IP(Br, g) = 95284.8 ± 0.5 cm^{-1}
$S°(298.15\ K)$ = 175.017 ± 0.003 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 117.92 ± 0.06 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 111.86 ± 0.06 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P°_{3/2}$	0.0	4
$^2P°_{1/2}$	3685.24	2

Enthalpy of Formation

The adopted value for the enthalpy of formation of Br(g) is derived from the spectroscopically determined dissociation energy of $Br_2(g)$ as reported by Barrow *et al.*[1,2] This value is also recommended by Brewer and Winn[3] and Huber and Herzberg.[4] The adopted value, $D_0°$ = 15895.6 ± 0.02 cm^{-1} (190.154 ± 0.001 $kJ·mol^{-1}$), has been corrected for the natural isotopic abundance from the dissociation energies of $^{79}Br_2$ and $^{81}Br_2$. The convergence limit in the absorption spectrum of the $^3\Pi_{0^+_u} - {}^1\Sigma^+_g$ system corresponds to dissociation to a ground state bromine atom ($^2P_{3/2}$) and a bromine atom in the $^2P_{1/2}$ excited state.

Using earlier data, the CODATA recommended value[5] was calculated using $D_0°$ (^{79}Br–^{81}Br) = 15893.1 ± 2 cm^{-1} based on Horsley and Barrow[6] and Sitterly.[7] LeRoy[8] recalculated the dissociation energy from these data; his result is correct only if Horsley and Barrow[6] missed many upper rotational levels of higher vibrational states in their interpretation of the absorption spectra. Subsequent to these initial CODATA evaluation, LeRoy and Bernstein,[9] using the band origins obtained by Horsley and Barrow,[6] derived $D_0°$ (^{79}Br–^{81}Br) = 15895.5 ± 0.5 cm^{-1}.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore.[10, 11] Only two levels are included in the calculation. All other levels (observed and predicted) lie above 63430 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[13] except for two minor differences. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ 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 $J·K^{-1}·mol^{-1}$ for the monatomic halogens arise due to the use of slightly different values for the relative atomic mass and for R; this table uses R = 8.31441 $J·K^{-1}·mol^{-1}$. Considering these minor changes, this table agrees within the estimated uncertainty with those by Hultgren *et al.*[14] Gurvich *et al.*[15] 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[17] and the 1973 values,[18] respectively.

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	117.917	117.917	INFINITE
100	20.786	152.310	193.497	−4.119	118.599	106.061	−55.400
200	20.786	166.717	176.918	−2.040	118.227	93.626	−24.453
250	20.786	171.356	175.359	−1.001	117.859	87.515	−18.285
298.15	20.786	175.017	175.017	0.	111.860	82.369	−14.431
300	20.786	175.145	175.017	0.038	111.828	82.186	−14.310
350	20.786	178.350	175.270	1.078	96.543	78.082	−11.653
400	20.787	181.125	175.832	2.117	96.667	75.436	−9.851
450	20.790	183.574	176.559	3.157	96.786	72.775	−8.447
500	20.798	185.765	177.372	4.196	96.900	70.100	−7.323
600	20.833	189.559	179.097	6.277	97.122	64.720	−5.634
700	20.908	192.776	180.827	8.364	97.339	59.302	−4.425
800	21.027	195.575	182.499	10.461	97.560	53.853	−3.516
900	21.184	198.060	184.093	12.571	97.788	48.376	−2.808
1000	21.365	200.301	185.603	14.698	98.028	42.873	−2.239
1100	21.559	202.347	187.034	16.844	98.283	37.345	−1.773
1200	21.752	204.231	188.389	19.010	98.552	31.794	−1.384
1300	21.937	205.979	189.676	21.195	98.837	26.219	−1.054
1400	22.107	207.611	190.899	23.397	99.134	20.622	−0.769
1500	22.258	209.142	192.065	25.615	99.443	15.004	−0.522
1600	22.388	210.583	193.178	27.848	99.761	9.364	−0.306
1700	22.497	211.943	194.242	30.092	100.085	3.704	−0.114
1800	22.586	213.232	195.262	32.346	100.412	−1.975	0.057
1900	22.657	214.455	196.240	34.609	100.740	−7.672	0.211
2000	22.710	215.619	197.180	36.877	101.066	−13.386	0.350
2100	22.748	216.728	198.085	39.150	101.387	−19.117	0.476
2200	22.772	217.786	198.956	41.426	101.701	−24.862	0.590
2300	22.785	218.799	199.797	43.704	102.006	−30.622	0.695
2400	22.788	219.769	200.609	45.983	102.301	−36.395	0.792
2500	22.782	220.699	201.394	48.262	102.585	−42.180	0.881
2600	22.769	221.592	202.154	50.539	102.856	−47.976	0.964
2700	22.750	222.451	202.890	52.815	103.114	−53.782	1.040
2800	22.727	223.278	203.603	55.089	103.360	−59.598	1.112
2900	22.699	224.075	204.296	57.360	103.592	−65.421	1.178
3000	22.669	224.844	204.968	59.629	103.813	−71.253	1.241
3100	22.635	225.587	205.621	61.894	104.023	−77.092	1.299
3200	22.600	226.305	206.256	64.156	104.222	−82.938	1.354
3300	22.564	227.000	206.875	66.414	104.411	−88.790	1.405
3400	22.526	227.673	207.476	68.669	104.593	−94.647	1.454
3500	22.489	228.325	208 063	70.919	104.767	−100.510	1.500
3600	22.450	228.958	208.634	73.166	104.936	−106.377	1.543
3700	22.412	229.573	209.192	75.409	105.101	−112.249	1.585
3800	22.374	230.170	209.736	77.649	105.263	−118.126	1.624
3900	22.336	230.751	210.268	79.884	105.423	−124.006	1.661
4000	22.298	231.316	210.787	82.116	105.582	−129.891	1.696
4100	22.261	231.866	211.294	84.344	105.743	−135.780	1.730
4200	22.225	232.402	211.791	86.568	105.904	−141.673	1.762
4300	22.189	232.925	212.276	88.789	106.069	−147.569	1.793
4400	22.154	233.434	212.751	91.006	106.237	−153.470	1.822
4500	22.120	233.932	213.216	93.220	106.409	−159.374	1.850
4600	22.087	234.418	213.672	95.430	106.587	−165.283	1.877
4700	22.055	234.892	214.118	97.637	106.770	−171.195	1.903
4800	22.023	235.356	214.556	99.841	106.960	−177.111	1.927
4900	21.992	235.810	214.985	102.042	107.156	−183.031	1.951
5000	21.962	236.254	215.406	104.239	107.359	−188.955	1.974
5100	21.933	236.689	215.819	106.434	107.570	−194.883	1.996
5200	21.905	237.114	216.225	108.626	107.789	−200.816	2.017
5300	21.878	237.531	216.623	110.815	108.016	−206.753	2.038
5400	21.851	237.940	217.014	113.002	108.251	−212.694	2.057
5500	21.825	238.341	217.398	115.186	108.495	−218.640	2.076
5600	21.800	238.734	217.775	117.367	108.746	−224.590	2.095
5700	21.776	239.119	218.146	119.546	109.007	−230.545	2.113
5800	21.752	239.498	218.511	121.722	109.275	−236.504	2.130
5900	21.730	239.870	218.870	123.896	109.552	−242.468	2.147
6000	21.708	240.235	219.223	126.068	109.838	−248.437	2.163

PREVIOUS June 1974 (1 atm) CURRENT. June 1982 (1 bar)

IP(Br^+, g) = 175870 ± 10 cm^{-1}
$S°$(298.15 K) = 176.872 ± 0.005 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1256.95 ± 0.13 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1257.091] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_2$	0.0	5
$^3P_1$	3136.4	3
$^3P_0$	3837.5	1
$^1D_2$	12089.1	5
$^1S_0$	27867.1	1

Enthalpy of Formation

$\Delta_f H°(Br^+, g, 0 K)$ is calculated from $\Delta_f H°(Br, g, 0 K)$[1] using the spectroscopic value of IP(Br) = 95284.8 ± 0.5 cm^{-1}(1139.86 ± 0.01 $kJ·mol^{-1}$) 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.

$\Delta_f H°(Br^+, g, 298.15 K)$ is calculated from $\Delta_f H°(Br, g, 0 K)$ by using IP(Br) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Br(g), $Br^+(g)$, and e^-(ref). $\Delta_f H°(Br \rightarrow Br^+ + e^-, 298.15 K)$ 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 93927 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 in $S°$(298.15 K) is due to uncertainties in the relative ionic mass, 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]

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
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	1256.951		
100	20.786	154.165	195.352	−4.119			
200	20.786	168.573	178.773	−2.040			
250	20.786	173.211	177.214	−1.001			
298.15	20.786	176.872	176.872	0.	1257.091	1220.792	−213.878
300	20.786	177.001	176.872	0.038	1257.098	1220.567	−212.520
350	20.788	180.205	177.125	1.078	1242.852	1215.232	−181.364
400	20.794	182.981	177.688	2.117	1244.016	1211.207	−158.167
450	20.809	185.431	178.415	3.157	1245.175	1207.037	−140.109
500	20.838	187.625	179.228	4.199	1246.330	1202.737	−125.649
600	20.953	191.433	180.954	6.287	1248.638	1193.802	−103.930
700	21.153	194.677	182.688	8.392	1250.952	1184.480	−88.387
800	21.426	197.519	184.368	10.520	1253.282	1174.825	−76.708
900	21.746	200.060	185.973	12.679	1255.637	1164.877	−67.608
1000	22.084	202.369	187.499	14.870	1258.020	1154.665	−60.313
1100	22.415	204.490	188.948	17.095	1260.432	1144.212	−54.334
1200	22.720	206.453	190.326	19.352	1262.872	1133.540	−49.342
1300	22.990	208.283	191.638	21.638	1265.336	1122.662	−45.109
1400	23.220	209.995	192.889	23.949	1267.821	1111.594	−41.474
1500	23.409	211.604	194.083	26.281	1270.322	1100.348	−38.318
1600	23.560	213.120	195.226	28.629	1272.835	1088.934	−35.550
1700	23.677	214.552	196.321	30.992	1275.355	1077.363	−33.103
1800	23.765	215.908	197.372	33.364	1277.879	1065.644	−30.924
1900	23.829	217.194	198.382	35.744	1280.403	1053.784	−28.971
2000	23.874	218.418	199.353	38.129	1282.924	1041.792	−27.209
2100	23.904	219.583	200.289	40.518	1285.440	1029.673	−25.612
2200	23.923	220.696	201.192	42.909	1287.948	1017.435	−24.157
2300	23.935	221.760	202.063	45.302	1290.447	1005.083	−22.826
2400	23.942	222.778	202.905	47.696	1292.935	992.623	−21.604
2500	23.946	223.756	203.720	50.091	1295.413	980.059	−20.477
2600	23.948	224.695	204.508	52.485	1297.880	967.396	−19.435
2700	23.950	225.599	205.273	54.880	1300.336	954.638	−18.469
2800	23.952	226.470	206.014	57.275	1302.781	941.790	−17.569
2900	23.955	227.310	206.734	59.671	1305.216	928.854	−16.730
3000	23.959	228.123	207.434	62.066	1307.643	915.835	−15.946
3100	23.964	228.908	208.114	64.462	1310.062	902.735	−15.211
3200	23.971	229.669	208.776	66.859	1312.474	889.557	−14.521
3300	23.979	230.407	209.420	69.257	1314.882	876.303	−13.871
3400	23.988	231.123	210.048	71.655	1317.286	862.977	−13.258
3500	23.997	231.818	210.660	74.054	1319.687	849.580	−12.679
3600	24.008	232.495	211.257	76.455	1322.088	836.114	−12.132
3700	24.018	233.153	211.840	78.856	1324.490	822.582	−11.613
3800	24.029	233.793	212.409	81.258	1326.893	808.985	−11.120
3900	24.040	234.418	212.966	83.662	1329.300	795.324	−10.652
4000	24.051	235.026	213.510	86.066	1331.711	781.602	−10.207
4100	24.061	235.620	214.042	88.472	1334.127	767.819	−9.782
4200	24.071	236.200	214.562	90.878	1336.550	753.977	−9.377
4300	24.080	236.767	215.072	93.286	1338.980	740.078	−8.990
4400	24.088	237.320	215.572	95.694	1341.418	726.122	−8.620
4500	24.095	237.862	216.061	98.104	1343.864	712.110	−8.266
4600	24.101	238.391	216.541	100.513	1346.320	698.044	−7.927
4700	24.107	238.910	217.011	102.924	1348.785	683.925	−7.601
4800	24.111	239.417	217.473	105.335	1351.260	669.753	−7.288
4900	24.114	239.915	217.926	107.746	1353.746	655.529	−6.988
5000	24.116	240.402	218.370	110.157	1356.242	641.254	−6.699
5100	24.116	240.879	218.807	112.569	1358.748	626.930	−6.421
5200	24.116	241.348	219.236	114.981	1361.265	612.556	−6.153
5300	24.114	241.807	219.658	117.392	1363.793	598.133	−5.895
5400	24.111	242.258	220.072	119.803	1366.332	583.663	−5.646
5500	24.107	242.700	220.479	122.214	1368.881	569.146	−5.405
5600	24.102	243.134	220.880	124.625	1371.440	554.582	−5.173
5700	24.096	243.561	221.274	127.035	1374.010	539.973	−4.948
5800	24.089	243.980	221.662	129.444	1376.590	525.318	−4.731
5900	24.081	244.392	222.044	131.853	1379.181	510.618	−4.521
6000	24.072	244.796	222.420	134.260	1381.780	495.875	−4.317

PREVIOUS. CURRENT. June 1982 (1 bar)

EA(Br, g) = 3.365 ± 0.003 eV
$S°(298.15\ K)$ = 163.491 ± 0.005 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -206.8 \pm 0.5\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-219.008]\ kJ·mol^{-1}$

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

Enthalpy of Formation

$\Delta_f H°(Br^-, g, 0\ K)$ is calculated from $\Delta_f H°(Br,g, 0\ K)$[1] using the adopted electron affinity of EA(Br) = 3.363 ± 0.003 eV (324.671 ± 0.289 $kJ·mol^{-1}$). This value, recommended by Hotop and Lineberger,[10] is based on plasma absorption and plasma emission studies.[5,6] Additional information on $Br^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2,10] Rosenstock *et al.*[3] and Massey.[4]

$\Delta_f H°(Br^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Br, g, 0\ K)$ by using EA(Br) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for $Br^-(g)$, Br(g), and e^-(ref). $\Delta_r H°(Br^- \rightarrow Br + e^-, 298.15\ K)$ 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 $kJ·mol^{-1}$ 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 $Br^-(g)$ 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 $J·K^{-1}·mol^{-1}$ with the values of Gurvich *et al.*[8] except for one minor difference. The entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ 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.

