.292	91.174	156.462	−364.911	83.135	−1.113
4000	40.501	132.318	92.190	160.512	−363.523	94.606	−1.235

PREVIOUS: CURRENT: September 1967

Cobalt (Co) **$Co_1(cr,l)$**

Cobalt (Co) IDEAL GAS $A_r = 58.9332$ Cobalt (Co) $Co_1(g)$

IP(Co, g) = 63430 ± 50 cm^{-1}
$S°(298.15\ K) = 179.52 \pm 0.01\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 425.1 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [426.7]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4F_{9/2}$	0	10
$^4F_{7/2}$	816.00	8
$^4F_{5/2}$	1406.84	6
$^4F_{3/2}$	1809.33	4
.	.	.
.	.	.
.	.	.
$^5H_6$	125969.5	13
IP	63430	

Enthalpy of Formation

The enthalpy of formation is the enthalpy of sublimation at 298.15 K. The adopted value is that reported by Edwards *et al.*[1] Their value is used because their vapor pressure measurements for Fe[1] and Cu[2] have proved to be very reliable. The results obtained by Vintaikin and Tomash[3] are rejected because their vapor pressure data for Fe[4] resulted in a value for the enthalpy of sublimation which was higher than the accepted value [refer to JANAF Fe(g) Table for details]. The remaining vapor pressure data are rejected either because the drift was too large or because there were not enough points. Second and third law analyses of the available vapor pressure data gave the following results, with reaction A corresponding to Co(c) = Co(g) and reaction B corresponding to Co(l) = Co(g).

Source	Reaction	Method	Data Points	T/K	$\Delta_r H°$(298.15 K), kcal·mol⁻¹ 2nd law	3rd law	Drift cal·K⁻¹·mol⁻¹	$\Delta_f H°$(298.15 K) kcal·mol⁻¹
Edwards[1]	A	Langmuir	9	1363–1522	101.0 ± 1.0	101.54	±0.4 ± 0.7	101.54
Kornev[5]	A	Knudsen	8*	1323–1523	98.8 ± 0.8	95.37	−2.4 ± 0.6	95.37
Dancy[6]	B	Langmuir	1	1823	—	90.51	—	94.82
Ruff[7]	B	Boiling Pt.	1	2648	—	99.35	—	103.66
Nesmeyanov[8]	A	Knudsen	3	1391–1540	82.4 ± 2.4	82.31	−0.1 ± 1.6	82.31
Nesmeyanov[9]	A	Knudsen	12*	1345–1541	91.7 ± 2.4	83.19	−5.9 ± 1.7	83.19
Vintaikin[3]	A	Knudsen	Eqn	1373–1523	102.9	103.34	+0.3	103.34

*One point rejected due to failure of a statistical test.

Heat Capacity and Entropy

The electronic levels are taken from Moore.[10] All observed levels were used but only the first few levels are listed above. Unobserved levels below 20,000 cm^{-1} are estimated.

References

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.360	425.087	425.087	INFINITE
100	20.793	156.132	198.942	−4.281	426.644	411.799	−215.102
200	21.452	170.670	181.570	−2.180	426.836	396.819	−103.639
250	22.214	175.536	179.892	−1.089	426.771	389.322	−81.344
298.15	23.024	179.518	179.518	0.	426.676	382.117	−66.945
300	23.054	179.660	179.518	0.043	426.673	381.841	−66.484
350	23.841	183.274	179.802	1.215	426.583	374.376	−55.873
400	24.508	186.503	180.441	2.425	426.487	366.924	−47.915
450	25.034	189.421	181.279	3.664	426.378	359.486	−41.728
500	25.425	192.080	182.229	4.926	426.250	352.060	−36.779
600	25.890	196.762	184.271	7.495	425.924	337.251	−29.360
700	26.093	200.771	186.349	10.095	425.489	322.504	−24.066
800	26.186	204.262	188.375	12.710	424.503	307.891	−20.103
900	26.251	207.350	190.315	15.331	423.781	293.356	−17.026
1000	26.320	210.119	192.159	17.960	422.837	278.913	−14.569
1100	26.399	212.631	193.908	20.596	421.637	264.576	−12.564
1200	26.480	214.932	195.565	23.240	420.145	250.361	−10.898
1300	26.558	217.054	197.138	25.892	418.214	236.287	−9.494
1400	26.624	219.025	198.632	28.551	415.716	222.383	−8.297
1500	26.673	220.864	200.053	31.216	414.233	208.628	−7.265
1600	26.705	222.586	201.408	33.885	413.009	194.962	−6.365
1700	26.719	224.206	202.702	36.556	411.885	181.369	−5.573
1800	26.715	225.733	203.939	39.228	394.495	168.135	−4.879
1900	26.697	227.177	205.125	41.899	393.116	155.597	−4.278
2000	26.666	228.546	206.262	44.567	391.734	143.132	−3.738
2100	26.626	229.846	207.354	47.232	390.348	130.736	−3.252
2200	26.579	231.083	208.405	49.892	388.958	118.406	−2.811
2300	26.528	232.264	209.417	52.547	387.564	106.139	−2.410
2400	26.475	233.391	210.392	55.198	386.164	93.933	−2.044
2500	26.423	234.471	211.334	57.842	384.758	81.786	−1.709
2600	26.375	235.507	212.244	60.482	383.348	69.695	−1.400
2700	26.331	236.501	213.124	63.118	381.933	57.658	−1.115
2800	26.293	237.458	213.976	65.749	380.514	45.674	−0.852
2900	26.264	238.380	214.802	68.377	379.092	33.740	−0.608
3000	26.243	239.270	215.603	71.002	377.667	21.856	−0.381
3100	26.233	240.130	216.380	73.626	376.241	10.019	−0.169
3184.943	26.233	240.840	217.023	75.854	----- FUGACITY = 1 bar -----		
3200	26.233	240.963	217.136	76.249	0.	0.	0.
3300	26.245	241.771	217.870	78.873	0.	0.	0.
3400	26.269	242.555	218.584	81.498	0.	0.	0.
3500	26.305	243.317	219.280	84.127	0.	0.	0.
3600	26.354	244.058	219.958	86.760	0.	0.	0.
3700	26.416	244.781	220.619	89.398	0.	0.	0.
3800	26.491	245.487	221.265	92.043	0.	0.	0.
3900	26.579	246.176	221.895	94.697	0.	0.	0.
4000	26.679	246.850	222.510	97.360	0.	0.	0.
4100	26.793	247.510	223.112	100.033	0.	0.	0.
4200	26.919	248.157	223.700	102.719	0.	0.	0.
4300	27.058	248.792	224.277	105.417	0.	0.	0.
4400	27.209	249.416	224.841	108.131	0.	0.	0.
4500	27.372	250.029	225.394	110.859	0.	0.	0.
4600	27.546	250.633	225.936	113.605	0.	0.	0.
4700	27.733	251.227	226.468	116.369	0.	0.	0.
4800	27.930	251.813	226.990	119.152	0.	0.	0.
4900	28.139	252.391	227.502	121.956	0.	0.	0.
5000	28.358	252.962	228.006	124.780	0.	0.	0.
5100	28.589	253.526	228.501	127.628	0.	0.	0.
5200	28.829	254.083	228.987	130.498	0.	0.	0.
5300	29.081	254.635	229.466	133.394	0.	0.	0.
5400	29.342	255.181	229.937	136.315	0.	0.	0.
5500	29.614	255.721	230.401	139.263	0.	0.	0.
5600	29.896	256.258	230.858	142.238	0.	0.	0.
5700	30.189	256.789	231.308	145.242	0.	0.	0.
5800	30.492	257.317	231.752	148.276	0.	0.	0.
5900	30.701	257.833	232.189	151.296	0.	0.	0.
6000	31.003	258.351	232.621	154.381	0.	0.	0.