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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	−6.197	−206.753		
100	20.786	140.783	181.971	−4.119			
200	20.786	155.191	165.392	−2.040			
250	20.786	159.829	163.833	−1.001			
298.15	20.786	163.491	163.491	0.	−219.008	−238.808	41.838
300	20.786	163.619	163.491	0.038	−219.078	−238.930	41.601
350	20.786	166.823	163.744	1.078	−235.403	−241.321	36.015
400	20.786	169.599	164.306	2.117	−236.318	−242.104	31.616
450	20.786	172.047	165.033	3.156	−237.239	−242.772	28.180
500	20.786	174.237	165.846	4.196	−238.164	−243.337	25.421
600	20.786	178.027	167.570	6.274	−240.023	−244.198	21.259
700	20.786	181.231	169.299	8.353	−241.893	−244.746	18.263
800	20.786	184.007	170.967	10.431	−243.769	−245.025	15.999
900	20.786	186.455	172.555	12.510	−245.651	−245.069	14.223
1000	20.786	188.645	174.056	14.589	−247.538	−244.904	12.792
1100	20.786	190.626	175.474	16.667	−249.429	−244.549	11.613
1200	20.786	192.435	176.813	18.746	−251.325	−244.021	10.622
1300	20.786	194.099	178.080	20.824	−253.226	−243.335	9.777
1400	20.786	195.639	179.280	22.903	−255.130	−242.503	9.048
1500	20.786	197.073	180.419	24.982	−257.040	−241.535	8.411
1600	20.786	198.415	181.502	27.060	−258.954	−240.439	7.850
1700	20.786	199.675	182.534	29.139	−260.875	−239.223	7.350
1800	20.786	200.863	183.520	31.217	−262.802	−237.893	6.903
1900	20.786	201.987	184.462	33.296	−264.736	−236.457	6.501
2000	20.786	203.053	185.365	35.375	−266.679	−234.918	6.135
2100	20.786	204.067	186.232	37.453	−268.631	−233.282	5.803
2200	20.786	205.034	187.065	39.532	−270.593	−231.553	5.498
2300	20.786	205.958	187.866	41.610	−272.566	−229.734	5.217
2400	20.786	206.843	188.639	43.689	−274.550	−227.830	4.959
2500	20.786	207.691	189.384	45.768	−276.545	−225.842	4.719
2600	20.786	208.506	190.104	47.846	−278.551	−223.774	4.496
2700	20.786	209.291	190.800	49.925	−280.569	−221.629	4.288
2800	20.786	210.047	191.474	52.004	−282.597	−219.409	4.093
2900	20.786	210.776	192.127	54.082	−284.636	−217.117	3.911
3000	20.786	211.481	192.761	56.161	−286.684	−214.754	3.739
3100	20.786	212.162	193.375	58.239	−288.739	−212.322	3.578
3200	20.786	212.822	193.973	60.318	−290.802	−209.824	3.425
3300	20.786	213.462	194.554	62.397	−292.871	−207.261	3.281
3400	20.786	214.082	195.119	64.475	−294.944	−204.636	3.144
3500	20.786	214.685	195.670	66.554	−297.020	−201.950	3.014
3600	20.786	215.271	196.206	68.632	−299.098	−199.204	2.890
3700	20.786	215.840	196.729	70.711	−301.176	−196.401	2.773
3800	20.786	216.394	197.239	72.790	−303.254	−193.541	2.660
3900	20.786	216.934	197.737	74.868	−305.329	−190.627	2.553
4000	20.786	217.461	198.224	76.947	−307.401	−187.659	2.451
4100	20.786	217.974	198.699	79.025	−309.469	−184.640	2.352
4200	20.786	218.475	199 164	81.104	−311.532	−181.571	2.258
4300	20.786	218.964	199 619	83.183	−313.588	−178.452	2.168
4400	20.786	219.442	200.064	85.261	−315.637	−175.286	2.081
4500	20.786	219.909	200.500	87.340	−317.678	−172.073	1.997
4600	20.786	220.366	200.927	89.418	−319.711	−168.815	1.917
4700	20.786	220.813	201.345	91.497	−321.735	−165.513	1.839
4800	20.786	221.250	201.755	93.576	−323.749	−162.167	1.765
4900	20.786	221.679	202.158	95.654	−325.754	−158.780	1.693
5000	20.786	222.099	202.552	97.733	−327.748	−155.352	1.623
5100	20.786	222.510	202.940	99.811	−329.732	−151.885	1.556
5200	20.786	222.914	203.320	101.890	−331.705	−148.378	1.490
5300	20.786	223.310	203.693	103.969	−333.667	−144.834	1.427
5400	20.786	223.699	204.060	106.047	−335.618	−141.253	1.366
5500	20.786	224.080	204.421	108.126	−337.559	−137.635	1.307
5600	20.786	224.454	204.775	110.204	−339.488	−133.983	1.250
5700	20.786	224.822	205.124	112.283	−341.407	−130.296	1.194
5800	20.786	225.184	205.466	114.362	−343.314	−126.576	1.140
5900	20.786	225.539	205.804	116.440	−345.212	−122.823	1.087
6000	20.786	225.889	206.135	118.519	−347.098	−119.038	1.036

PREVIOUS: CURRENT June 1982 (1 bar)

$S°(298.15\ K) = 252.89 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -41.3 \pm 41.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -49.4 \pm 41.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$X\ ^2\Sigma^+$	0	2	$D\ ^2\Sigma$	30190.6	2
$A_1\ ^2\Pi_{1/2}$	15922.5	2	$E\ ^2\Sigma$	33942.2	2
$A_2\ ^2\Pi_{3/2}$	15985.8	2	[F $^2\Pi$]	[35000]	[4]
$B\ ^2\Sigma$	16380.0	2	[G $^2\Delta$]	[36000]	[4]
$C_1\ ^2\Pi$	25314.0	2	[H $^2\Sigma$]	36798.7	[2]
$C_2\ ^2\Pi_{3/2}$	25537.5	2			

$\omega_e = 284.56\ cm^{-1}$ $\omega_e x_e = 0.86\ cm^{-1}$ $\sigma = 1$
$B_e = [0.09637]\ cm^{-1}$ $\alpha_e = [0.000389]\ cm^{-1}$ $r_e = [2.56]$ Å

Enthalpy of Formation

The selected value, $\Delta_f H°(0\ K) = -41.258\ kJ\ mol^{-1}$, is obtained from an analysis of spectroscopic data. The adopted values of the ground state vibrational constants, ω_e and $\omega_e x_e$, give $D_0° = 2.90$ eV for CaBr(g) by a linear Birge–Sponer extrapolation. Based on the ionicity correction suggested by Hildenbrand,[1] this value adjusts to 3.50 eV (337.696 $kJ \cdot mol^{-1}$) which is adopted. The adopted value for $D_0°$ gives $D_0°(CaBr)/\Delta_a H°(CaBr_2) = 0.43$ which is quite consistent with values of this ratio for other alkaline earth halide systems.[2] Also, Hildenbrand[3,4] found that the ionicity parameter brings thermochemical and spectroscopic dissociation energies for CaF(g) and CaCl(g) into reasonable agreement. $\Delta_f H°(298.15\ K)$ corresponds to $-49.4\ kJ \cdot mol^{-1}$.

Ionic model calculations have led to $D_0°$ values of 5.29 eV[5] and 3.4 eV.[6] The latter result is believed to represent a minimum value for $D_0°$. Two other experimental values, which bracket the selected value, have also been reported. Flame studies[7] gave $D_0° = 3.29$ eV and chemiluminescence[8] from reaction of Ca atoms with Br gave a lower limit to $D_0°$ of 4.22 eV. We assign an uncertainty of ±41.8 kJ mol^{-1} to $\Delta_f H°(0\ K)$ to include the possibility that these studies are correct.

Heat Capacity and Entropy

The value of r_e is obtained from that for gaseous $CaBr_2$[9] with $r_e(CaBr)/r_e(CaBr_2) = 0.96$. The value of this ratio is calculated from bond lengths[2] for several other alkaline earth halide systems. Our adopted value for r_e is supported by an estimate ($r_e = 2.6$ Å) of Krasnov and Karaseva[6] while another estimated value[5] is only 0.14 Å larger than ours. The rotational constant is calculated from the estimated value of r_e. The value of α_e is obtained from a Morse potential function.

The vibrational constants are those recently determined from a complete vibrational analysis of the $D\ ^2\Sigma$–$X\ ^2\Sigma$ system by Shah.[10] These two values are corrected for the natural isotopic abundances of Br. The electronic levels with the exception of those for the D, F, G, and H states are from the compilation of Rosen.[11] The D state energy is from Shah.[10] The two doublet states (F and G) are estimated by analogy with those for SrBr.[9] Recently, Reddy *et al.*[12] reported observing a new system of bands in the visible emission spectrum of CaBr which was associated with $^2\Sigma$ – A $^2\Pi$ transition. The upper state of this system is assigned the H $^2\Sigma$ state by analogy with SrBr.

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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	−9.854	−41.259	−41.259	INFINITE
100	31.560	215.410	284.258	−6.885	−40.667	−57.919	30.254
200	35.141	238.594	256.190	−3.519	−42.021	−74.700	19.510
250	35.915	246.526	253.491	−1.741	−42.901	−82.771	17.294
298.15	36.381	252.894	252.894	0.	−49.396	−89.707	15.716
300	36.395	253.119	252.895	0.067	−49.447	−89.957	15.663
350	36.713	258.755	253.339	1.896	−65.250	−95.832	14.302
400	36.935	263.673	254.330	3.737	−65.652	−100.174	13.081
450	37.100	268.033	255.615	5.588	−66.084	−104.463	12.126
500	37.227	271.949	257.056	7.446	−66.554	−108.703	11.356
600	37.413	278.754	260.122	11.179	−67.624	−117.035	10.189
700	37.548	284.532	263.207	14.927	−68.883	−125.173	9.341
800	37.654	289.553	266.193	18.688	−71.193	−133.014	8.685
900	37.743	293.993	269.040	22.458	−72.831	−140.646	8.163
1000	37.822	297.974	271.738	26.236	−74.760	−148.080	7.735
1100	37.894	301.582	274.289	30.022	−76.988	−155.307	7.375
1200	37.962	304.882	276.703	33.815	−87.252	−161.695	7.038
1300	38.026	307.923	278.989	37.614	−88.852	−167.834	6.744
1400	38.088	310.744	281.158	41.420	−90.451	−173.849	6.486
1500	38.149	313.373	283.219	45.232	−92.049	−179.750	6.259
1600	38.209	315.837	285.181	49.050	−93.646	−185.545	6.057
1700	38.269	318.156	287.054	52.873	−95.242	−191.240	5.876
1800	38.331	320.345	288.843	56.703	−245.513	−194.630	5.648
1900	38.395	322.419	290.556	60.540	−245.698	−191.798	5.273
2000	38.463	324.390	292.199	64.383	−245.889	−188.956	4.935
2100	38.536	326.268	293.777	68.232	−246.091	−186.104	4.629
2200	38.615	328.063	295.295	72.090	−246.306	−183.243	4.351
2300	38.703	329.781	296.757	75.956	−246.539	−180.371	4.096
2400	38.800	331.430	298.168	79.831	−246.792	−177.489	3.863
2500	38.908	333.016	299.530	83.716	−247.071	−174.596	3.648
2600	39.028	334.545	300.848	87.613	−247.381	−171.691	3.449
2700	39.161	336.020	302.123	91.522	−247.726	−168.773	3.265
2800	39.307	337.447	303.359	95.445	−248.113	−165.842	3.094
2900	39.468	338.829	304.559	99.384	−248.545	−162.896	2.934
3000	39.644	340.170	305.723	103.340	−249.030	−159.935	2.785
3100	39.835	341.473	306.856	107.313	−249.573	−156.956	2.645
3200	40.041	342.741	307.957	111.307	−250.178	−153.959	2.513
3300	40.262	343.976	309.030	115.322	−250.852	−150.942	2.389
3400	40.498	345.182	310.076	119.360	−251.600	−147.903	2.272
3500	40.748	346.359	311.096	123.422	−252.427	−144.842	2.162
3600	41.013	347.511	312.091	127.510	−253.338	−141.755	2.057
3700	41.291	348.638	313.064	131.625	−254.336	−138.642	1.957
3800	41.582	349.743	314.015	135.769	−255.426	−135.501	1.863
3900	41.885	350.827	314.945	139.942	−256.610	−132.330	1.772
4000	42.199	351.892	315.855	144.146	−257.892	−129.127	1.686
4100	42.524	352.938	316.747	148.382	−259.272	−125.891	1.604
4200	42.858	353.966	317.621	152.651	−260.751	−122.620	1.525
4300	43.201	354.979	318.478	156.954	−262.332	−119.313	1.449
4400	43.552	355.976	319.319	161.291	−264.009	−115.968	1.377
4500	43.910	356.959	320.144	165.664	−265.770	−112.584	1.307
4600	44.274	357.928	320.955	170.074	−267.634	−109.160	1.240
4700	44.643	358.884	321.752	174.519	−269.594	−105.694	1.175
4800	45.016	359.828	322.536	179.002	−271.643	−102.185	1.112
4900	45.394	360.760	323.306	183.523	−273.778	−98.633	1.051
5000	45.773	361.681	324.064	188.081	−275.993	−95.036	0.993
5100	46.155	362.591	324.811	192.677	−278.285	−91.395	0.936
5200	46.538	363.491	325.546	197.312	−280.642	−87.708	0.881
5300	46.921	364.381	326.271	201.985	−283.068	−83.974	0.828
5400	47.303	365.261	326.984	206.696	−285.553	−80.194	0.776
5500	47.685	366.133	327.688	211.446	−288.090	−76.368	0.725
5600	48.065	366.996	328.383	216.233	−290.664	−72.496	0.676
5700	48.442	367.850	329.067	221.059	−293.286	−68.577	0.628
5800	48.817	368.695	329.743	225.921	−295.942	−64.612	0.582
5900	49.188	369.533	330.411	230.822	−298.626	−60.601	0.537
6000	49.555	370.363	331.070	235.759	−301.330	−56.544	0.492

PREVIOUS: December 1974 (1 atm) CURRENT December 1974 (1 bar)

$S°(298.15\ K) = 240.001\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 22.087 \pm 1.25\ kJ·mol^{-1}$
$\Delta H°(298.15\ K) = 14.644 \pm 1.25\ kJ·mol^{-1}$

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

$\omega_e = 443.1\ cm^{-1}$ $\omega_e x_e = 1.8\ cm^{-1}$ $\sigma = 1$
$B_e = 0.150797\ cm^{-1}$ $\alpha_e = 0.0007597\ cm^{-1}$ $r_e = 2.136$ Å

Enthalpy of Formation

The average $\Delta_r H°(298.15\ K) = 0.406\ kcal·mol^{-1}$ for the reaction $Br_2(g) + Cl_2(g) = 2BrCl(g)$ and the $\Delta_f H°(298.15\ K) = 3.694\ kcal·mol^{-1}$ for 1/2 Br_2(g) from JANAF tables were used to calculate the $\Delta_f H°(298.15\ K) = 3.5 \pm 0.3\ kcal·mol^{-1}$ ($14.644 \pm 1.25\ kJ·mol^{-1}$). Other equilibrium measurements not included below have been summarized by Beeson and Yost.[3]

Source	T, K	Method	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1}
[1]	301	Light absorption	.51
[2]	298	Light absorption	0.34
[3]	372–492	Total pressure Run III	0.39
[3]	372–492	Total pressure Run II	0.47
[4]	313 ± 5	Mass spectrometric	0.32
		Average	0.406

Heat Capacity and Entropy

All spectroscopic and molecular constants were obtained from Evans *et al* [5] except r_e which was calculated from B_e. The value of r_e was reported to be 2.13 Å and 2.11 Å by Beeson and Yost[3] and Cole and Elverum,[6] respectively. Ground state configuration was taken from Herzberg.[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	−9.402	22.087	22.087	INFINITE
100	29.709	204.809	269.641	−6.483	22.153	13.815	−7.216
200	32.987	226.411	243.147	−3.347	21.320	5.776	−1.509
250	34.180	233.907	240.573	−1.666	20.783	1.950	−0.407
298.15	34.990	240.001	240.001	0.	14.644	−0.967	0.169
300	35.015	240.218	240.002	0.065	14.607	−1.063	0.185
350	35.604	245.662	240.430	1.831	−0.811	−2.829	0.422
400	36.029	250.445	241.389	3.622	−0.810	−3.117	0.407
450	36.344	254.708	242.637	5.432	−0.809	−3.405	0.395
500	36.586	258.550	244.039	7.256	−0.808	−3.694	0.386
600	36.927	265.253	247.032	10.932	−0.807	−4.271	0.372
700	37.157	270.964	250.053	14.637	−0.807	−4.848	0.362
800	37.323	275.937	252.984	18.362	−0.809	−5.426	0.354
900	37.452	280.340	255.784	22.101	−0.812	−6.003	0.348
1000	37.557	284.292	258.441	25.851	−0.817	−6.579	0.344
1100	37.646	287.876	260.956	29.612	−0.823	−7.155	0.340
1200	37.724	291.155	263.338	33.380	−0.832	−7 730	0.336
1300	37.793	294.177	265.596	37.156	−0.842	−8.305	0.334
1400	37.858	296.980	267.738	40.939	−0.855	−8.878	0.331
1500	37.918	299.594	269.776	44.727	−0.871	−9.451	0.329
1600	37.974	302.043	271.717	48.522	−0.891	−10.022	0.327
1700	38.028	304.347	273.569	52.322	−0.916	−10.592	0.325
1800	38.081	306.522	275.340	56.128	−0.946	−11.160	0.324
1900	38.131	308.583	277.036	59.938	−0.984	−11.727	0.322
2000	38.180	310.540	278.663	63.754	−1.029	−12.291	0.321
2100	38.229	312.404	280.225	67.574	−1.085	−12.853	0.320
2200	38.276	314.183	281 729	71.400	−1.152	−13.412	0.318
2300	38.323	315.886	283.177	75.230	−1.232	−13.967	0.317
2400	38.369	317.518	284.574	79.064	−1.326	−14.519	0.316
2500	38.414	319.085	285.923	82.903	−1.434	−15.066	0.315
2600	38.460	320.592	287.228	86.747	−1.558	−15.609	0.314
2700	38.504	322.045	288.491	90.595	−1.698	−16.147	0.312
2800	38.549	323.446	289.714	94.448	−1.853	−16.680	0.311
2900	38.593	324.799	290.901	98.305	−2.023	−17.206	0.310
3000	38.637	326.108	292.053	102.166	−2.208	−17.726	0.309
3100	38.681	327.376	293.172	106.032	−2.407	−18.240	0.307
3200	38.724	328.605	294.260	109.903	−2.617	−18.748	0.306
3300	38.768	329.797	295.319	113.777	−2.838	−19.248	0.305
3400	38.811	330.955	296.350	117.656	−3.068	−19.742	0.303
3500	38.854	332.081	297.355	121.539	−3.303	−20.230	0.302
3600	38.897	333.176	298.335	125.427	−3.543	−20.710	0.300
3700	38.940	334.242	299.291	129.319	−3.784	−21.183	0.299
3800	38.983	335.281	300.225	133.215	−4.025	−21.650	0.298
3900	39.026	336.294	301.137	137.115	−4.263	−22.111	0.296
4000	39.068	337.283	302.028	141.020	−4.495	−22.566	0.295
4100	39.111	338.248	302.900	144.929	−4.719	−23.015	0.293
4200	39.154	339.191	303 752	148.842	−4.933	−23.458	0.292
4300	39.196	340.113	304.587	152.760	−5.135	−23.897	0.290
4400	39.239	341.015	305.405	156.682	−5.322	−24.331	0.289
4500	39.281	341.897	306.206	160.608	−5.493	−24.761	0.287
4600	39.323	342.761	306.992	164.538	−5.645	−25.187	0.286
4700	39.366	343.607	307.762	168.472	−5.777	−25.611	0.285
4800	39.408	344.436	308.517	172.411	−5.888	−26.032	0.283
4900	39.450	345.249	309.258	176.354	−5.975	−26.450	0.282
5000	39.492	346.046	309.986	180.301	−6.039	−26.868	0.281
5100	39.535	346.829	310.701	184.252	−6.077	−27.284	0.279
5200	39.577	347.597	311.403	188.208	−6.089	−27.700	0.278
5300	39.619	348.351	312.093	192.168	−6.074	−28.115	0.277
5400	39.661	349.092	312.772	196.132	−6.032	−28.531	0.276
5500	39.703	349.820	313.439	200.100	−5.961	−28.948	0.275
5600	39.745	350.536	314.095	204.072	−5.861	−29.367	0.274
5700	39 788	351.240	314.740	208.049	−5.732	−29.788	0.273
5800	39.830	351 932	315.375	212.030	−5.574	−30.212	0.272
5900	39.872	352 614	316.001	216.015	−5.387	−30.638	0.271
6000	39.914	353.284	316.617	220 004	−5.170	−31.068	0.270

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

$S°(298.15\ K) = 228.967\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -50.815 \pm 1.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -58.463 \pm 1.7\ kJ·mol^{-1}$

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

$\omega_e = 673\ cm^{-1}$ $\omega_e x_e = 4\ cm^{-1}$ $\sigma = 1$
$B_e = 0.356319\ cm^{-1}$ $\alpha_e = 0.005206\ cm^{-1}$ $r_e = 1.7555$ Å

Enthalpy of Formation

The equilibrium constant for the reaction $Br_2(g) + BrF_3(g) = 3BrF(g)$ has been measured over the temperature range 328–380 K by Steunenberg *et al.*[1] 3rd law analysis of the data yields a $\Delta_r H°(298.15\ K) = 11.785 \pm 0.2$ kcal·mol^{-1}, with a drift of -0.6 ± 1.2 cal·K^{-1}·mol^{-1}. 2nd law analysis yields $\Delta_r H°(298.15\ K) = 11.98 \pm 0.45$ kcal mol^{-1}, thus it is obvious that the data is thermodynamically self consistent. There is an uncertainty in the entropy of BrF_3(g) of ± 1 cal·K^{-1}·mol^{-1} but this corresponds only to ± 0.35 kcal·mol^{-1} in $\Delta_r H°(298.15\ K)$, thus a best value of $\Delta_r H°(298\ 15\ K) = 11.78 \pm 0.5$ kcal·mol^{-1} is adopted. This yields $\Delta_f H°$(BrF, g, 298.15 K) = -13.973 ± 0.4 kcal·mol^{-1} (-58.463 ± 1.7 kJ·mol^{-1}), the uncertainty in the enthalpy of formation being a maximum value comprising the sum of the uncertainties in Br_2, BrF_3 and $\Delta_f H°$.

Attempts have been made to analyze the spectra of BrF to obtain a dissociation energy. Brodersen and Sicre,[2] obtained two dissociation limits for BrF of 65.62 kcal·mol^{-1} and 54.98 kcal·mol^{-1}. The difference corresponds to the $Br(^2P_{1/2}) - Br(^2P_{3/2})$ excitation energy, indicating that the upper state goes to $F(^2P_{3/2})$ and $Br(^2P_{1/2})$. This yields an enthalpy of formation of BrF of -10.23 kcal·mol^{-1} Since this value is well outside the possible uncertainty limits of the equilibrium data we must conclude that the extrapolation is in error Evans *et al.*[3] have also analyzed the spectra and conclude that an enthalpy of formation of -14.4 kcal·mol^{-1} is possible. However, Evans[4] now believes that the dissociating state was too strongly perturbed for meaningful extrapolation.