PREVIOUS September 1967 (1 atm)   CURRENT. September 1967 (1 bar)

Cobalt, Ion (Co^+) IDEAL GAS $M_r = 58.93265$ Cobalt, Ion (Co^+) $Co_1^+(g)$

IP(Co^+, g) = 137795 ± 10 cm^{-1}
$S°(298.15\ K) = 178.346 \pm 0.05\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1183.88 \pm 1.0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [1191.597]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weights State	ϵ_i, cm^{-1}	g_i
$^3F_4$	0.00	9
$^3F_3$	950.51	7
$^3F_2$	1597.32	5
$^5F_5$	3350.58	9
.	.	.
.	.	.
.	.	.
$^5H_6$	125969.5	13
IP	137795	

Enthalpy of Formation

$\Delta_f H°(Co^+, g, 0\ K)$ is calculated from $\Delta_f H°(Co, g, 0\ K)$[1] using the spectroscopic value of IP(Co) = 63430 ± 10 cm^{-1} (758.79 ± 0.12 $kJ \cdot mol^{-1}$) from Sugar and Corliss.[2] The ionization limit is converted from cm^{-1} to $kJ \cdot mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ \cdot mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Co^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Co, g, 0\ K)$ by using IP(Co) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for Co(g), $Co^+(g)$, and e^-(ref). $\Delta_r H°(Co \rightarrow Co^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Sugar and Corliss,[2] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground, the first excited state, the highest observed excited state, and the ionization potential for $Co^+(g)$, all levels listed by Sugar and Corliss,[2] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for $Co^+(g)$, the thermodynamic functions are independent of the estimated missing levels (for n = 3), the cut–off procedure, and the inclusion of n = 7 levels up to 1000 K, the Gibbs energy function showing variations of 0.05% at this temperature. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass, and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n>7), and use of different fill and cut–off procedures.[6]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.291	1183.879		
100	20.787	155.255	197.384	−4.213			
200	21.116	169.718	180.341	−2.125			
250	21.635	174.482	178.709	−1.057			
298.15	22.272	178.346	178.346	0.	1191.597	1141.133	−199.922
300	22.297	178.484	178.346	0.041	1191.630	1140.819	−198.634
350	22.981	181.973	178.620	1.173	1192.539	1132.279	−168.983
400	23.606	185.083	179.237	2.338	1193.438	1123.609	−146.728
450	24.133	187.895	180.045	3.532	1194.323	1114.827	−129.406
500	24.559	190.461	180.961	4.750	1195.190	1105.947	−115.538
600	25.165	194.996	182.932	7.238	1196.863	1087.940	−94.714
700	25.585	198.908	184.941	9.777	1198.444	1069.660	−79.819
800	25.946	202.348	186.906	12.354	1199.499	1051.222	−68.638
900	26.307	205.425	188.796	14.966	1200.846	1032.605	−59.931
1000	26.681	208.216	190.601	17.615	1202.002	1013.848	−52.958
1100	27.067	210.777	192.320	20.303	1202.932	994.985	−47.248
1200	27.485	213.150	193.958	23.030	1203.602	976.049	−42.486
1300	28.002	215.369	195.521	25.803	1203.871	957.072	−38.456
1400	28.740	217.469	197.014	28.638	1203.626	938.094	−35.001
1500	29.883	219.488	198.445	31.564	1204.484	919.101	−32.006
1600	31.654	221.469	199.822	34.635	1205.740	900.036	−29.383
1700	34.287	223.462	201.154	37.924	1207.312	880.883	−27.066
1800	37.981	225.521	202.450	41.528	1192.933	861.922	−25.012
1900	42.853	227.700	203.721	45.560	1194.993	843.479	−23.189
2000	48.890	230.047	204.978	50.138	1197.599	824.913	−21.545
2100	55.916	232.599	206.232	55.371	1200.861	806.202	−20.053
2200	63.578	235.375	207.492	61.342	1204.861	787.318	−18.693
2300	71.383	238.374	208.769	68.091	1209.639	768.234	−17.447
2400	78.752	241.570	210.069	75.604	1215.180	748.927	−16.300
2500	85.120	244.919	211.395	83.808	1221.413	729.374	−15.239
2600	90.025	248.358	212.751	92.579	1228.212	709.559	−14.255
2700	93.179	251.820	214.134	101.755	1235.416	689.476	−13.339
2800	94.494	255.238	215.541	111.153	1242.843	669.120	−12.483
2900	94.073	258.552	216.967	120.595	1250.314	648.498	−11.681
3000	92.159	261.713	218.406	129.918	1257.665	627.620	−10.928
3100	89.071	264.687	219.852	138.988	1264.763	606.500	−10.219
3200	85.153	267.455	221.297	147.705	896.695	586.930	−9.581
3300	80.724	270.008	222.735	156.002	904.447	577.129	−9.135
3400	76.057	272.349	224.160	163.842	911.740	567.100	−8.712
3500	71.364	274.486	225.568	171.212	918.561	556.863	−8.311
3600	66.801	276.432	226.954	178.119	924.913	546.438	−7.929
3700	62.471	278.202	228.316	184.580	930.815	535.842	−7.565
3800	58.437	279.814	229.650	190.623	936.291	525.093	−7.218
3900	54.728	281.283	230.955	196.279	941.371	514.205	−6.887
4000	51.353	282.626	232.231	201.580	946.088	503.191	−6.571
4100	48.306	283.856	233.475	206.560	950.474	492.064	−6.269
4200	45.568	284.986	234.688	211.251	954.558	480.833	−5.980
4300	43.119	286.029	235.870	215.683	958.370	469.508	−5.703
4400	40.933	286.995	237.021	219.884	961.936	458.098	−5.438
4500	38.985	287.893	238.142	223.878	965.280	446.609	−5.184
4600	37.250	288.730	239.233	227.688	968.422	435.048	−4.940
4700	35.707	289.514	240.294	231.334	971.384	423.420	−4.706
4800	34.332	290.251	241.327	234.835	974.180	411.732	−4.481
4900	33.107	290.946	242.333	238.206	976.826	399.986	−4.264
5000	32.015	291.604	243.312	241.461	979.335	388.189	−4.055
5100	31.040	292.228	244.265	244.613	981.718	376.342	−3.855
5200	30.168	292.822	245.193	247.672	983.985	364.449	−3.661
5300	29.386	293.390	246.097	250.649	986.145	352.514	−3.474
5400	28.686	293.932	246.978	253.552	988.206	340.540	−3.294
5500	28.056	294.453	247.837	256.389	990.173	328.528	−3.120
5600	27.489	294.953	248.673	259.166	992.053	316.481	−2.952
5700	26.978	295.435	249.490	261.889	993.851	304.401	−2.790
5800	26.517	295.900	250.286	264.563	995.570	292.290	−2.632
5900	26.099	296.350	251.063	267.193	997.259	280.147	−2.480
6000	25.721	296.785	251.821	269.784	998.843	267.979	−2.333

PREVIOUS: September 1967 (1 atm) CURRENT: June 1984 (1 bar)

Cobalt, Ion (Co^-) IDEAL GAS $M_r = 58.93375$ Cobalt, Ion (Co^-) $Co_1^-(g)$

EA(Co, g) = 0.661 ± 0.010 eV
$S°(298.15\ K) = 178.412 \pm 0.005\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 361.31 \pm 4.7\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [356.649]\ kJ{\cdot}mol^{-1}$

Electonic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^3F_4$	0	9
$^3F_3$	910	7
$^3F_2$	1560	5

Enthalpy of Formation

$\Delta_f H°(Co^-, g, 0\ K)$ is calculated from $\Delta_f H°(Co, g, 0\ K)$[1] using the adopted electron affinity of EA(Co) = 0.661 ± 0.010 eV (63.776 ± 0.965 $kJ{\cdot}mol^{-1}$). This value, recommended by Hotop and Lineberger[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on $Co^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2, 4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Co^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Co, g, 0\ K)$ by using EA(Co) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, or $Co^-(g)$, Co(g), and e^-(ref). $\Delta_r H°(Co^- \rightarrow Co + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 $kJ{\cdot}mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state and fine-structure separations for $Co^-(g)$ have been experimentally determined by Corderman *et al.*[3] Lacking any experimental evidence as to the existence of stable excited states, we assume no stable excited states exist.