Heat Capacity and Entropy

All molecular constants were obtained from Evans *et al.*,[3] except r_e and the ground state configuration which were taken from Herzberg.[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	−9.019	−50.815	−50.815	INFINITE
100	29.162	195.677	256.772	−6.109	−50.755	−59.112	30.877
200	30.760	216.261	231.914	−3.131	−51.692	−67.137	17.534
250	31.940	223.252	229.504	−1.563	−52.283	−70.931	14.820
298.15	32.956	228.967	228.967	0.	−58.463	−73.809	12.931
300	32.991	229.171	228.968	0.061	−58.501	−73.904	12.868
350	33.852	234.324	229.373	1.733	−73.949	−75.622	11.286
400	34.537	238.891	230.283	3.443	−73.968	−75.859	9.906
450	35.080	242.991	231.471	5.184	−73.982	−76.095	8.833
500	35.513	246.710	232.812	6.949	−73.991	−76.329	7.974
600	36.148	253.245	235.688	10.535	−74.002	−76.796	6.686
700	36.584	258.852	238.606	14.172	−74.009	−77.261	5.765
800	36.900	263.759	241.450	17.847	−74.015	−77.725	5.075
900	37.140	268.119	244.175	21.550	−74.022	−78.188	4.538
1000	37.330	272.043	246.769	25.274	−74.030	−78.651	4.108
1100	37.487	275.608	249.231	29.015	−74.041	−79.112	3.757
1200	37.620	278.876	251.567	32.770	−74.054	−79.573	3.464
1300	37.736	281.892	253.785	36.538	−74.071	−80.032	3.216
1400	37.840	284.692	255.894	40.317	−74.092	−80.490	3.003
1500	37.934	287.306	257.902	44.106	−74.118	−80.946	2.819
1600	38.021	289.757	259.817	47.903	−74.149	−81.400	2.657
1700	38.102	292.064	261.647	51.710	−74.186	−81.852	2.515
1800	38.179	294.244	263.398	55.524	−74.229	−82.302	2.388
1900	38.252	296.311	265.076	59.345	−74.278	−82.749	2.275
2000	38.323	298.275	266.688	63.174	−74.332	−83.193	2.173
2100	38.391	300.146	268.237	67.010	−74.392	−83.635	2.080
2200	38.457	301.933	269.728	70.852	−74.457	−84.073	1.996
2300	38.522	303.644	271.166	74.701	−74.524	−84.509	1.919
2400	38.585	305.285	272.553	78.556	−74.595	−84.942	1.849
2500	38.647	306.862	273.894	82.418	−74 665	−85.371	1.784
2600	38.708	308.379	275.192	86.286	−74 735	−85.798	1.724
2700	38.769	309.841	276.448	90.160	−74.802	−86.222	1.668
2800	38.828	311.252	277.666	94.040	−74.865	−86.644	1.616
2900	38.887	312.615	278.848	97.925	−74.920	−87.064	1.568
3000	38.946	313.934	279.995	101.817	−74.967	−87.482	1.523
3100	39.003	315.212	281.111	105.714	−75.003	−87.898	1.481
3200	39.061	316.452	282.196	109.618	−75.025	−88.314	1.442
3300	39 118	317.654	283.252	113.527	−75.033	−88.729	1.404
3400	39.175	318.823	284.282	117.441	−75.023	−89.144	1.370
3500	39.232	319.960	285.285	121.362	−74.995	−89.560	1.337
3600	39.288	321.065	286.263	125.288	−74.946	−89.977	1.306
3700	39.344	322.143	287.219	129.219	−74.875	−90.395	1.276
3800	39.400	323.193	288.152	133.156	−74.781	−90.816	1.248
3900	39.455	324.217	289.063	137.099	−74.662	−91.239	1.222
4000	39.511	325.216	289.955	141.047	−74.517	−91.666	1.197
4100	39.566	326.193	290.827	145.001	−74.345	−92.097	1.173
4200	39.622	327.147	291.680	148.961	−74.145	−92.532	1.151
4300	39.677	328.080	292.516	152.926	−73.917	−92.973	1.129
4400	39 732	328.993	293.334	156.896	−73.660	−93.419	1.109
4500	39.786	329.886	294.137	160.872	−73.374	−93.871	1.090
4600	39.841	330.761	294.923	164.853	−73.058	−94.330	1.071
4700	39.896	331.619	295.695	168.840	−72.712	−94.796	1.054
4800	39.951	332.459	296.452	172.832	−72.336	−95.270	1.037
4900	40.005	333.283	297.196	176.830	−71.930	−95.752	1.021
5000	40.060	334.092	297.925	180.833	−71.494	−96.242	1.005
5100	40.114	334.886	298.642	184.842	−71.029	−96.742	0.991
5200	40.168	335.665	299.347	188.856	−70.533	−97.251	0.977
5300	40.223	336.431	300.039	192.876	−70.008	−97.769	0.964
5400	40.277	337.183	300.720	196.901	−69.454	−98.298	0.951
5500	40.331	337.923	301.390	200.931	−68.871	−98.838	0.939
5600	40.385	338.650	302.049	204.967	−68.260	−99.388	0.927
5700	40.439	339.365	302.697	209.008	−67.621	−99.950	0.916
5800	40.494	340.069	303.336	213.055	−66.955	−100.523	0.905
5900	40.548	340.762	303.964	217.107	−66.261	−101.107	0.895
6000	40.602	341.444	304.583	221.164	−65.541	−101.704	0.885

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

$S°(298.15\ K) = 292.397\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -244.37 \pm 2.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -255.59 \pm 2.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
674 (1)	613 (1)
[528](1)	[384](1)
[300](1)	[289](1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: $Br–F_1 = Br–F_3 = 1.8061Å$; $Br–F_2 = 1.721Å$
Bond Angles: $F_1–Br–F_2 = 86°12.6'$; $F_2–Br–F_3 = 86°12.6'$; $F_3–Br–F_1 = 187°4.8'$
Product of the Moment of Inertia: $I_A I_B I_C = 4.48703 \times 10^{-114}\ g^3·cm^6$

Enthalpy for Formation

$\Delta_f H°(298.15\ K) = -255.588 \pm 2.9\ kJ·mol^{-1}$ is from Stein[1] and was derived from enthaply of reaction of F_2 with Br_2 which were measured in an adiabatic calorimeter. Stein's value for the $\Delta_f H°(298.15\ K) = -271.040\ kJ\ mol^{-1}$ was based upon gaseous Br_2, which has been adjusted to the liquid Br_2 reference state at 298.15 K.

Heat Capacity and Entropy

Magnuson[2] determined the moments of inertia and quadrupole coupling coefficients of both $^{79}BrF_3$ and $^{81}BrF_3$ from a number f microwave transitions. From the moment of inertia the bromine trifluoride molecule was found to have a distorted "T" structure with one short, 1.721 Å, and two long, 1.810 Å Br–F bonds. The FBrF angle was found to be 86°12.6'.

Claasen *et al.*,[3] observed two of the six vibrational levels in the vapor, and calculated the other four levels from a normal coordinate treatment of the molecule. They also obtained a measured entropy of BrF_3(g), from low temperature data combined with vapor pressure data and an approximate correction for dimerization. This value is $300.9\ J·K^{-1}·mol^{-1}$ at 316.27 K compared with a value of $296.42\ J·K^{-1}·mol^{-1}$ from this table, the difference is probably within the uncertainty of the data. The principal moments of inertia are: $I_A = 7.7525 \times 10^{-39}$, $I_B = 20.4920 \times 10^{-39}$, and $I_C = 28.2445 \times 10^{-39}\ g·cm^2$.

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	−14.275	−244.370	−244.370	INFINITE
100	39.106	235.530	343.752	−10.822	−246.675	−241.980	126.398
200	55.795	267.920	298.179	−6.052	−248.749	−236.395	61.740
250	62.017	281.071	293.468	−3.099	−249.458	−233.222	48.729
298.15	66.497	292.397	292.397	0.	−255.588	−229.383	40.187
300	66.644	292.808	292.398	0.123	−255.622	−229.221	39.911
350	70.048	303.351	293.223	3.545	−270.908	−223.983	33.428
400	72.571	312.877	295.094	7.113	−270.700	−217.293	28.376
450	74.468	321.539	297.558	10.791	−270.444	−210.632	24.450
500	75.918	329.464	300.358	14.553	−270.155	−204.002	21.312
600	77.935	343.498	306.409	22.253	−269.525	−190.829	16.613
700	79.228	355.616	312.593	30.116	−268.859	−177.765	13.265
800	80.100	366.255	318.649	38.085	−268.180	−164.798	10.760
900	80.713	375.727	324.475	46.127	−267.501	−151.916	8.817
1000	81.160	384.256	330.034	54.222	−266.828	−139.110	7.266
1100	81.495	392.007	335.321	62.355	−266.166	−126.370	6.001
1200	81.752	399.110	340.345	70.518	−265.518	−113.690	4.949
1300	81.954	405.662	345.120	78.704	−264.887	−101.063	4.061
1400	82.115	411.741	349.664	86.908	−264.274	−88.485	3.301
1500	82.246	417.411	353.994	95.126	−263.680	−75.949	2.645
1600	82.353	422.723	358.125	103.356	−263.108	−63.453	2.072
1700	82.443	427.718	362.073	111.596	−262.557	−50.991	1.567
1800	82.518	432.433	365.853	119.844	−262.025	−38.561	1.119
1900	82.581	436.896	369.475	128.099	−261.512	−26.161	0.719
2000	82.636	441.133	372.953	136.360	−261.016	−13.787	0.360
2100	82.683	445.166	376.297	144.626	−260.533	−1.438	0.036
2200	82.723	449.014	379.515	152.897	−260.058	10.889	−0.259
2300	82.759	452.692	382.617	161.171	−259.589	23.195	−0.527
2400	82.790	456.214	385.611	169.448	−259.121	35.480	−0.772
2500	82.818	459.595	388.503	177.729	−258.647	47.745	−0.998
2600	82.842	462.843	391.300	186.012	−258.164	59.991	−1.205
2700	82.864	465.970	394.008	194.297	−257.666	72.218	−1.397
2800	82.884	468.984	396.633	202.584	−257.149	84.427	−1.575
2900	82.901	471.893	399.178	210.874	−256.606	96.617	−1.740
3000	82.917	474.704	401.649	219.165	−256.035	108.787	−1.894
3100	82.931	477.423	404.050	227.457	−255.430	120.937	−2.038
3200	82.944	480.056	406.384	235.751	−254.788	133.068	−2.172
3300	82.956	482.609	408.655	244.046	−254.105	145.179	−2.298
3400	82.967	485.085	410.867	252.342	−253.379	157.267	−2.416
3500	82.977	487.490	413.022	260.639	−252.605	169.334	−2.527
3600	82.986	489.828	415.123	268.937	−251 783	181.378	−2.632
3700	82.995	492.102	417.173	277.236	−250.909	193.398	−2.730
3800	83.002	494.315	419.174	285.536	−249.983	205.394	−2.823
3900	83.010	496.471	421.129	293.837	−249.002	217.365	−2.911
4000	83.016	498.573	423.039	302.138	−247.966	229.310	−2.994
4100	83.022	500.623	424.906	310.440	−246.875	241.229	−3.073
4200	83.028	502.624	426.733	318.743	−245.727	253.120	−3.148
4300	83.033	504.578	428.520	327.046	−244.522	264.983	−3.219
4400	83.038	506.487	430.271	335.349	−243.261	276.817	−3.286
4500	83.043	508.353	431.985	343.653	−241.943	288.623	−3.350
4600	83.047	510.178	433.665	351.958	−240.569	300.398	−3.411
4700	83.051	511.964	435.312	360.263	−239.139	312.143	−3.469
4800	83.055	513.713	436.928	368.568	−237.654	323.857	−3.524
4900	83.059	515.425	438.512	376.874	−236.115	335.539	−3.577
5000	83.062	517.103	440.067	385.180	−234.522	347.189	−3.627
5100	83.065	518.748	441.594	393.486	−232.877	358.807	−3.675
5200	83.068	520.361	443.093	401.793	−231.180	370.393	−3.721
5300	83.071	521.943	444.566	410.100	−229.433	381.945	−3.764
5400	83.074	523.496	446.013	418.407	−227.636	393.464	−3.806
5500	83.076	525.021	447.436	426.715	−225.790	404.948	−3.846
5600	83.079	526.517	448.835	435.023	−223.898	416.399	−3.884
5700	83.081	527.988	450.211	443.331	−221.959	427.816	−3.920
5800	83.083	529.433	451.564	451.639	−219.975	439.198	−3.955
5900	83.085	530.853	452.896	459.947	−217.948	450.546	−3.989
6000	83.087	532.250	454.207	468.256	−215.878	461.859	−4.021

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

$S°(298.15\ K) = 323.682\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -413.58 \pm 2.1\ kJ·mol^{-1}$
$(298.15\ K) = -428.72 \pm 2.1\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
683 (1)	535 (1)	644 (2)
587 (1)	[281](1)	415 (2)
369 (1)	312 (1)	245 (2)

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: C_{4v}
Bond Distances: Br–F = 1.79 Å; Br–F* = 1.68 Å
Bond Angles: F–Br–F = [90]° and F*–Br–F = [90]°
(* axial)
Product of the Moments of Inertia: $I_A I_B I_C = 3.20483 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K) = -428.718 \pm 2.1\ kJ\ mol^{-1}$ is from Stein[1] and was derived from enthalpies of reaction of F_2 with Br_2 which were measured in an adiabatic calorimeter. Stein's value for the $\Delta_f H°(298.15\ K) = -444.17\ kJ·mol^{-1}$ was based upon gaseous Br_2 which has been adjusted to the liquid Br_2 reference state at 298.15 K.