References

[1] JANAF Thermochemical Tables: Co(g), 9–30–67; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.307	361.311		
100	20.788	155.256	197.536	−4.228			
200	21.191	169.734	180.420	−2.137			
250	21.768	174.521	178.777	−1.064			
298.15	22.438	178.412	178.412	0.	356.649	318.675	−55.831
300	22.465	178.550	178.412	0.042	356.607	318.440	−55.445
350	23.154	182.066	178.688	1.182	355.445	312.170	−46.589
400	23.755	185.198	179.310	2.355	354.274	306.068	−39.968
450	24.233	188.025	180.123	3.556	353.087	300.114	−34.836
500	24.582	190.597	181.044	4.777	351.878	294.292	−30.745
600	24.937	195.117	183.024	7.256	349.385	283.007	−24.638
700	24.962	198.966	185.033	9.753	346.767	272.150	−20.308
800	24.794	202.290	186.987	12.242	343.577	261.739	−17.090
900	24.531	205.195	188.852	14.709	340.621	251.684	−14.607
1000	24.233	207.765	190.618	17.147	337.409	241.972	−12.639
1100	23.932	210.060	192.283	19.555	333.902	232.595	−11.045
1200	23.646	212.130	193.852	21.934	330.067	223.552	−9.731
1300	23.383	214.012	195.331	24.285	325.756	214.847	−8.633
1400	23.144	215.736	196.728	26.611	320.846	206.496	−7.704
1500	22.931	217.326	198.049	28.915	316.924	198.467	−6.911
1600	22.740	218.799	199.300	31.198	313.235	190.691	−6.225
1700	22.571	220.173	200.488	33.464	309.627	183.143	−5.627
1800	22.420	221.458	201.618	35.713	289.736	176.101	−5.110
1900	22.286	222.667	202.694	37.948	285.842	169.894	−4.671
2000	22.166	223.807	203.722	40.171	281.936	163.892	−4.280
2100	22.059	224.886	204.704	42.382	278.018	158.086	−3.932
2200	21.964	225.910	205.645	44.583	274.090	152.468	−3.620
2300	21.878	226.884	206.547	46.775	270.154	147.027	−3.339
2400	21.800	227.814	207.414	48.959	266.209	141.758	−3.085
2500	21.731	228.702	208.248	51.135	262.257	136.654	−2.855
2600	21.668	229.553	209.051	53.305	258.298	131.708	−2.646
2700	21.611	230.370	209.826	55.469	254.333	126.915	−2.455
2800	21.559	231.155	210.574	57.627	250.363	122.268	−2.281
2900	21.511	231.910	211.296	59.781	246.387	117.763	−2.121
3000	21.468	232.639	211.996	61.930	242.408	113.396	−1.974
3100	21.429	233.342	212.673	64.074	238.424	109.161	−1.839
3200	21.392	234.022	213.330	66.215	−140.377	106.828	−1.744
3300	21.359	234.680	213.967	68.353	−142.942	114.593	−1.814
3400	21.328	235.317	214.585	70.487	−145.512	122.435	−1.881
3500	21.300	235.935	215.187	72.619	−148.088	130.354	−1.945
3600	21.273	236.534	215.771	74.747	−150.671	138.346	−2.007
3700	21.249	237.117	216.340	76.873	−153.262	146.409	−2.067
3800	21.227	237.683	216.895	78.997	−155.862	154.544	−2.124
3900	21.206	238.234	217.435	81.119	−158.472	162.746	−2.180
4000	21.186	238.771	217.961	83.238	−161.094	171.016	−2.233
4100	21.168	239.294	218.475	85.356	−163.728	179.351	−2.285
4200	21.151	239.804	218.977	87.472	−166.376	187.751	−2.335
4300	21.135	240.301	219.467	89.586	−169.040	196.214	−2.384
4400	21.120	240.787	219.946	91.699	−171.719	204.739	−2.431
4500	21.106	241.262	220.415	93.810	−174.415	213.325	−2.476
4600	21.093	241.725	220.873	95.920	−177.129	221.972	−2.521
4700	21.080	242.179	221.322	98.029	−179.863	230.677	−2.564
4800	21.069	242.622	221.761	100.136	−182.617	239.441	−2.606
4900	21.058	243.057	222.191	102.243	−185.393	248.263	−2.647
5000	21.047	243.482	222.613	104.348	−188.191	257.141	−2.686
5100	21.038	243.899	223.026	106.452	−191.013	266.076	−2.725
5200	21.028	244.307	223.431	108.555	−193.859	275.066	−2.763
5300	21.020	244.708	223.829	110.658	−196.731	284.111	−2.800
5400	21.011	245.100	224.219	112.759	−199.629	293.211	−2.836
5500	21.004	245.486	224.602	114.860	−202.554	302.364	−2.872
5600	20.996	245.864	224.979	116.960	−205.508	311.571	−2.906
5700	20.989	246.236	225.348	119.059	−208.492	320.831	−2.940
5800	20.982	246.601	225.712	121.158	−211.506	330.144	−2.973
5900	20.976	246.959	226.069	123.256	−214.506	339.506	−3.006
6000	20.970	247.312	226.420	125.353	−217.573	348.921	−3.038

PREVIOUS: CURRENT. June 1984 (1 bar)

Cobalt Fluoride (CoF$_2$) CRYSTAL $M_r = 96.930006$ Cobalt Fluoride (CoF$_2$) Co$_1$F$_2$(cr)

$\Delta_f H°(0\ K) = -670.4 \pm 4.2\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 82.026 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -671.53 \pm 4.2\ kJ \cdot mol^{-1}$

$T_{fus} = 1400 \pm 7.0\ K$ $\Delta_{fus} H° = 58.819 \pm 12.6\ kJ\ mol^{-1}$

Enthalpy of Formation

Heus and Egan[1] measured the emf of a solid state galvanic cell which involved the reactions: $Al(cr) + 3/2\ CoF_2(cr) \rightarrow AlF_3(cr) + 3/2\ Co(cr)$, E(873 K) = 1.611 volts; $Mg(cr) + CoF_2(cr) \rightarrow MgF_2(cr) + Co(cr)$, E(873 K) = 2.231 volts. Combining these results with auxiliary thermodynamic data[2] for the reactants and products, we derive $\Delta_f H°(CoF_2, cr, 298.15\ K) = -160.2$ and $-159.95\ kcal \cdot mol^{-1}$.

Several equilibrium studies[3-5] involving CoF$_2$(cr) have been reported in the literature. 2nd and 3rd law analyses of these equilibrium data are summarized below, auxiliary data for CoO(cr) and CoCl$_2$(cr) are from.[6]

Source	Reaction	T/K	Data Points	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	*$\Delta_f H°$(298.15 K) kcal·mol^{-1}
3	$CoF_2(cr) + 2HCl(g) \rightarrow CoCl\ (_2cr) + 2HF(g)$	588–805	3	4.1	1.75 ± 0.4	−1.7 ± 0.1	−162.6 ± 2.0
4	$CoF_2(cr) + H_2(g) \rightarrow Co(cr) + 2HF(g)$	673–873	3	35.2	31.5 ± 1.0	−4.2 ± 3.5	−161.8 ± 2.0
5	$CoF_2(cr) + H_2O(g) \rightarrow CoO(cr) + 2HF(g)$	773–1023	5	30.2	31.1 ± 0.2	0.9 ± 0.3	−160.45 ± 1.0

*3rd law values except for the first reaction.

We note that Heus and Egan,[1] in the same paper, measured $\Delta_f H°(AlF_3, cr, 298.15\ K) = -360.2\ kcal \cdot mol^{-1}$ which is in excellent agreement with the JANAF value[2]. Domange[5] also measured similar equilibria for MgF$_2$ and CaF$_2$, which were very consistent with the JANAF enthalpies of formation.[2] Jellinek and Rudat[4] reported similar equilibria for PbF$_2$(cr), which show excellent consistency with the JANAF enthalpy of formation.[2] Thus, it is apparent that these three sets are probably quite reliable, and we adopt $\Delta_f H°(CoF_2, cr, 298.15\ K) = -160.5 \pm 1\ kcal \cdot mol^{-1}$ ($-671.532 \pm 4.2\ kJ \cdot mol^{-1}$).

Heat Capacity and Entropy

Catalano and Stout[7] measured low temperature heat capacities in the temperature range 10 to 300 K. Heat capacity data above 300 K are calculated from the high temperature (468–1400 K) enthalpy data of Binford *et al.*[8] Both sets of data were smoothed by computer and joined at 298.15 K.

The value of $S°(298.15\ K)$ is obtained from the low temperature heat capacity data of Catalano and Stout[7] and is based on $S°(10\ K) = 0.013\ cal \cdot K^{-1} \cdot mol^{-1}$ ($0.05439\ J \cdot K^{-1} \cdot mol^{-1}$).

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Kana'an *et al.*[9] made sublimation studies of CoF$_2$ using Knudsen and Langmuir techniques over the temperature range 972–1241 K. 2nd and 3rd law analyses of these sublimation pressures are summarized below.

Method	T/K	Data Points	$\Delta_{sub} H°$(298.15 K) kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
Knudsen	1058–1242	17	75.0	75.1 ± 0.1	0.1 ± 0.2
Langmuir	972–1032	8	72.8	75.5 ± 0.2	2.6 ± 1.4

The selected value is $\Delta_{sub} H°(298.15\ K) = 75.3 \pm 3.0\ kcal \cdot mol^{-1}$ ($315.055 \pm 12.6\ kJ \cdot mol^{-1}$).