Heat Capacity and Entropy

Begun *et al.*[2] report the infrared (gas phase) and Raman (liquid phase) spectra and correlate the observations by means of normal coordinate calculations for the similar molecules BrF_5, IF_5, ClF_5 and $XeOF_4$. The fundamental frequencies are taken from Begun *et al.*[2] except for υ_9 which was beyond the range of their infrared measurements. The value $\upsilon_9 = 245\ cm^{-1}$ for the gas has been observed by McDowell and Asprey[3] and is confirmed by 237 cm^{-1} found in the Raman spectra of the liquid. Raman values from the liquid were used for the infrared inactive fundamentals υ_4 and υ_6. One Raman active frequency, persumably , υ_5 is not observed in any of the four molecules. The value $\upsilon_5 = 281\ cm^{-1}$ was obtained from the normal coordinate calculation. Previous Raman studies were reported by Stephenson and Jones.[4]

A tetragonal pyramidal structure (C_{4v} symmetry) with the above parameters was used by Begun *et al.*[2] in the analysis of the spectra. This symmetry is consistent with the NMR spectra of Gutowsky and Hoffman,[5] with the dipole moment determined by Rogers *et al.*,[6] and with the X-ray crystal structure obtained by Robinson and Bensey.[7] Bond distances were based on those in the crystal and the bond angle was assumed to be 90°, slightly larger than those in the crystal (80.5–86.5°) Begun *et al.*[2] indicate that the angle in the gaseous molecule is probably not exactly 90° but that the normal coordinate calculations are not sensitive to this angle The three principal moments of inertia are $I_A = 40.4333 \times 10^{-39}$ and $I_B = I_C = 28.1536 \times 10^{-39}\ g·cm^2$.

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−19.180	−413.581	−413.581	INFINITE
100	47.334	243 616	398.823	−15.521	−418.586	−397.662	207 717
200	80.797	287.176	332.382	−9.041	−421.879	−375.246	98.004
250	92.816	306.562	325.307	−4.686	−422.688	−363.487	75.946
298.15	101.404	323.682	323.682	0.	−428.718	−351.379	61.560
300	101.685	324.310	323.684	0.188	−428 745	−350.899	61.097
350	108.182	340.499	324 948	5.443	−443.787	−337.105	50.310
400	112.985	355.274	327.829	10.978	−443.243	−321.901	42.036
450	116.590	368.799	331.640	16.721	−442.588	−306.771	35.609
500	119.343	381.232	335.986	22.623	−441.858	−291 719	30.476
600	123.169	403.356	345.417	34.763	−440.261	−261.839	22.795
700	125.618	422.540	355.095	47.211	−438.561	−232.235	17.330
800	127.270	439.429	364.603	59.861	−436.812	−202.879	13.247
900	128.431	454.490	373.768	72.649	−435.041	−173 744	10 084
1000	129.277	468.067	382.531	85.537	−433.265	−144.806	7.564
1100	129.911	480.420	390.877	98.497	−431.496	−116.046	5.511
1200	130.398	491.745	398.817	111.514	−429.740	−87.447	3.806
1300	130.780	502.198	406.373	124.573	−428.004	−58.993	2.370
1400	131.085	511.902	413.568	137.667	−426.291	−30.672	1.144
1500	131.332	520.954	420.429	150.789	−424.606	−2.472	0.086
1600	131.535	529.437	426.979	163.932	−422.948	25.616	−0.836
1700	131 704	537.416	433.243	177.094	−421.320	53.601	−1.647
1800	131.846	544.949	439.242	190.272	−419 719	81.491	−2.365
1900	131 966	552.080	444.995	203.463	−418.142	109.293	−3.005
2000	132.069	558.852	450.520	216.665	−416.586	137 013	−3.578
2100	132 158	565.298	455.833	229.876	−415.044	164.654	−4.096
2200	132.235	571 448	460.950	243.096	−413.510	192.223	−4.564
2300	132.302	577.327	465.883	256.323	−411 976	219.723	−4.990
2400	132.361	582 959	470.644	269.556	−410.435	247.155	−5.379
2500	132.413	588.364	475.246	282.795	−408.878	274.522	−5.736
2600	132.460	593.558	479.697	296.038	−407.297	301.827	−6.064
2700	132.501	598.558	484.007	309.287	−405.682	329.071	−6.366
2800	132.538	603.377	488.185	322.539	−404.028	356.253	−6.646
2900	132.571	608 029	492.238	335.794	−402.325	383 377	−6 905
3000	132 601	612.524	496.173	349.053	−400.567	410.440	−7.146
3100	132.628	616.872	499.997	362.314	−398.748	437 443	−7.371
3200	132 653	621.083	503.715	375.578	−396 861	464.387	−7.580
3300	132.676	625 166	507.334	388.845	−394.903	491.271	−7 776
3400	132.696	629 127	510.858	402.113	−392.868	518.095	−7.960
3500	132 715	632 973	514.292	415.384	−390.753	544.857	−8.132
3600	132.732	636 712	517.641	428.656	−388.555	571.559	−8.293
3700	132.748	640.349	520 909	441 930	−386.271	598.197	−8.445
3800	132.763	643.890	524.099	455.206	−383.900	624.772	−8.588
3900	132.776	647.338	527.215	468.483	−381.439	651.285	−8 723
4000	132.789	650 700	530.260	481.761	−378.889	677.733	−8.850
4100	132 800	653.979	533.238	495.040	−376.248	704.115	−8 971
4200	132.811	657 180	536.151	508.321	−373.516	730.433	−9.084
4300	132.821	660.305	539.002	521.603	−370.695	756.684	−9.192
4400	132 831	663.358	541.794	534.885	−367.783	782.869	−9.294
4500	132.839	666.344	544.528	548.169	−364.782	808.987	−9.390
4600	132.848	669.263	547.208	561.453	−361.693	835.036	−9.482
4700	132.855	672 120	549.836	574.738	−358.518	861.018	−9.569
4800	132.862	674 918	552.413	588.024	−355.256	886.932	−9.652
4900	132.869	677.657	554 941	601.311	−351.911	912.776	−9.730
5000	132.876	680.342	557.422	614.598	−348.483	938.551	−9.805
5100	132.882	682.973	559.858	627.886	−344.975	964.257	−9.876
5200	132 887	685.553	562.250	641.174	−341.387	989.894	−9.944
5300	132.893	688.085	564.601	654.463	−337.723	1015.461	−10.008
5400	132.898	690.569	566.911	667.753	−333.983	1040.957	−10.069
5500	132.902	693.007	569.181	681.043	−330.169	1066.383	−10.128
5600	132.907	695.402	571 414	694.333	−326.285	1091.741	−10.183
5700	132.911	697.754	573.610	707.624	−322.330	1117.027	−10.236
5800	132.915	700 066	575.770	720.916	−318.308	1142.243	−10.287
5900	132.919	702.338	577.896	734.207	−314.220	1167.392	−10.335
6000	132.923	704.572	579.989	747.499	−310.068	1192.468	−10.381

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

$S°(298.15\ K) = [333.648 \pm 2.1]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-953.5 \pm 59]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-972.8 \pm 59]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
848 (1)	621 (1)	580 (2)
694 (1)	[325](1)	423 (2)
597 (1)	502 (1)	225 (2)
279 (1)	892 (2)	

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: C_{4v}
Bond Distances: S–F = 1.597 Å; S-Br = 2.1902 Å
Bond Angles: Br–S–F* = [92°]; F*-S-F* = 90°
(* equatorial)
Product of Moments of Inertia: $I_A I_B I_C = [1.66563 \times 10^{-112}]\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(BrSF_5, g, 0\ K) = -953.529 \pm 59\ kJ·mol^{-1}$ is calculated from a S–Br bond energy of $173.0 \pm 42\ kJ·mol^{-1}$ by combining $D_0°$ with JANAF enthalpies of formation[1] for SF_5 and Br. We estimate the strength of the S–Br bond in $BrSF_5$ from bond energy correlations. In the case of related sulfur chlorine molecules, we calculate that the ratio of the S–Cl bond strength in $ClSF_5$[1] is 1.1 times the mean S–Cl bond energy in $SOCl_2$.[2] Assuming that this relationship holds for $BrSF_5$ and $SOBr_2$, we obtain the adopted value for $D_0°(SF_5–Br)$ from $D_0°(SOBr–Br)$, 157.3 $kJ·mol^{-1}$.

The enthalpy of atomization and mean S–F bond energy are calculated to be $1730.5 \pm 67\ kJ·mol^{-1}$ and $311.3\ kJ·mol^{-1}$, respectively. The latter value is identical with that found for $ClSF_5$, indicating that the sulfur fluorine bonding is very similar in these two molecules. This conclusion is supported by spectroscopic data.[1,3,4]

Heat Capacity and Entropy

Microwave[3] and vibrational spectroscopic[4] measurements indicate that $BrSF_5$ is a symmetrical top molecule possessing C_{4v} symmetry. We adopt the structural parameters proposed by Neuvar and Jache[3] from an analysis of the observed rotational spectrum The adopted bond lengths were calculated assuming that the Br–S–F* bond angle was 92° which was estimated from the value (91.6°) for the Cl–S–F* angle in $ClSF_5$ reported by Kewley *et al.*[5] A more plausible value for the Cl–S–F* angle is 90.7 ± 0.2,[1] indicating that the bond lengths reported by Neuvar and Jache[3] may be slightly biased. We place the values of $S°(298.15\ K)$ and $I_A I_B I_C$ in brackets to emphasize this uncertainty.

The vibrational frequencies are based on the infrared and laser-excited Raman spectra of $BrSF_5$ recorded under matrix (argon) isolation conditions by Smardzewski *et al.*[4] We adjust their reported frequencies for a matrix effect which is estimated as 5 cm^{-1} from gas phase[1] and argon–matrix[4] spectral data for $ClSF_5$. Evidence available for ClS_5[1] indicates that $\nu_6 = 220\ cm^{-1}$ by Smardzewski *et al.*[4] should be reassigned. We believe that this Raman band is the low frequency mode (S–Br wag) and that ν_6 has not been resolved. We estimate $\nu_6 = 325\ cm^{-1}$ from the force-field value for $ClSF_5$.[1]

The principal moments of inertia are: $I_A = 32.1450 \times 10^{-39}\ g\ cm^2$ and $I_B = I_C = 71.9835 \times 10^{-39}\ g·cm^2$.

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	−19.433	−953.526	−953.526	INFINITE
100	47.160	252.860	410.417	−15.756	−959.203	−937.951	489.936
200	81.206	296.049	342.686	−9.327	−964.189	−914.603	238.870
250	95.727	315.781	335.351	−4.893	−965.938	−901.996	188.462
298.15	107.073	333.648	333.648	0.	−972.822	−888.897	155.731
300	107.459	334.312	333.650	0.198	−972.880	−888.376	154.680
350	116.682	351.599	334.995	5.811	−988.731	−873.408	130.349
400	123.876	367.669	338.087	11.833	−991.131	−856.830	111.891
450	129.504	382.598	342.213	18.173	−991.805	−840.009	97.506
500	133.940	396.481	346.954	24.763	−992.388	−823.108	85.990
600	140.315	421.507	357.341	38.499	−992.781	−789.203	68.706
700	144.531	443.474	368.109	52.755	−992.620	−755.280	56.360
800	147.434	462.974	378.772	67.362	−992.125	−721.405	47.103
900	149.507	480.466	389.116	82.215	−1044.546	−686.525	39.845
1000	151.033	496.301	399.055	97.245	−1042.483	−646.855	33.788
1100	152.186	510.752	408.562	112.409	−1040.383	−607.393	28.843
1200	153.077	524.034	417.639	127.674	−1038.265	−568.124	24.730
1300	153.779	536.315	426.302	143.018	−1036.147	−529.031	21.257
1400	154.341	547.733	434.572	158.425	−1034.040	−490.102	18.286
1500	154.798	558.397	442.476	173.882	−1031.951	−451.322	15.716
1600	155.175	568.400	450.037	189.382	−1029.886	−412.681	13.473
1700	155.488	577.817	457.279	204.915	−1027.849	−374.168	11.497
1800	155.753	586.713	464.225	220.478	−1025.840	−335.774	9 744
1900	155.977	595.140	470.895	236.065	−1023.857	−297.492	8.179
2000	156.169	603 145	477.309	251.672	−1021.896	−259.312	6.773
2100	156.335	610.769	483.485	267.297	−1019.953	−221.232	5.503
2200	156.479	618.045	489.437	282.938	−1018.020	−183.243	4.351
2300	156.605	625.004	495.181	298.593	−1016.091	−145.341	3.301
2400	156.715	631.671	500.730	314.259	−1014.158	−107.524	2.340
2500	156.813	638.071	506.096	329.935	−1012.212	−69.787	1.458
2600	156.900	644.223	511.291	345.621	−1010.244	−32.129	0.645
2700	156.977	650.146	516.325	361.315	−1008.246	5.453	−0.105
2800	157.047	655.856	521.207	377.016	−1006.210	42.960	−0.801
2900	157.109	661.368	525.946	392.724	−1004.128	80.394	−1.448
3000	157.166	666.695	530.549	408.438	−1001.994	117.755	−2.050
3100	157.217	671.849	535.024	424.157	−999.800	155.044	−2.612
3200	157.263	676.841	539.379	439.881	−997.541	192.261	−3.138
3300	157.305	681.681	543.618	455.609	−995.213	229.407	−3.631
3400	157.344	686.378	547.748	471.342	−992.810	266.480	−4 094
3500	157.379	690.940	551.774	487.078	−990.330	303.482	−4.529
3600	157.412	695.373	555.702	502.818	−987.769	340.413	−4.939
3700	157.441	699.687	559.535	518.560	−985.125	377.271	−5.326
3800	157 469	703.886	563.279	534.306	−982.397	414.055	−5.692
3900	157.494	707.977	566.937	550.054	−979.582	450.768	−6.037
4000	157.518	711.964	570.513	565.805	−976.681	487.407	−6.365
4100	157.540	715.854	574.011	581.558	−973.693	523.972	−6.675
4200	157.560	719.651	577.433	597.313	−970.618	560.464	−6.970
4300	157.579	723.358	580.784	613.070	−967.457	596.880	−7.251
4400	157.597	726.981	584.066	628.828	−964.211	633.223	−7.517
4500	157.613	730.523	587.281	644.589	−960.880	669.491	−7.771
4600	157.629	733.987	590.433	660.351	−957.467	705.684	−8.013
4700	157.643	737.378	593.523	676.115	−953.971	741.802	−8.244
4800	157.657	740.697	596.555	691.880	−950.396	777.845	−8.465
4900	157.670	743.948	599.530	707.646	−946.742	813.812	−8.675
5000	157.682	747.133	602.450	723.414	−943.011	849.704	−8.877
5100	157.693	750.256	605.318	739.182	−939.207	885.521	−9.070
5200	157.704	753.318	608.135	754.952	−935.329	921.262	−9.254
5300	157.714	756.322	610.902	770.723	−931.381	956.928	−9.431
5400	157.723	759.270	613.623	786 495	−927.364	992.519	−9.601
5500	157.732	762.164	616.297	802.268	−923.280	1028.034	−9.763
5600	157.741	765.006	618.928	818.041	−919.132	1063.476	−9.920
5700	157.749	767.798	621.515	833.816	−914.922	1098.842	−10.070
5800	157.757	770.542	624.061	849.591	−910.650	1134.133	−10.214
5900	157.764	773.239	626.566	865.367	−906.320	1169.352	−10.353
6000	157.771	775.890	629.033	881.144	−901.933	1204.496	−10.486