References

[1] R. J. Heus and J. J. Egan, Z. Phys. Chem. 49, 38 (1966).
[2] JANAF Thermochemical Tables: AlF$_3$(cr), 6–30–70; MgF$_2$(cr), 3–31–66; PbF$_2$(cr), 6–30–69; CaF$_2$(cr), 12–31–68.
[3] K. Jellinek and R. Koop, Z. Phys. Chem. A145, 305 (1929).
[4] K. Jellinek and A. Rudat, Z. Anorg. Chem. 175, 281 (1928).
[5] L. Domange, Ann. Chim. 7, 225 (1937).
[6] U. S. Nat. Bur. Stand. Tech. Note 270–4, 141 pp. (1969).
[7] E. Catalano and J. W. Stout, J. Chem. Phys. 23, 1803 (1955).
[8] J. S. Binford, Jr., J. M. Strohmenger, and T. H. Hebert, J. Phys. Chem. 71, 2404 (1967).
[9] A. S. Kana'an, G. Besenbruch, and J. L. Margrave, J. Inorg. Nucl. Chem. 28, 1035 (1966).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K$_f$
0	0.	0.	INFINITE	−12.459	−670.395	−670.395	INFINITE
100	33.492	25.002	134.693	−10.969	−672.334	−657.029	343.197
200	57.584	56.746	87.999	−6.250	−672.454	−641.555	167.557
298.15	68.909	82.026	82.026	0.	−671.532	−626.562	109 771
300	69.041	82.453	82.028	0.128	−671.508	−626.283	109.046
400	75 714	103.350	84.831	7.408	−670.016	−611.424	79.844
500	78.927	120.625	90.315	15.155	−668.372	−596.965	62.365
600	80.789	135.193	96.613	23.148	−666.746	−582.837	50.741
700	82.015	147 744	103.041	31.292	−665.190	−568.977	42.458
800	82.902	158 756	109.331	39.540	−664.152	−555.271	36.255
900	83.592	168.562	115.378	47.866	−662.824	−541.742	31.442
1000	84.161	177.400	121.145	56.254	−661.698	−528.351	27.598
1100	84.646	185.444	126.631	64.695	−660.813	−515.062	24.458
1200	85.077	192.828	131.844	73.182	−660.208	−501.841	21.845
1300	85.475	199 654	136.801	81.710	−660.032	−488.654	19.634
1400	85.839	206.002	141.519	90.276	−660.415	−475.460	17.740
1400.000	85.839	206.002	141.519	90.276	--- CRYSTAL <--> LIQUID ---		
1500	86.186	211.936	146.018	98.877	−659.771	−462.269	16.098
1600	86.517	217.509	150.314	107.512	−658.858	−449.131	14.663
1700	86.831	222.764	154.423	116.180	−657.832	−436.054	13.398
1800	87.140	227.736	158.359	124.878	−673.055	−422.744	12.268
1900	87.441	232.455	162.135	133.607	−672.247	−408.860	11.240
2000	87.734	236.948	165.765	142.366	−671.420	−395.019	10.317

PREVIOUS: CURRENT: June 1970

Cobalt Fluoride (CoF_2) LIQUID $M_r = 96.930006$ Cobalt Fluoride (CoF_2) $Co_1F_2(l)$

$S°(298.15\ K) = [86.238]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-637.691]\ kJ·mol^{-1}$

$T_{fus} = 1400 \pm 7.0\ K$ $\Delta_{fus}H° = 58.819 \pm 12.6\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(CoF_2,\ l,\ 298.15\ K)$ is calculated from $\Delta_f H°(CoF_2,\ cr,\ 298.15\ K)$ by adding the enthalpy of fusion the difference in enthalpy, $H°(1400\ K)-H°(298.15)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of liquid CoF_2 is estimated by comparison with those for $FeCl_2(l)$, $MgF_2(l)$, and $PbF_2(l)$ and is assumed constant in the temperature range 298–3000 K. Binford *et al.*[1] reported $C_p = 30.3\ cal·K^{-1}·mol^{-1}$ for liquid CoF_2 at 1444 K. This value is based on only two enthalpy points near the melting point and appears high in comparison with heat capacities for other liquid metal dihalides. Therefore, the value is not adopted.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

$T_{fus} = 1400$ K is from the high temperature enthalpy studies of Binford *et al.*[1] $\Delta_{fus}H°$ is calculated from their enthalpy data. Premelting of the sample is assumed to be responsible for the rapid rise in enthalpy near the melting point. This enthalpy is included in $\Delta_{fus}H°$.

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change for the process $CoF_2(l) \rightarrow CoF_2(g)$ equals zero. The difference between the enthalpy of formation of the gas and liquid at T_{vap} is $\Delta_{vap}H°$.

Reference

[1] J. S. Bindord, Jr., J. M. Strohmenger, and T. H. Hebert, J. Phys. Chem., **71**, 2404 (1967).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	104.600	86.238	86.238	0.	−637.691	−593.977	104.062
300	104.600	86.885	86.240	0.194	−637.602	−593.706	103.373
400	104.600	116.976	90.343	10.654	−632.929	−579.787	75.712
500	104.600	140.317	98.090	21.114	−628.573	−567.012	59.235
600	104.600	159.388	106.765	31.574	−624.480	−555.088	48.325
700	104.600	175.512	115.464	42.034	−620.608	−543.832	40.581
800	104.600	189.480	123.863	52.494	−617.358	−533.055	34.805
900	104 600	201.800	131.851	62.954	−613.896	−522.728	30.338
1000	104.600	212.820	139.407	73.414	−610.698	−512.772	26.784
1100	104.600	222.790	146.541	83.874	−607.794	−503.123	23.891
1200	104.600	231.891	153.280	94.334	−605.216	−493.723	21.491
1300	104.600	240.264	159.653	104.794	−603.108	−484.522	19.468
1400	104.600	248.015	165.691	115.254	−601.596	−475.460	17.740
1400.000	104.600	248.015	165.691	115.254	--- CRYSTAL <--> LIQUID ---		
1500	104.600	255.232	171.423	125.714	−599.094	−466.535	16.246
1600	104.600	261.983	176.874	136.174	−596.356	−457.786	14.945
1700	104.600	268.324	182.069	146.634	−593.537	−449.212	13.803
1800	104.600	274.303	187.029	157.094	−606.999	−440.510	12.783
1900	104.600	279.958	191.772	167.554	−604.461	−431.330	11.858
2000	104.600	285.324	196.317	178.014	−601.932	−422.283	11.029
2100	104.600	290.427	200.678	188.474	−599.409	−413.362	10.282
2200	104.600	295.293	204.869	198.934	−596.889	−404.562	9.606
2300	104.600	299.943	208.902	209.394	−594.367	−395.876	8.991
2400	104.600	304.394	212.789	219.854	−591.840	−387.301	8.429
2500	104.600	308.664	216.539	230.314	−589.305	−378.830	7.915
2600	104.600	312.767	220.162	240.774	−586.757	−370.461	7.443
2700	104.600	316.714	223.665	251.234	−584.194	−362.191	7.007
2800	104.600	320.519	227.057	261.694	−581.612	−354.016	6.604
2900	104.600	324.189	230.343	272.154	−579.007	−345.933	6.231
3000	104.600	327.735	233.531	282.614	−576.379	−337.941	5.884

PREVIOUS: CURRENT: June 1970

Cobalt Fluoride (CoF_2) $Co_1F_2(l)$

Cobalt Fluoride (CoF_2)

CRYSTAL-LIQUID

0 to	1400 K	crystal
above		1400 K	liquid

Refer to the individual tables for details.

$M_r = 96.930006$ Cobalt Fluoride (CoF_2) $Co_1F_2(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−12.459	−670.395	−670.395	INFINITE
100	33.492	25.002	134.693	−10.969	−672.334	−657.029	343.197
200	57.584	56.746	87.999	−6.250	−672.454	−641.555	167.557
298.15	68.909	82.026	82.026	0.	−671.532	−626.562	109.771
300	69.041	82.453	82.028	0.128	−671.508	−626.283	109.046
400	75.714	103.350	84.831	7.408	−670.016	−611.424	79.844
500	78.927	120.625	90.315	15.155	−668.372	−596.965	62.365
600	80.789	135.193	96.613	23.148	−666.746	−582.837	50.741
700	82.015	147.744	103.041	31.292	−665.190	−568.977	42.458
800	82.902	158.756	109.331	39.540	−664.152	−555.271	36.255
900	83.592	168.562	115.378	47.866	−662.824	−541.742	31.442
1000	84.161	177.400	121.145	56.254	−661.698	−528.351	27.598
1100	84.646	185.444	126.631	64.695	−660.813	−515.062	24.458
1200	85.077	192.828	131.844	73.182	−660.208	−501.841	21.845
1300	85.475	199.654	136.801	81.710	−660.032	−488.654	19.634
1400	85.839	206.002	141.519	90.276	−660.415	−475.460	17.740
1400.000	85.839	206.002	141.519	90.276	CRYSTAL <--> LIQUID TRANSITION		
1400.000	104.600	248.015	141.519	149.094			
1500	104.600	255.232	148.862	159.554	−599.094	−466.535	16.246
1600	104.600	261.983	155.724	170.014	−596.356	−457.786	14.945
1700	104.600	268.324	162.163	180.474	−593.537	−449.212	13.803
1800	104.600	274.303	168.228	190.934	−606.999	−440.510	12.783
1900	104.600	279.958	173.961	201.394	−604.461	−431.330	11.858
2000	104.600	285.324	179.396	211.854	−601.932	−422.283	11.029
2100	104.600	290.427	184.563	222.314	−599.409	−413.363	10.282
2200	104.600	295.293	189.487	232.774	−596.889	−404.562	9.606
2300	104.600	299.943	194.189	243.234	−594.367	−395.876	8.991
2400	104.600	304.394	198.688	253.694	−591.840	−387.301	8.429
2500	104.600	308.664	203.003	264.154	−589.305	−378.830	7.915
2600	104.600	312.767	207.146	274.614	−586.757	−370.461	7.443
2700	104.600	316.714	211.131	285.074	−584.194	−362.191	7.007
2800	104.600	320.519	214.971	295.534	−581.612	−354.016	6.604
2900	104.600	324.189	218.674	305.994	−579.007	−345.933	6.231
3000	104.600	327.735	222.250	316.454	−576.379	−337.941	5.884