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

$S°(298.15\ K) = 198.699 \pm 0.033\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -28.60 \pm 0.25\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -36.44 \pm 0.17\ kJ·mol^{-1}$

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

$\omega_e = 2649.1816 \pm 0.007\ cm^{-1}$ $\omega_e x_e = 45.2245 \pm 0.003\ cm^{-1}$ $\sigma = 1$
$B_e = 8.466203 \pm 0.000025\ cm^{-1}$ $\alpha_e = 0.233332 \pm 0.00004\ cm^{-1}$ $r_e = 1.414435$ Å

Enthaply of Formation

For HBr(g), CODATA[1] recommended the key value $\Delta_f H°(298.15\ K) = -36.38 \pm 0.17\ kJ·mol^{-1}$ which is adopted. References 2–9 were cited by CODATA.

Heat Capacity and Entropy

The values of ω_e, $\omega_e x_e$, B_e, and α_e are taken from Rank *et al.*[10] after correction to the averge isotopic species. See also James and Thibault,[11] Jones and Gordy,[12] Plyler,[13] and Mould *et al.*[14] The ground state configuration is from Huber and Herzberg[15] where molecular constants for *HBr(g) are also given.*

Our evaluations lead to $S°(298.15\ K) = 198.589\ J·K^{-1}·mol^{-1}$ in agreement with the CODATA recommended value[1] of $198.585 \pm 0.033\ J·K^{-1}·mol^{-1}$, both values based on a reference pressure of one atm. The value adopted, $S°(298.15\ K) = 198.694 \pm 0.033\ J·K^{-1}·mol^{-1}$, is the CODATA value corrected, by $0.109\ J·K^{-1}·mol^{-1}$, to a reference pressure of one bar.

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
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−8.648	−28.603	−28.603	INFINITE
100	29.115	166.884	224.595	−5.771	−28.622	−37.581	19.630
200	29.124	187.067	201.363	−2.859	−29.507	−46.237	12.076
250	29.130	193.567	199.178	−1.403	−30.157	−50.348	10.520
298.15	29.141	198.699	198.699	0.	−36.443	−53.513	9.375
300	*29.141*	*198.879*	*198.699*	0.054	−36.485	−53.619	9.336
350	29.167	203.373	199.054	1.512	−52.077	−55.615	8.300
400	29.220	207.270	199.843	2.971	−52.261	−56.108	7.327
450	29.313	210.717	200.863	4.434	−52.449	−56.577	6.567
500	29.453	213.812	202.006	5.903	−52.636	−57.026	5.957
600	29.870	219.216	204.437	8.868	−52.996	−57.869	5.038
700	30.427	223.861	206.887	11.882	−53.320	−58.655	4.377
800	31.055	227.965	209.270	14.956	−53.599	−59.398	3.878
900	31.698	231.660	211.556	18.093	−53.830	−60.109	3.489
1000	32.319	235.032	213.737	21.294	−54.018	−60.796	3.176
1100	32.897	238.140	215.816	24.556	−54.168	−61.466	2.919
1200	33.425	241.025	217.798	27.872	−54.287	−62.124	2.704
1300	33.902	243.720	219.690	31.239	−54.381	−62.773	2.522
1400	34.329	246.248	221.497	34.651	−54.455	−63.416	2.366
1500	34.711	248.630	223.228	38.103	−54.517	−64.054	2.231
1600	35.053	250.881	224.886	41.592	−54.568	−64.688	2.112
1700	35.360	253.015	226.479	45.113	−54.614	−65.319	2.007
1800	35.635	255.044	228.010	48.663	−54.658	−65.947	1.914
1900	35.884	256.978	229.484	52.239	−54.703	−66.573	1.830
2000	36.109	258.824	230.905	55.838	−54.751	−67.196	1.755
2100	36.313	260.591	*232.277*	*59.460*	*−54.805*	*−67.817*	1.687
2200	36.500	262.285	233.603	63.101	−54.865	−68.436	1.625
2300	36.672	263.911	234.885	66.759	−54.935	−69.051	1.568
2400	36.830	265.475	236.128	70.434	−55.014	−69.663	1.516
2500	36.976	266.982	237.332	74.125	−55.104	−70.272	1.468
2600	37.111	268.435	238.500	77.829	−55.205	−70.877	1.424
2700	37.238	269.838	239.635	81.547	−55.317	−71.477	1.383
2800	37.357	271.194	240.738	85.277	−55.440	−72.074	1.345
2900	37.468	272.507	241.811	89.018	−55.574	−72.665	1.309
3000	37.573	273.779	242.856	92.770	−55.719	−73.252	1.275
3100	37.673	275.013	243.873	96.532	−55.872	−73.834	1.244
3200	37.767	276.210	244.865	100.304	−56.034	−74.411	1.215
3300	37.857	277.374	245.833	104.086	−56.203	−74.983	1.187
3400	37.943	278.505	246.777	107.876	−56.378	−75.549	1.161
3500	38.025	279.606	247.699	111.674	−56.558	−76.110	1.136
3600	38.104	280.678	248.601	115.481	−56.742	−76.666	1.112
3700	38.181	281.724	249.482	119.295	−56.928	−77.217	1.090
3800	*38.254*	*282.743*	*250.344*	*123.117*	−57.116	−77.763	1.069
3900	38.325	283.737	251.187	126.946	−57.304	−78.304	1.049
4000	38.394	284.709	252.013	130.782	−57.492	−78.840	1.030
4100	38.461	285.657	252.822	134.624	−57.677	−79.372	1.011
4200	38.526	286.585	253.615	138.474	−57.860	−79.898	0.994
4300	38.589	287.492	254.392	142.329	−58.039	−80.421	0.977
4400	38.651	288.380	255.155	146.191	−58.214	−80.940	0.961
4500	38.711	289.249	255.903	150.059	−58.384	−81.454	0.945
4600	38.770	290.101	256.637	153.934	−58.548	−81.965	0.931
4700	38.828	290.935	257.358	157.814	−58.705	−82.472	0.917
4800	38.885	291.753	258.066	161.699	−58.856	−82.976	0.903
4900	38.941	292.556	258.762	165.591	−58.999	−83.478	0.890
5000	38.996	293.343	259.446	169.487	−59.134	−83.975	0.877
5100	39.050	294.116	260.118	173.390	−59.260	−84.471	0.865
5200	39.103	294.875	260.779	177.297	−59.378	−84.964	0.853
5300	39.155	295.620	261.429	181.210	−59.487	−85.455	0.842
5400	39.207	296.352	262.069	185.128	−59.585	−85.944	0.831
5500	39.258	297.072	262.699	189.052	−59.675	−86.432	0.821
5600	39.309	297.780	263.319	192.980	−59.753	−86.917	0.811
5700	39.359	298.476	263.930	196.913	−59.822	−87.402	0.801
5800	39.408	299.161	264.531	200.852	−59.879	−87.885	0.791
5900	39.457	299.835	265.124	204.795	−59.925	−88.368	0.782
6000	39.506	300.499	265.708	208.743	−59.960	−88.850	0.774

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

$S°(298.15\ K) = 262.47 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-61.84 \pm 17]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-78.24 \pm 17]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2200 (I)	2209.2(2)
930.3 (I)	946.3(2)
430.6 (I)	632.6(2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: Si–H = 1.486 ± 0.008 Å; Si–Br = 2.210 Å
Bond Angles: H–Si–H = 110.42° ± 0.5°; H–Si–Br = 108.5° ± 0.5°
Product of the Moments of Inertia: $I_A I_B I_C = 3.79963 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy for Formation

$\Delta_f H°(298.15\ K)$ is estimated by linear interpolation between the values[1] of $SiBr_4$(g) and SiH_4(g) The only experimental value for $SiHBr_3$(g) appears to be too uncertain to justify a nonlinear interpolation such as that adopted for SiH_3Cl.[1] ormally we would seek a comparison with $\Delta_f H°$ values of CH_nBr_{4-n}. These were recently reviewed by Kudchadker and Kudchadker.[2] They adopted a cubic variation of $\Delta_f H°$ with n, based on $\Delta_f H°$ values of $CHBr_3$ and CBr_4 selected by Wagman *et al.*[3] We presume that Wagman's values are calculated rather than experimental. Uncertainty in these values[4–6] precludes their use as a comparison for SiH_nBr_{4-n}. We conclude, as did Hunt and Sirtl,[15] that the available data justify only linear interpolation of $\Delta_f H°$.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Kewley *et al.*[7] 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 structural determinations.[8] The principal moments of inertia are $I_A = 0.9971 \times 10^{-39}$ and $I_B = I_C = 19.5210 \times 10^{-39}\ g \cdot cm^2$.

Vibrational frequencies are from gas–phase infrared spectra[9] measured with a grating spectrometer by Buerger *et al* [9] Assignments were based on analysis of band contours and rotational fine structure. These results supersede Shimanouchi's selected frequencies[10] which derive from lower resolution spectra. The new data agree with unpublished data cited by Ball *et al.*[11]

We neglect excited states and assume the electronic ground state to be $^1A_1$ by analogy with CH_3Br.[12] SiH_3Br has several high–lying electronic absorptions and a diffuse band with a maximum at ~52000 cm^{-1}.[13] Comparison[12,13] with CH_3Br[12,14] suggests that the lowest excited state in SiH_3Br is near 40000 cm^{-1}. Contributions due to excited states should be unimportant.

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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	−11.769	−61.836	−61.836	INFINITE
100	34.071	217.875	302.187	−8.431	−64.660	−68.263	35 657
200	42.240	243.595	266.964	−4.674	−68.572	−70.393	18.385
250	47.756	253.612	263.308	−2.424	−70.675	−70.606	14.752
298.15	52.865	262.466	262.466	0.	−78.241	−69.751	12.220
300	53.052	262 794	262.467	0.098	−78.330	−69.698	12.135
350	57.817	271.337	263.131	2.872	−95.089	−67.304	10.045
400	62.019	279.337	264.662	5.870	−96.278	−63.252	8.260
450	65.736	286.861	266.715	9 066	−97.318	−59.060	6.856
500	69.060	293.962	269.088	12.437	−98.219	−54.760	5.721
600	74.795	307.077	274.345	19.639	−99.646	−45.926	3.998
700	79.577	318.976	279.884	27.365	−100.645	−36.888	2.753
800	83.586	329.872	285 461	35.529	−101.295	−27.732	1.811
900	86.942	339.917	290.961	44.060	−101.669	−18.512	1.074
1000	89.747	349.227	296.328	52.899	−101.834	−9.261	0.484
1100	92.092	357.894	301.535	61.994	−101.845	−0.002	0.
1200	94.058	365.993	306.573	71.304	−101.747	9.252	−0.403
1300	95.712	373.589	311.439	80.795	−101.577	18.496	−0.743
1400	97.111	380.735	316.136	90.438	−101.368	27.724	−1.034
1500	98.299	387.476	320.669	100.210	−101.141	36.937	−1.286
1600	99.315	393.854	325.046	110.092	−100.917	46.135	−1.506
1700	100.188	399.902	329.273	120.069	−150.886	55.766	−1.713
1800	100.942	405.650	333.358	130.126	−150.476	67.911	−1.971
1900	101.597	411.126	337.308	140.254	−150.062	80.032	−2.200
2000	102.169	416.352	341.130	150.443	−149.650	92.132	−2.406
2100	102.671	421.349	344.832	160.685	−149.247	104.211	−2.592
2200	103.114	426.136	348.420	170.975	−148.858	116.271	−2.761
2300	103.505	430.728	351.899	181.306	−148.485	128.314	−2.914
2400	103.854	435 141	355.276	191.675	−148.132	140.341	−3.054
2500	104.165	439.387	358.556	202.076	−147.801	152.354	−3.183
2600	104.443	443.478	361 744	212.506	−147.493	164.353	−3.302
2700	104.694	447.424	364.845	222.964	−147.209	176.342	−3.412
2800	104 920	451.236	367.863	233 444	−146.951	188.321	−3.513
2900	105.124	454.921	370.802	243.947	−146.717	200.291	−3.608
3000	105.310	458.488	373.665	254.469	−146.508	212.253	−3.696
3100	105 478	461.944	376.458	265.008	−146.324	224.208	−3 778
3200	105.633	465.295	379.182	275.564	−146.164	236.158	−3.855
3300	105.774	468.548	381.841	286.134	−146.027	248.104	−3.927
3400	105.903	471 708	384.438	296.718	−145.912	260.045	−3.995
3500	106.022	474.779	386 975	307.314	−145.818	271.984	−4.059
3600	106.132	477.767	389.456	317.922	−529.897	294.381	−4.271
3700	106.233	480 677	391.882	328.540	−529.430	317.271	−4 479
3800	106.326	483.511	394.256	339.168	−528.983	340.148	−4.676
3900	106.413	486.274	396.580	349.806	−528.555	363.015	−4.862
4000	106.494	488.969	398.857	360.451	−528.145	385.870	−5.039
4100	106.569	491.600	401.087	371.104	−527.752	408.716	−5.207
4200	106.638	494.169	403.272	381.764	−527.374	431.552	−5.367
4300	106.704	496.679	405.416	392.432	−527.010	454.379	−5.520
4400	106.764	499.133	407.518	403.105	−526.660	477.198	−5.665
4500	106.821	501.532	409.580	413.784	−526.323	500.009	−5.804
4600	106.875	503.881	411.605	424.469	−525.997	522.813	−5.937
4700	106.925	506.180	413.593	435.159	−525.683	545.610	−6.064
4800	106.972	508.432	415.545	445.854	−525.378	568.400	−6.185
4900	107.016	510.638	417.463	456.553	−525.082	591.184	−6.302
5000	107.058	512.800	419.349	467.257	−524.795	613.962	−6.414
5100	107.097	514.921	421.202	477.965	−524.515	636.734	−6.521
5200	107.134	517.000	423.024	488.677	−524.243	659.501	−6.625
5300	107.169	519.042	424.817	499.392	−523.976	682.263	−6.724
5400	107.203	521.045	426.580	510.110	−523.715	705.020	−6.820
5500	107.234	523.012	428.316	520.832	−523.457	727.771	−6.912
5600	107.264	524.945	430.024	531.557	−523.204	750.519	−7.001
5700	107.292	526.844	431.706	542.285	−522.953	773.262	−7.086
5800	107.319	528.710	433.362	553.016	−522.705	796.001	−7.169
5900	107.345	530.545	434.994	563.749	−522.457	818.734	−7.249
6000	107.369	532.349	436.602	574.484	−522.209	841.464	−7.326

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

$S°(298.15\ K) = 112.84\ J·K^{-1}·mol^{-1}$
$T_{trs} = 411\ K$
$T_{fus} = 815.2\ K$

$\Delta_f H°(0\ K) = -255.0 \pm 1.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -271.5 \pm 1.3\ kJ·mol^{-1}$
$\Delta_{trs} H° = 3.222\ kJ·mol^{-1}$
$\Delta_{fus} H° =$ Unknown

Enthalpy of Formation

The equilibrium pressures for the reaction $NH_4Br(cr) \rightarrow NH_3(g) + HBr(g)$ have been measured by several investigators. Using the densi–tensimeter, Smits and Purcell,[2] determined both the equilibrium pressures and vapor densities of the decomposition products, simultaneously, at several temperatures. In order to check the density values obtained, the authors applied the "extrapolation method," from which it was calculated that the corresponding vapor density agreed with complete dissociation. Based on this conclusion, the reported equilibrium pressures were employed to evaluate the enthalpy changes ($\Delta_r H°$) of the decomposition reaction by both the 2nd and 3rd law methods. The results obtained are presented as follows.

Source	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Equipment Used
Smith and Calvert[1]	576.40–676.02	45.12 ± 0.13	44.93	Isoteniscope
Smits and Purcell[2]	604.95–668.15	45.50 ± 0.17	45.08	Densi–tensimeter
Johnson[3]	573.15–667.75	45.41 ± 0.44	44.85	Spiral Manometer

The value of $\Delta_r H°(298.15\ K)$ adopted is $45.2 \pm 0.2\ kcal·mol^{-1}$. Using $\Delta_f H°(298.15\ K) = -10.97$ and $-8.71\ kcal·mol^{-1}$ for $NH_3(g)$ and HBr(g), respectively, the value of $\Delta_f H°(298.15\ K)$ for $NH_4Br(cr)$ is evaluated as $-64.9 \pm 0.3\ kcal·mol^{-1}$ ($-271.542 \pm 1.3\ kJ·mol^{-1}$). The corresponding $\Delta_r H°(298.15\ K)$ value evaluated from solution data, selected by Parker[4] is $45.5 \pm 0.2\ kcal·mol^{-1}$.

The vapor densities (573–661 K) of dissociation products of $NH_4Br(cr)$ were also measured by Smith and Lombard.[5] Using the equilibrium pressures reported by Smith and Calvert,[1] they derived the corresponding degrees of dissociation of $NH_4Br(cr)$ at different temperatures. The calculated results indicated that only 48% of $NH_4Br(cr)$ decomposed at 573 K and as reaction temperatures increased to 661 K the degree of dissocation decreased to 10%. This conclusion was stated to be erroneous by Smits and Purcell[2] probably because of incorrect density determinations.

Heat Capacity and Entropy

The low temperature (13–305 K) heat capacities and $S°(298.15\ K)$ were obtained from Sorai *et al.*[6] The $C_p°$ values above 305 K were estimated by comparison with those for NaCl(cr), NaBr(cr) and $NH_4Cl(cr)$. The low temperature heat capacities were also measured by Ewald,[7] 139–301 K, and by Simon *et al.*,[8] 201.2–277.1 K.

Transition Data

The temperature (T_{trs}) and enthalpy of transition ($\Delta_{trs} H°$) were given by Bridgman.[9] $T_{trs} = 419.5 \pm 0.6$ K was reported Markowitz and Boryta,[10] which was determined by differential thermal analysis. According to Sorai *et al.*,[6] there are three solid phase transitions, namely Phase IV (CsCl) → Phase III (tetragonal) at 108 K, Phase III (tetragonal) → Phase II (CsCl) at 235 K and Phase II (CsCl) → Phase I (NaCl) at 411 K.

Fusion Data

The value of T_{fus} was taken from Rassow,[11] determined under pressure.

Decomposition Data

The temperature of decomposition was calculated as 670 K, i.e. the temperature at which the total pressure of the decomposition products for the reaction $NH_4Br(cr) \rightarrow NH_3(g) + HBr(g)$ equals 1 atm. Values of 674 and 668.4 K were reported by Luft[12] and Markowitz and Boryta,[10] respectively.

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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	-16.954	-254.971	-254.971	INFINITE
100	44.283	35.690	183.887	-14.820	-261.683	-234.424	122.450
200	78.680	77.864	120.813	-8.590	-264.747	-205.814	53.753
298.15	88.676	112.842	112.842	0.	-271.542	-176 007	30.836
300	88.893	113.392	112.844	0.164	-271.581	-175.414	30.542
400	92 717	139.666	116.401	9.306	-286.950	-140.189	18.307
411.000	92.844	142.183	117.057	10.327	II <--> I		
411.000	72.867	150.022	117.057	13.548	TRANSITION		
500	87.195	165.676	124.323	20.677	-284.740	-104.074	10.873
600	102.424	182.959	132.660	30.179	-284.447	-67.944	5.915
700	115.060	199.708	141.050	41.061	-282.832	-31.971	2.386
800	126.775	215.856	149.397	53.167	-280.062	3.690	-0.241
900	136.817	231.376	157.650	66.353	-276.295	38.943	-2.260
1000	146.022	246.276	165.772	80.503	-271.660	73.728	-3.851
1100	154.102	260.577	173.745	95.515	-266.266	108.012	-5.129
1200	161.502	274.308	181.557	111.301	-260.207	141.775	-6.171
1300	168.127	287.500	189.203	127.787	-253.560	175.007	-7.032
1400	174.264	300.187	196.680	144 910	-246.386	207.708	-7.750
1500	179.912	312.406	203.990	162.623	-238.733	239.879	-8.353

PREVIOUS: March 1962 CURRENT: September 1965

$S°(298.15\ K) = 271.538\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 115.5 \pm 38\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 104.2 \pm 38\ kJ·mol^{-1}$

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

$\omega_e = 187.29\ cm^{-1}$ $\omega_e x_e = 0.9665\ cm^{-1}$ $\sigma = 1$
$B_e = [0.0545]\ cm^{-1}$ $\alpha_e = [0.0003]\ cm^{-1}$ $r_e = [2.33]$ Å

Enthalpy of Formation

Gaydon[1] gives 0.7 ± 0.4 eV for the dissociation energy into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants from Wieland[2] were weighted according to their natural isotopic abundances. The bond length was estimated to be 0.965 of the mercuric bond length by analogy with the mercury chlorides. Rotational constants were estimated.[3]

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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	−10.252	115.527	115.527	INFINITE
100	33.918	232.289	304.036	−7.175	115.502	98.688	−51.549
200	36.493	256.811	274.923	−3.622	114.019	82.403	−21.522
250	36.940	265.007	272.149	−1.786	110.751	74.762	−15.621
298.15	37.210	271.538	271.538	0.	104.182	68.581	−12.015
300	37.218	271.768	271.538	0.069	104.129	68.360	−11.902
350	37.413	277.521	271.992	1.935	88.280	63.279	−9.444
400	37.561	282.526	273.003	3.809	87.864	59.736	−7.801
450	37.681	286.958	274.312	5.690	87.457	56.245	−6.529
500	37.783	290.933	275.779	7.577	87.058	52.798	−5.516
600	37.956	297.837	278.897	11.364	86.271	46.020	−4.006
700	38.105	303.700	282.032	15.168	26.732	45.945	−3.428
800	38.242	308.797	285.066	18.985	26.594	48.699	−3.180
900	38.372	313.309	287.958	22.816	26.464	51.470	−2.987
1000	38.497	317.358	290.699	26.659	26.342	54.255	−2.834
1100	38.619	321.033	293.292	30.515	26.228	57.051	−2.709
1200	38.738	324.399	295.746	34.383	26.121	59.858	−2.606
1300	38.857	327.504	298.071	38.263	26.022	62.674	−2.518
1400	38.974	330.388	300.278	42.154	25.930	65.497	−2.444
1500	39.090	333.081	302.376	46.057	25.845	68.326	−2.379
1600	39.206	335.607	304.375	49.972	25.767	71.161	−2.323
1700	39.322	337.988	306.283	53.899	25.694	74.000	−2.274
1800	39.437	340.238	308.107	57.837	25.627	76.843	−2.230
1900	39.552	342.374	309.855	61.786	25.563	79.690	−2.191
2000	39.666	344.405	311.532	65.747	25.503	82.541	−2.156
2100	39.780	346.343	313.144	69.719	25.444	85.394	−2.124
2200	39.895	348.197	314.695	73.703	25.388	88.250	−2.095
2300	40.009	349 973	316.191	77.698	25.331	91.109	−2.069
2400	40.123	351.678	317.634	81.705	25.276	93.970	−2.045
2500	40.237	353.318	319.029	85.723	25.220	96.834	−2.023
2600	40.350	354.898	320.378	89.752	25.164	99.699	−2.003
2700	40.464	356.423	321.685	93.793	25.108	102.567	−1.984
2800	40.578	357.897	322.952	97.845	25.054	105.437	−1.967
2900	40.691	359.323	324.182	101.908	25.000	108.309	−1.951
3000	40.805	360.704	325.377	105.983	24.948	111.182	−1.936
3100	40.919	362.044	326.538	110.069	24.900	114.057	−1.922
3200	41.032	363.345	327.668	114.167	24.856	116.934	−1.909
3300	41.146	364 609	328.768	118.276	24.818	119.812	−1.896
3400	41.259	365.839	329.841	122.396	24.787	122.691	−1.885
3500	41.372	367.037	330.886	126.527	24.763	125.571	−1.874
3600	41.486	368.204	331.907	130.670	24.750	128.452	−1.864
3700	41.599	369.342	332.903	134.825	24.747	131.332	−1.854
3800	41.713	370.453	333.877	138.990	24.756	134.213	−1.845
3900	41.826	371.538	334.829	143.167	24.778	137.093	−1.836
4000	41.939	372.599	335.760	147.355	24.815	139.972	−1.828
4100	42.053	373.635	336.671	151.555	24.868	142.851	−1.820
4200	42.166	374.650	337.563	155.766	24.936	145.728	−1.812
4300	42.279	375.644	338.437	159.988	25.022	148.603	−1.805
4400	42.393	376.617	339.294	164.222	25.126	151.475	−1.798
4500	42.506	377.571	340.134	168.467	25.249	154.346	−1.792
4600	42.619	378.506	340.958	172.723	25.391	157.213	−1.785
4700	42.733	379.424	341.767	176.991	25.552	160.077	−1.779
4800	42.846	380.325	342.561	181.270	25.733	162.937	−1.773
4900	42.959	381.210	343.340	185.560	25.934	165.794	−1.767
5000	43.072	382.079	344.106	189.861	26.156	168.646	−1.762
5100	43.186	382.933	344 859	194.174	26.398	171.493	−1.756
5200	43.299	383.772	345.600	198.499	26.660	174.336	−1.751
5300	43.412	384.598	346.328	202.834	26.942	177.173	−1.746
5400	43.525	385.411	347.044	207.181	27.244	180.005	−1.741
5500	43.639	386.211	347.749	211.539	27.565	182.831	−1.736
5600	43.752	386.998	348.443	215.909	27.906	185.651	−1.732
5700	43.865	387.773	349.126	220.290	28.265	188.464	−1.727
5800	43.978	388.537	349.799	224.682	28.643	191.271	−1.723
5900	44.092	389.290	350.462	229.085	29.039	194 072	−1.718
6000	44.205	390.032	351.115	233.500	29.452	196.866	−1.714