PREVIOUS: CURRENT: June 1970

Cobalt Fluoride (CoF_2) $Co_1F_2(cr,l)$

Cobalt Fluoride (CoF_2) **IDEAL GAS** **M_r = 96.930006 Cobalt Fluoride (CoF_2)** **$Co_1F_2(g)$**

$S°(298.15\ K) = 278.04 \pm 12.6\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -355.82 \pm 12.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -356.48 \pm 12.6\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^4\Sigma$	0	4
	[300]	[4]
	[4000]	[4]
	[9000]	[4]

Vibrational Frequencies and Degenracies

υ, cm^{-1}
[600](1)
[151](1)
762 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Co–F = [1.72] Å
Bond Angle: F–Co–F = [165]°
Product of Moments of Inertia: $I_A I_B I_C = 6.57815 \times 10^{-116}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(CoF_2, g, 298.15\ K) = -85.2 \pm 3.0\ kcal \cdot mol^{-1}$ ($-355.477 \pm 12.6\ kJ \cdot mol^{-1}$), is calculated from the enthalpy of formation of the crystal, $\Delta_f H°(CoF_2, cr, 298.15\ K) = -160.5 \pm 4.0\ kcal \cdot mol^{-1}$, and the enthalpy of sublimation, $\Delta_{sub} H°(298.15\ K) = 75.3 \pm 3.0\ kcal \cdot mol^{-1}$ The sublimation value is determined from a 3rd law analysis of the vapor pressure data for CoF_2 reported by Kana'an *et al.*[1] Refer to the crystal table for details.

Heat Capacity and Entropy

Buchler *et al.*[2] investigated the deflection of a molecular beam of $CoF_2(g)$ by an electric field and found that within the sensitivity of the apparatus the molecule was nonpolar and consequently possessed a linear structure. Hastie *et al.*[3] recently investigated the infrared absorption spectra of several transition metal difluorides through the use of matrix isolation techniques. Isoptopic shift measurements for matrix isolated NiF_2, ZnF_2, and CuF_2 in neon and argon indicated that these species were slightly bent. Based upon these results, the authors estiamted the F–Co–F angle as 165°. This value is adopted here. The bond length was estimated by Brewer *et al.*[4] The principal moments of inertia are: $I_A = 0.1934 \times 10^{-39}$, $I_B = 18.3484 \times 10^{-39}$, and $I_C = 18.5417 \times 10^{-39}\ g \cdot cm^2$.

Hastie *et al.*[3] isolated CoF_2 in neon and argon matrices and observed the υ_3 fundamental at 762 cm^{-1} They also calculated $\upsilon_1 = 600$ cm^{-1} by a valence force field method and estimated υ_2 as 151 cm^{-1} by applying the variation in the frequencies for the chlorides of Co, Ni, Cu, and Zn to the fluorides. The electronic levels and quantum weights are estimated by comparison with the electronic energy levels for $Co^{++}(g)$ ion[5] and those for $CoCl_2(g)$ observed by Hougen *et al.*[6]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.940	−355.821	−355.821	INFINITE
100	41.091	227.574	320.907	−9.333	−355.643	−360.595	188.355
200	47.569	258.314	282.621	−4.861	−356.010	−365.424	95.439
250	49.634	269.160	278.877	−2.429	−356.236	−367.752	76.838
298.15	51.210	278.042	278.042	0.	−356.477	−369.949	64.813
300	51.263	278.359	278.043	0.095	−356.486	−370.032	64.428
350	52.536	286.361	278.672	2.691	−356.741	−372.270	55.558
400	53.528	293.444	280.084	5.344	−357.024	−374.470	48.901
450	54.305	299.795	281.928	8.040	−357.343	−376.632	43.718
500	54.920	305.550	284.007	10.772	−357.700	−378.756	39.568
600	55.822	315.648	288.462	16.312	−358.528	−382.892	33.334
700	56.459	324.303	292.979	21.927	−359.500	−386.878	28.869
800	56.956	331.876	297.377	27.599	−361.038	−390.652	25.507
900	57.377	338.609	301.591	33.316	−362.319	−394.279	22.883
1000	57.753	344 674	305.601	39.073	−363.824	−397.752	20.776
1100	58.095	350.195	309.408	44.865	−365.588	−401.062	19.045
1200	58.410	355.263	313.021	50.691	−367.644	−404.198	17.594
1300	58.699	359.950	316.453	56.546	−370.141	−407.147	16.359
1400	58.964	364.310	319.718	62.430	−373.205	−409.882	15.293
1500	59.205	368.387	322.828	68.338	−375.255	−412.428	14.362
1600	59.424	372.215	325.796	74.270	−377.045	−414 847	13.543
1700	59.622	375.823	328.634	80.223	−378.734	−417.157	12.818
1800	59.801	379.236	331.351	86.194	−396.684	−419.075	12.161
1900	59.963	382.474	333.957	92.182	−398.618	−420.267	11.554
2000	60.108	385.554	336.461	98.186	−400.545	−421.356	11.005
2100	60.239	388.489	338.869	104.203	−402.465	−422.350	10.505
2200	60.356	391.295	341.189	110.233	−404.375	−423.252	10.049
2300	60.461	393.980	343.426	116.274	−406.272	−424.067	9.631
2400	60.555	396.555	345.586	122.325	−408.154	−424.800	9.246
2500	60.638	399.029	347.675	128.385	−410.019	−425.455	8.889
2600	60.712	401.409	349.696	134.452	−411.864	−426.036	8.559
2700	60.777	403.701	351.654	140.527	−413.686	−426.547	8.252
2800	60.834	405.912	353.553	146.608	−415.483	−426.990	7.966
2900	60.882	408.048	355.395	152.693	−417.253	−427.370	7.698
3000	60.924	410.113	357.185	158.784	−418.994	−427.689	7.447
3100	60.959	412.111	358.925	164.878	−420.705	−427.951	7.211
3200	60.988	414.047	360.617	170.975	−797.197	−426.385	6.960
3300	61.011	415.924	362.265	177.075	−797.416	−414.793	6.566
3400	61.029	417.746	363.870	183.177	−797.604	−403.196	6.194
3500	61.041	419.515	365.435	189.281	−797.761	−391.593	5.844
3600	61.050	421.235	366.961	195.385	−797.888	−379.986	5.513
3700	61.054	422.907	368.450	201.491	−797.986	−368.377	5.201
3800	61.054	424.536	369.905	207.596	−798.056	−356.765	4.904
3900	61.051	426.121	371.326	213.701	−798.101	−345.151	4.623
4000	61.044	427.667	372.715	219.806	−798.121	−333.536	4.356
4100	61.035	429.174	374.074	225.910	−798.119	−321.922	4.101
4200	61.023	430.645	375.404	232.013	−798.096	−310.307	3.859
4300	61.009	432.081	376.705	238.115	−798.055	−298.694	3.628
4400	60.992	433.483	377.980	244.215	−797.996	−287.082	3.408
4500	60.973	434.853	379.228	250.313	−797.924	−275.471	3.198
4600	60.953	436.193	380.452	256.409	−797.838	−263.862	2.996
4700	60.931	437.504	381.652	262.504	−797.742	−252.254	2.803
4800	60.908	438.787	382.829	268.595	−797.637	−240.649	2.619
4900	60.883	440.042	383.984	274.685	−797.526	−229.047	2.442
5000	60.858	441.272	385.118	280.772	−797.410	−217.446	2.272
5100	60.831	442.477	386.230	286.857	−797.291	−205.848	2.108
5200	60.804	443.658	387.323	292.938	−797.171	−194.252	1.951
5300	60.776	444.816	388.397	299.017	−797.052	−182.659	1.800
5400	60.747	445.951	389.453	305.094	−796.936	−171.068	1.655
5500	60.718	447.066	390.490	311.167	−796.825	−159.479	1.515
5600	60.689	448.160	391.510	317.237	−796.721	−147.891	1.379
5700	60.659	449.234	392.513	323.305	−796.625	−136.306	1.249
5800	60.629	450.288	393.501	329.369	−796.539	−124.723	1.123
5900	60.599	451.324	394.472	335.430	−796.420	−113.143	1.002
6000	60.569	452.343	395.428	341.489	−796.348	−101.563	0.884

PREVIOUS. June 1970 (1 atm) CURRENT: June 1970 (1 bar)

Cobalt Fluoride (CoF_2) **$Co_1F_2(g)$**

Cobalt Fluoride (CoF_3) CRYSTAL $M_r = 115.928409$ Cobalt Fluoride (CoF_3) $Co_1F_3(cr)$

$S°(298.15\ K) = [94.6 \pm 12.6]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$T_{fus} = [1200 \pm 200]\ K$

$\Delta_f H°(0\ K) = $ Unknown

$\Delta_f H°(298.15\ K) = -790.36 \pm 12.6\ kJ{\cdot}mol^{-1}$

$\Delta_{fus} H° = $ Unknown

Enthalpy of Formation

Fowler *et al.*[1] determined calorimetrically the enthalpy of fluorination of crystalline CoF_2 at 473.15 K. For the reaction $2\ CoF_2(cr) + F_2(g) \rightarrow CoF_3(cr)$ they reported $\Delta_r H°(473.15\ K) = -52.0 \pm 3.0$ kcal mol^{-1} which yields $\Delta_r H°(298.15\ K) = -52.4 \pm 3.0$ kcal·mol^{-1} based upon our functions for $CoF_2(cr)$ and $CoF_3(cr)$. Combining this result with the enthalpy of formation of $CoF_2(cr)$,[2] we derive $\Delta_f H°(CoF_3$, cr, 298.15 K$) = -186.7 \pm 3.0$ kcal·mol^{-1}.

Jessup *et al.*[3] investigated calorimetrically this same fluorination reaction and reported $\Delta_r H°(523.15\ K) = -56.1 \pm 2.0$ kcal·mol^{-1}. This result leads to $\Delta_f H°(CoF_3$, cr, 298.15 K$) = -188.8 \pm 2.0$ kcal·mol^{-1}. In the same investigation Jessup *et al.*[3] reported $\Delta_r H°(608\ K) = -74.0 \pm 4.0$ kcal·mol^{-1} for the reduction reaction $2\ CoF_3(cr) + H_2(g) \rightarrow 2\ CoF_2(cr) + 2\ HF(g)$. Corrected to 298.15 K we calculate $\Delta_r H°(298.15\ K) = -73.3 \pm 4.0$ kcal·mol^{-1}. Combining this result with enthalpy of formation data for CoF_2cr).[2] and HF(g),[4] we derive $\Delta_f H°(CoF_3$, cr, 298.15 K$) = -189.0 \pm 4.0$ kcal·mol^{-1}. We note that the addition of these two results by Jessup *et al.*[3] leads to $\Delta_r H°(298.15\ K) = -129.9 \pm 6.0$ kcal·mol^{-1} for the reaction $H_2(g) + F_2(g) \rightarrow 2\ HF(g)$ which is quite consistent with the result -130.28 ± 0.4 kcal·mol^{-1} calculated from the selected value for the enthalpy of formation of HF(g).[4] Thus, it is apparent that these two results are probably quite reliable, and we adopted $\Delta_f H°(CoF_3$, cr, 298.15 K$) = -188.9 \pm 3.0$ kcal·mol^{-1} (-790.358 ± 12.6 kJ·mol^{-1}).

Jellinek and Koop[5] reported equilibrium constants for the reduction reaction given above in the temperature range 470–595 K. 2nd and 3rd law analyses of these equilibrium data give $\Delta_r H°(298.15\ K)$ of 31.7 and 29.3 ± 0.6 kcal·mol^{-1}, respectively; the drift is -4.7 ± 1.5 cal·K^{-1}·mol^{-1}. These values are in considerable disagreement with the calorimetric value of -73.3 ± 4.0 kcal·mol^{-1} given by Jessup *et al.* [3], and no weight is given to these equilibrium data.

Heat Capacity and Entropy

Heat capacity data for $CoF_3(cr)$ are estimated by comparison with those for $FeF_2(cr)$, $FeF_3(cr)$, $TiF_3(cr)$, and $CoF_2(cr)$. $S°(298.15\ K)$ is estimated to be 22.6 cal·K^{-1}·mol^{-1} (94.5584 J·K^{-1}·mol^{-1}) from the ionic entropy contributions given by Kubaschewski, Evans, and Alcock.[6] We note that this method leads to $S°(298.15\ K) = 19.4$ cal·K^{-1}·mol^{-1} for $CoF_2(cr)$ which is in good agreement with the experimental value of 19.60 ± 0.10 cal·K^{-1}·mol^{-1}.[2]

Fusion Data

T_{fus} is estimated by comparison with those for other transition metal halides. We note that Ruff and Ascher[7] reported $CoF_3(cr)$ being thermally unstable around 900 K, while Stewart[8] recently showed that $CoF_2(cr)$ was formed by hydrolytic reactions and not by thermal decomposition. The derived $\Delta_f G°$ values for $CoF_3(cr)$ indicate that it is thermodynamically more stable than $CoF_2(cr)$ in agreement with the findings of Stewart.[8] In the temperature range 298–900 K, the Gibbs energy change for the decomposition reaction $2\ CoF_3(cr) \rightarrow 2CoF_2(cr) + F_2(g)$ are in the range + 10–20 kcal·mol^{-1}.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	91.797	94.558	94.558	0.	−790.358	−718.893	125 947
300	92.471	95.128	94.560	0 170	−790.320	−718.450	125.093
400	97.470	122.481	98.255	9.691	−788.197	−694.811	90.733
500	99 701	144.498	105.375	19.561	−786.113	−671.708	70.173
600	100 454	162.742	113.461	29.569	−784.209	−649.010	56.501
700	101.219	178.285	121.638	39.653	−782.489	−626.614	46.759
800	101.981	191.849	129.584	49.812	−781.344	−604.393	39 463
900	102.839	203.909	137.185	60.051	−779.930	−582.361	33.799
1000	103.868	214.796	144.410	70.386	−778.703	−560.477	29.276
1100	105.027	224.750	151.268	80.830	−777.675	−538.706	25.581
1200	106.248	233.940	157.779	91.393	−776.867	−517.019	22.505
1300	107.587	242.497	163.970	102.084	−776.412	−495.386	19.905
1400	108.935	250.519	169.869	112.910	−776.429	−473.771	17.677
1500	110.320	258.082	175.500	123.873	−775.330	−452.188	15.747

PREVIOUS: CURRENT: December 1970

Cobalt Oxide (CoO) CRYSTAL $M_r = 74.9326$ Cobalt Oxide (CoO) $Co_1O_1(cr)$

$S°(298.15\ K) = 52.993 \pm 0.34\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 2103 \pm 10\ K$

$\Delta_f H°(0\ K) = -238.1 \pm 0.4\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -237.7 \pm 0.4\ kJ{\cdot}mol^{-1}$
$\Delta_{fus} H° =$ Unknown

Enthalpy Reference Temperature = T_r = 298.15 K						Standard State Pressure = $p°$ = 0.1 MPa	
	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.434	−238.056	−238.056	INFINITE
100	19.038	9.109	97.044	−8.794	−239.390	−230.867	120.593
200	45.376	30.904	58.385	−5.496	−239.458	−222.172	58.025
298.15	55.279	52.993	52.993	0.	−237.735	−213 988	37.490
300	54.831	53.333	52.994	0.102	−237.706	−213.840	37.233
400	52.932	68.698	55.099	5.439	−236.422	−206.088	26.912
500	53.932	80.628	59.052	10.788	−235.342	−198.632	20.751
600	54.312	90.497	63.495	16.201	−234.402	−191.381	16.661
700	54.513	98.883	67.966	21.642	−233.625	−184.275	13.751
800	54.819	106.180	72.297	27.107	−233.428	−177.207	11.570
900	55.312	112.664	76.428	32.612	−232.970	−170.209	9.879
1000	56.011	118.526	80.349	38.176	−232.709	−163.251	8.527
1100	56.886	123 904	84.068	43.820	−232.656	−156.309	7.423
1200	57.915	128.897	87.598	49.559	−232.827	−149.363	6.502
1300	59 070	133.578	90.957	55.407	−233.353	−142.390	5.721
1400	60.329	138.001	94.160	61.377	−234.348	−135.357	5.050
1500	61.672	142.208	97.224	67.476	−234.217	−128.288	4.467
1600	63.086	146.233	100.163	73.713	−233.707	−121.241	3.958
1700	64.559	150.102	102.987	80.095	−232.966	−114.234	3.510
1800	66.078	153.835	105.709	86.627	−248.354	−106.981	3.105
1900	67.639	157.449	108.337	93.312	−247.588	−99.147	2.726
2000	69.233	160.959	110.881	100.156	−246.676	−91.357	2.386
2100	70.856	164.376	113.347	107.160	−245.615	−83.617	2.080
2200	72.505	167.710	115.743	114.328	−244.401	−75.930	1.803
2300	74.174	170.970	118.074	121.662	−243.033	−68.303	1.551
2400	75.860	174.162	120.344	129.163	−241.508	−60.738	1.322
2500	77.563	177.294	122.560	136.834	−239.825	−53.240	1.112
2600	79.283	180.369	124.724	144.676	−237.981	−45.813	0.920
2700	81.011	183.394	126.841	152.691	−235.975	−38.459	0.744
2800	82.747	186.371	128.914	160.879	−233.806	−31.183	0.582
2900	84.496	189.305	130.946	169.241	−231.473	−23.987	0.432
3000	86.253	192.199	132.940	177.778	−228.974	−16.874	0.294

PREVIOUS: CURRENT: December 1970

Enthalpy of Formation

Boyle *et al.*[1] measured the enthalpy of combustion of metallic cobalt at 303.16 K. Their analyses of the combustion products indicated that some overoxidation of the metal had occurred. Correction of their results to correspond to CoO was made on the assumption that the excess oxygen was combined as Co_3O_4. Also the analyses indicated that the combustion products had attacked the silica–glass capsules, used to hold the metal samples, resulting in appreciable amounts of silicate formation. Corrections for these two side reactions amounted to three percent of the total measured energy of combustion. From these data, we derive $\Delta_f H°$(CoO, cr, 298.15 K) = −57.0 ± 0.3 kcal·mol^{-1}. Roth and Havekoss[2] also investigated calorimetrically the combustion of metallic cobalt and reported $\Delta_f H°$(CoO, cr, 298.15 K) = −57.2 ± 0.2 kcal·mol^{-1}.

2nd and 3rd law analyses of several equilibrium studies,[3-12] emf measurements,[13] and mass–spectrometric studies[14] involving CoO(cr) are discussed in the JANAF Thermochemical Tables,[18] $\Delta_f H°$(CoO, cr, 298.15 K) = −56.82 ± 0.10 kcal·mol^{-1}(−237.735 ± 0.4 kJ·mol^{-1}) was adopted. A recent critical evaluation by Cyr *et al.*[19] recommended $\Delta_f H°$(CoO, cr, 298.15 K) = −237.5 ± 0.4 kJ mol^{-1}, based on 2nd and 3rd law analyses. Since this value differs from the value previously adopted by JANAF by only 0.2 kJ mol^{-1} and includes ten new references in the evaluation, it is adopted for the current table.

Heat Capacity and Entropy

The adopted heat capacities for CoO(cr) in the temperature range 51–298 K are those of King[15]. These data have a pronounced maximum at 287.3 K, at which point the heat capacity is greater than 17.6 cal·K^{-1}·mol^{-1}. Assayag and Bizette[16] also measured heat capacities for CoO(cr) between 180–400 K and reported a maximum at 298.7 K. Presumably this anomaly is of the magnetic type. Heat capacity data above 300 K are calculated from the high temperature (400–1800 K) enthalpy data of King and Christensen.[17] Both sets of data were smoothed by computer and joined at 298.15 K.

The value of $S°$(298.15 K) is obtained from the low temperature heat capacity dataof King[15] and is based on $S°$(51 K) = 0.42 cal·K^{-1}·mol^{-1}.

Fusion Data

The adopted T_{fus} of 2103 ± 10 K was recommended by IUPAC [20] based on the work of Coutures.[21]

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Cobalt Sulfate (CoSO$_4$)   CRYSTAL(α–β) $M_r = 154.9908$

$S°(298\ 15\ \mathrm{K}) = 117.377 \pm 4.2\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$
$T_{trs}\ (\alpha \rightarrow \beta) = 964 \pm 5\ \mathrm{K}$

$\Delta_f H°(0\ \mathrm{K}) = -878.95 \pm 1.3\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_f H°(298.15\ \mathrm{K}) = -888.26 \pm 1.3\ \mathrm{kJ\cdot mol^{-1}}$
$\Delta_{trs} H° = 2.134 \pm 0.4\ \mathrm{kJ\cdot mol^{-1}}$

Enthalpy of Formation

Adami and King[1] determined calorimetrically the enthalpies of solution of crystalline CoO and α–CoSO$_4$ in hydrochloric acid solution. From these measurements they derived the enthalpy for the reaction CoO(cr) + H$_2$SO$_4$ 7.068 H$_2$O(l → CoSO$_4$(cr) + 8.068 H$_2$O (l) as $\Delta_r H°(298.15\ \mathrm{K}) = -14.280 \pm 0.110\ \mathrm{kcal\cdot mol^{-1}}$. Combining this result with enthalpies of formation for CoO[2] H$_2$SO$_4$·7.068 H$_2$O[3], and H$_2$O[3], we derive $\Delta_f H°(\alpha\text{–CoSO}_4,\ \mathrm{cr},\ 298.15\ \mathrm{K}) = -212.3 \pm 0.3\ \mathrm{kcal\cdot mol^{-1}}(-888.263 \pm 1.3\ \mathrm{kJ\cdot mol^{-1}})$ which is adopted.

The total pressures of SO$_3$(g), SO$_2$(g), and O$_2$(g) over CoSO$_4$(cr) in the temperature range 1100–1300 K have been determined by manometric[4-7] and transpiration[8] methods. Previous investigators[4-6] analyzed these data solely in terms of two equilibria, namely (A) CoSO$_4$(cr) = CoO(cr) + SO$_3$(g) and (B) SO$_3$(g) = SO$_2$(g) + 0.5 O$_2$(g). However, Warner[10] has shown that CoSO$_4$ takes part in three successive, univariant, decomposition equilibria as the temperature is increased. Co$_3$O$_4$ is the decomposition product at low temperatures (<1150 K), a mixture of Co$_3$O$_4$ and CoO at intermediate tempertures, and CoO at high temperatures. Second and third law analyses of those points involving only equilibria (A) and (B) are given below. The appearance of Co$_3$O$_4$ as a decomposition product was determined by comparing the oxygen partial pressures that were calculated from the total pressure data with those for the decomposition reaction (C) Co$_3$O$_4$(cr) → 3 CoO(cr) + 0.5 O$_2$(g)[2]. Espelund and Flengas[9] measured the Gibbs energy of reaction (A) in a high temperature solid electrolytic cell. Here, no Co$_3$O$_4$ was formed over the entire temperature range (827–1133 K), since the oxygen pressures in the cell were too low to oxidize the CoO. Results of an analysis of these data are also given below:

Source	Reaction	Method	Data Points	T/K	$\Delta_r H°(298.15\ \mathrm{K})$, kcal·mol^{-1} 2nd law	$\Delta_r H°(298.15\ \mathrm{K})$, kcal·mol^{-1} 3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ \mathrm{K})$ kcal·mol^{-1}
Marchal[4]	A	Manometric	17	1143–1303	54.5	60.4 ± 0.5	4.9 ± 0.6	−211.8 ± 0.8
Schenck and Raub[5]	A	Manometric	14	1099–1243	68.5	60.9 ± 0.7	−6.3 ± 1.1	−212.3 ± 1.0
Warner[6]	A	Manometric	2	1164–1175	56.9	59.3 ± 0.3	2.1	−210.8 ± 0.3
Ingraham[7]	A	Manometric	9	1144–1210	59.1	59.1 ± 0.1	0.04 ± 0.91	−210.6 ± 0.4
Alcock *et al.*[8]	D**	Transpiration	8	1131–1217	−191.1	−166.8 ± 1.4	20.2 ± 5.5	−211.2 ± 1.5
Espelund and Flengas[9]	A	emf	28	827–1177	59.5	59.5 ± 0.3	0.08 ± 0.22	−211.0 ± 0.6

** Reaction: (D) 2 CoO(cr) + 2 SO$_2$(g) + O$_2$(g) = 2 CoSO$_4$(cr)

These results indicate that the Gibbs energy functions and equilibrium data are consistent within experimental error.

Heat Capacity and Entropy

The low temperature (52–298 K) heat capacities are those reported by Weller.[11] No anomalies appear in these data. Heat capacities in the temperature range 300–2000 K are estimated by comparison with those for CuSO$_4$.[2]

$S°(298.15\ \mathrm{K})$ is determined from the C_p data based on $S°(51\ \mathrm{K}) = 1.56 + 2.75\ \mathrm{cal\cdot K^{-1}\cdot mol^{-1}}$. The 1.56 is a lattice contribution, while the 2.75 is the entropy associated with the ordering of the Co^{+2} spin moments. In assigning the magnetic entropy, it is assumed that all of the contribution remains to be extracted below the minimum temperature (52 K) of the heat capacity measurements.[11]

Transition Data

The temperature (T_{trs}) and the heat ($\Delta_{trs}H°$) of the α–β transition for CoSO$_4$ are from the differential thermal analysis studies of Ingraham and Marier.[12] Other temperatures reported for the transition are 890[6] and 903 K.[13]

Decomposition Data

T_{dcm} is the temperature at which the Gibbs energy change for the process CoSO$_4$(cr) → CoO(cr) + SO$_3$(g) is zero.

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Cobalt Sulfate (CoSO$_4$)   Co$_1$O$_4$S$_1$(cr)

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K$_f$
0	0.	0.	INFINITE	−17.238	−878.952	−878.952	INFINITE
100	44 454	37.748	192.584	−15.484	−884.218	−851.311	444.679
200	80.281	80.789	126.133	−9.069	−887.177	−817.096	213.403
298.15	103.219	117.377	117.377	0.	−888.263	−782.408	137.075
300	103.638	118.017	117.379	0.191	−888.269	−781.751	136.115
400	119.286	150.056	121.642	11.366	−890.202	−746.171	97.440
500	131.545	178.049	130.182	23.933	−890.418	−710.133	74.187
600	140.666	202.877	140.269	37.565	−889.584	−674.139	58.689
700	147.277	225.081	150.827	51.977	−888.064	−638.344	47.634
800	152.047	245.074	161.380	66.955	−886.571	−602.736	39.355
900	155.394	263.190	171.702	82.339	−937.599	−566.301	32.867
964 000	156.792	273.916	178.135	92.332	ALPHA <- -> BETA TRANSITION		
964.000	157.221	276.129	178.135	94.466			
1000	158.113	281.910	181.767	100.142	−932.148	−525.304	27.439
1100	160.415	297.089	191.571	116.071	−928.946	−484.775	23.020
1200	162.465	311.137	200.956	132.217	−925.920	−444.531	19.350
1300	164.306	324.215	209.941	148.556	−923.232	−404.528	16.254
1400	165.979	336.453	218.545	165.071	−921.020	−364.713	13.608
1500	167.569	347 959	226.793	181.749	−917.705	−325.090	11.321
1600	169.075	358.822	234.708	198.582	−914.048	−285.700	9.327
1700	170.498	369.115	242.314	215.561	−910.211	−246.545	7.575
1800	171.921	378.901	249.633	232.683	−922.559	−207.326	6.016
1900	173.259	388.232	256.684	249.942	−918.819	−167.692	4.610
2000	174.598	397.153	263.486	267.335	−915.002	−128.257	3.350

PREVIOUS: CURRENT: December 1971

Cobalt Oxide (Co_3O_4) CRYSTAL $M_r = 240.7972$ Cobalt Oxide (Co_3O_4) $Co_3O_4(cr)$

$\Delta_f H°(0\ K) = -896.3 \pm 4.0\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 114.29 \pm 4.2\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = -910.0 \pm 4.0\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Bugden and Pratt[1] measured Gibbs energies of reaction for (a) $2Cu(cr) + Co_3O_4(cr) \rightarrow 3CoO(cr) + Cu_2O(cr)$ and (b) $Ni(cr) + Co_3O_4(cr) \rightarrow 3CoO(cr) + NiO(cr)$ from high temperature solid electrolytic cells. These data were subjected to 2nd and 3rd law analyses with results summarized in the following table:

Source	Reaction	Method	T/K	No. of Points	$\Delta_f H°$(298.15 K) kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298. 15K)*
Bugden and Pratt[1]	a	emf	900–1150	Eqn	5.1	6.3 ± 0.2	1.1	−217.5 ± 0.8
	b	emf	850–1100	Eqn	−12.0	−10.6 ± 0.2	1.3	−217.1 ± 0.8
Foote and Smith[3]	c	Manometric	1073–1243	6	34.5	47.2 ± 1.4	10.6 ± 1.3	−217.7 ± 1.5
Watanabe[4]	c	Manometric	1128–1233	4	38.1	47.9 ± 0.7	8.3 ± 0.8	−218.4 ± 1.0
Chufarov *et al.*[5]	c	Manometric	973–1173	4	27.9	46.4 ± 2.9	17.0 ± 0.6	−216.9 ± 3.0
Balakirev and Chufarov[6]	c	Manometric	923–1173	5	33.8	46.1 ± 2.5	11.3 ± 2.5	−216.6 ± 3.0
Roiter and Paladine[7]	c	Manometric	1139–1220	5	36.4	47.1 ± 0.6	9.0 ± 2.0	−217.6 ± 1.0
Ingraham[8] Set I	c	Manometric	1101–1159	6	41.4	46.8 ± 0.2	4.5 ± 0.4	−217.3 ± 0.5
Set II	c	Manometric	1086–1219	19	35.6	46.9 ± 0.8	9.7 ± 0.2	−217.4 ± 1.0
O'Bryan and Parravano[9]	c	X–ray & Wt. Loss	1073–1243	Eqn	40.3	47.3 ± 0.8	5.9	−217.8 ± 1.0

*3rd law values based on $\Delta_f H°(CoO,cr,\ 298.15\ K) = -56.82 \pm 0.1\ kcal{\cdot}mol^{-1}$.[2]

Both sets of emf data are much more compatible with the adopted functions than the dissociation pressure data (refer to the discussion below). The results obtained with the Cu/Cu_2O reference couple are judged to be more reliable and lead to the adopted enthalpy of formation, $\Delta_f H°(Co_3O_4,cr,\ 298.15\ K) = -217.5 \pm 1.0\ kcal{\cdot}mol^{-1}$, when used in conjunction with JANAF[2] enthalpies of formation for CoO and Cu_2O.

Equilibrium oxygen pressures for the reaction (c) $Co_3O_4(cr) = 3CoO(cr) + 0.5\ O_2(g)$ have been determined by numerous investigators.[3-9] 2nd and 3rd law analyses of these data are given in the above table. Within each set the 2nd and 3rd law $\Delta_f H°$(298.15 K) values are not in agreement, and all sets contain large positive drifts. Warner[10] has suggested that these discrepancies arise as a result of an error in the measured standard entropy[11] for Co_3O_4. However, once the magnetic contribution is included (see entropy write-up) the real error in this value is probably no greater than one cal·K^{-1}·mol^{-1}. The other possible source of error is lack of true equilibrium conditions. Recent thermogravimetric,[9] X–ray,[9] and kinetic,[9, 12] studies of the Co_3O_4–CoO–O_2 system all point to an irreversible reaction. Therefore, no weight has been given to the dissociation pressure data in our evaluation.

Heat Capacity and Entropy

The low temperature heat capacities (54–296.3 K) are those reported by King.[11] Heat capacities in the temperature range 300–1000 K are calculated from the high temperature enthalpy data of King and Christensen,[13] a constrained curve fitting technique was used to join smoothly these data with the low temperature data at 298 K. No anomalies appear in either set of data. Roth[14] observed a maximum in the magnetic susceptibility of Co_3O_4 at 40 K, while Mossbauer studies by Kundig *et al.*[15] indicated a Neel temperature of 33.0 ± 1.0 K. With the assumption that Co_3O_4 is a normal 2-3 spinel,[16] this transition can be associated with the antiferromagnetic ordering of the Co^{+2} ion spin moments. Therefore, the entropy is based on $S°(51\ K) = 1.36 + 2.75 = 4.11\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, where 1.36 is a lattice contribution and 2.75 is the magnetic entropy. In assigning the magnetic entropy, it is assumed that all of the contribution remains to be extracted below the minmum temperature (54 K) of the heat capacity measurements.

Decomposition Data

T_{dcm} is the temperature at which the Gibbs energy change for the process $Co_3O_4(cr \rightarrow 3CoO(cr) + 0.5\ O_2(g)$ is zero.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.968	−896.309	−896.309	INFINITE
100	34.368	31.487	198.112	−16.663	−902.377	−868.560	453.689
200	87.595	72.039	124.547	−10.501	−907.767	−832.428	217.408
298.15	123.051	114.286	114.286	0.	−910.020	−794.871	139.258
300	123.512	115.049	114.289	0.228	−910.038	−794.157	138.275
400	142.666	153.657	119.423	13.694	−910.220	−755.468	98.654
500	152.850	186.590	129.647	28.471	−909.774	−716.825	74.886
600	162.808	215.325	141.580	44.247	−908.999	−678.302	59.051
700	173.628	241.224	153.992	61.062	−907.802	−639.941	47.753
800	185.272	265.161	166.410	79.001	−907.337	−601.601	39.280
900	197.552	287.688	178.645	98.139	−905.043	−563.516	32.706
1000	210.296	309.158	190.630	118.528	−902.293	−525.712	27.460
1100	223.384	329.814	202.350	140.210	−899.139	−488.203	23.183
1200	236.727	349.821	213.809	163.214	−895.639	−450.998	19.631
1300	250.262	369.303	225.024	187.562	−892.206	−414.087	16.638
1400	263.943	388.349	236.012	213.272	−889.197	−377.422	14.082
1500	277.742	407.029	246.793	240.355	−881.838	−341.108	11.878

PREVIOUS December 1970 CURRENT December 1971