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

$S°(298.15\ K) = 258.95\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 49.815 \pm 0.08\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 40.878 \pm 0.08\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights					
State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
X $^1\Sigma^+$	0	1	B' 0^+	16880	1
A $^3\Pi_1$	12230	6	C ($\Pi_{1,2}$)	[51677]	2
B $^3\Pi_{0^+}$	[16155]	5	D ($\Pi_{1,0}$)	[56349]	2

$\omega_e = 267.38\ cm^{-1}$ $\omega_e x_e = 0.774\ cm^{-1}$ $\sigma = 1$
$B_e = 0.05568\ cm^{-1}$ $\alpha_e = 0.00034\ cm^{-1}$ $r_e = 2.485$ Å

Enthalpy for Formation

The equilibrium constants for the reaction (A) $I_2(g) + Br_2(g) = 2\ IBr(g)$ were determined to be 0.01124 and 0.01303 at 547.7 and 578 K, respectively, by Muller[1] who studied the rate of reaction between $H_2(g)$ and $Br_2(g)$ in the presence of $I_2(g)$. Bodenstein and Schmidt[2] derived two values of the equilibrium constants at 1495 K for the same reaction by vapor density studies on the system I_2, I, Br_2, Br and BrI. The equilibrium between $CuBr_2$(cr), I_2(g), CuBr(cr) and IBr(g) was investigated by McMorris and Yost[3] and the equilibrium constants at 115.0, 151.2 and 176.0°C for reaction (A) were evaluated. Based on these reported equilibrium constants, the corresponding enthalpy changes for reaction (A) are calculated by both the 2nd and 3rd law methods.

Badger and Yost[4] observed the infrared bands of IBr and classified them as the $A^3\Pi_2$–$X^1\Sigma$ transition. They have shown that the dissociation products of the upper state are normal atoms. Brown[5] assigned a faint set of bands in the red as the $B^3\Pi_0$–$X^1\Sigma$ system. By means of a vibrational analysis he found that the absorption spectrum of IBr is analogous to that of ICl. The dissociation energy for IBr was evaluated to be 14,660 ± 5 cm^{-1} or 1.817 eV. Hence the enthalpy change for the reaction (B) $IBr(g) = I(g) + Br(g)$ is calculated as 41.92 $kcal·mol^{-1}$.

The enthaplies of formation for IBr(g) derived from the enthalpy changes for reaction (A) and (B) are presented in the following table. The value of $\Delta_f H°$(IBr, g, 298.15 K) adopted is 9.77 ± 0.02 $kcal·mol^{-1}$ (40.878 ± 0.08 $kJ·mol^{-1}$).

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}	$\Delta_f H°$(298.15K) kcal·mol^{-1}
Muller[1]	A	547.7, 578	2	−3.07	−3.38	−0.55	9.47
Bodenstein and Schmidt[2]	A	1495	1	–	−2.92	–	9.70
McMorris and Yost[3]	A	388.2–449.2	14	−2.46	−2.85	−0.9 ± 0.4	9.73
Brown[5]	B	298	–	–	41.92**	–	9.77**

**The value is derived from $D_0°$(I–Br).

Heat Capacity and Entropy

The ground state configuration, electronic levels, quantum weights, ω_e and $\omega_e x_e$ are obtained from Herzberg.[6] The values of B_e, α_e(corrected to the average isotopic species) and r_e were reported by Jaseja[7] who analyzed the microwave spectrum of IBr, corresponding to the transitions $J = 4 \rightarrow 5$ and $J = 5 \rightarrow 6$, for the two isotopic species, $^{127}I^{79}Br$ and $^{127}I\ ^{81}Br$.

The infrared absorption spectrum of IBr at 8000–6800 Å, associated with a $^1\Pi_1$–$X^1\Sigma^+$ transition, was observed by Selin.[8] The derived rotational constants are different from those reported by Jaseja.[7]

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^{-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	−9.917	49.815	49.815	INFINITE
100	31.904	221.168	290.519	−6.935	49.875	33.500	−17.499
200	35.387	244.574	262.265	−3.538	48.355	17.678	−4.617
250	36.103	252.554	259.552	−1.749	47.422	10.114	−2.113
298.15	36.531	258.952	258.952	0.	40.878	3.675	−0.644
300	36.544	259.178	258.953	0.068	40.825	3.444	−0.600
350	36.836	264.835	259.399	1.903	24.929	−1.903	0.284
400	37.042	269.768	260.394	3.750	16.448	−5.428	0.709
450	37.196	274.140	261.683	5.606	15.367	−8.098	0.940
500	37.316	278.066	263.128	7.469	−5.777	−8.748	0.914
600	37.494	284.886	266.203	11.210	−5 773	−9.342	0.813
700	37.627	290.676	269.296	14.966	−5.769	−9.937	0.742
800	37 734	295.708	272.290	18.734	−5.767	−10.533	0.688
900	37.827	300.158	275.144	22.513	−5.766	−11.129	0.646
1000	37.911	304 147	277.848	26.300	−5.767	−11.724	0.612
1100	37.989	307.764	280.406	30.095	−5.771	−12.320	0.585
1200	38.066	311.073	282.825	33.897	−5.781	−12.915	0.562
1300	38.143	314.123	285.117	37.708	−5 798	−13.509	0.543
1400	38.227	316.953	287.291	41.526	−5.828	−14.101	0.526
1500	38.323	319.593	289.358	45.354	−5.874	−14 690	0.512
1600	38.437	322.070	291.326	49.191	−5.939	−15.276	0.499
1700	38.576	324.405	293.203	53.042	−6.027	−15.857	0.487
1800	38.748	326 614	294.999	56.908	−6.139	−16.432	0.477
1900	38 962	328.715	296.718	60.793	−6.273	−17.000	0.467
2000	39.223	330.720	298.369	64.702	−6.427	−17.561	0 459
2100	39.538	332.641	299.955	68.639	−6.596	−18.114	0.451
2200	39.911	334.488	301.483	72.611	−6 771	−18.658	0.443
2300	40.347	336.272	302.957	76.624	−6.944	−19.194	0.436
2400	40.845	337.999	304.382	80.683	−7.104	−19.724	0.429
2500	41.408	339.678	305.760	84.795	−7.239	−20.247	0.423
2600	42.033	341.314	307.096	88.966	−7.337	−20.765	0.417
2700	42.718	342.913	308.393	93.203	−7.386	−21.280	0.412
2800	43.457	344.480	309.654	97.512	−7.374	−21.795	0.407
2900	44.245	346.018	310.882	101.896	−7.290	−22.311	0.402
3000	45.076	347.532	312.078	106.362	−7.124	−22.832	0.398
3100	45.942	349.024	313.246	110.913	−6.866	−23.359	0.394
3200	46.834	350.497	314.387	115.551	−6.508	−23.897	0.390
3300	47.745	351.952	315.503	120.280	−6.044	−24.447	0.387
3400	48.664	353.391	316.597	125.101	−5.469	−25.013	0.384
3500	49.585	354.815	317.668	130.013	−4.779	−25.597	0.382
3600	50.497	356.224	318.720	135.017	−3.972	−26.203	0.380
3700	51.393	357.620	319.752	140.112	−3.046	−26.833	0.379
3800	52.264	359.002	320.767	145.295	−2.001	−27.490	0.378
3900	53.105	360.371	321.765	150.564	−0.839	−28.176	0.377
4000	53.909	361.726	322.747	155.915	0.439	−28.893	0.377
4100	54.671	363.066	323.714	161.344	1.829	−29.643	0.378
4200	55.386	364.392	324.667	166.847	3.327	−30.429	0.378
4300	56.050	365.704	325.606	172.420	4.929	−31.251	0.380
4400	56.661	366.999	326.532	178.056	6.630	−32.112	0.381
4500	57.217	368.279	327.446	183.750	8.425	−33.012	0.383
4600	57.717	369.542	328.347	189.497	10.307	−33.954	0.386
4700	58.161	370.788	329.237	195.292	12.272	−34 937	0.388
4800	58.548	372.017	330.115	201.127	14.312	−35.963	0.391
4900	58.881	373.228	330.983	206.999	16.423	−37.032	0.395
5000	59.159	374.420	331.840	212.902	18.598	−38.145	0.398
5100	59.387	375.594	332.686	218.829	20.830	−39.302	0.403
5200	59.565	376.749	333.522	224.777	23.116	−40.503	0.407
5300	59.696	377.885	334.349	230.741	25.448	−41 749	0.411
5400	59.782	379.001	335.165	236.715	27.822	−43.039	0.416
5500	59.828	380.099	335.972	242.696	30.233	−44.373	0.421
5600	59.836	381.177	336.770	248.679	32.675	−45.751	0.427
5700	59.809	382.236	337.558	254.662	35.145	−47.174	0.432
5800	59.749	383.276	338.338	260.640	37.639	−48.640	0.438
5900	59 661	384.296	339.108	266.611	40.152	−50.149	0.444
6000	59.546	385.298	339.869	272.571	42.681	−51.701	0.450

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

$S°(298.15\ K) = 95.94 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1007\ K$

$\Delta_f H°(0\ K) = -386.674 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -393.798 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 25.5\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of solution, $\Delta_{sol}H$, of KBr(cr) in H_2O(l) has been measured by many investigators. The results were reviewed in detail by Parker.[1] Eight pertinent $\Delta_{sol}H°$(aq, ∞) values are reproduced in the table below. Adopting the best value, $\Delta_r H°(298.15\ K) = 4.75 \pm 0.02$ kcal·mol^{-1}, for the reaction KBr(cr) = K^+(aq, ∞) + Br^-(aq, ∞), we derive $\Delta_f H°(298.15\ K) = -94.12$ kcal·mol^{-1} for KBr(cr) (−393.798 kJ·mol^{-1}). The auxiliary values $\Delta_f H°(298.15\ K) = -60.32$ and −29.05 kcal·mol^{-1} for K^+(aq, ∞) and Br^-(∞H_2O), respectively, are obtained from reference.[2]

$\Delta_{sol}H°$(aq, ∞)* kcal·mol^{-1}	T/°C	m**	Source
4.727	16.6	0.28	Walden[3]
4.777	25	0.37	Wust and Lange[4]
7.753	25	0.09	Chipman *et al.*[5]
4.684	20	0.19	Popov *et al.*[6]
4.889	23.5	0.14	Fedorov and Sil'chenko[7]
4.783	25	0.13	Lange and Martin[8]
4.542	20.5	0.12	Popov *et al.*[9]
4.739	25	0.28	Hietala[10]

*Values are adjusted to 298.15 K and to infinite dilution.
**Lowest experimental molality.

Heat Capacity and Entropy

The low temperature heat capacities, 2.9–272.2 K, were measured by Berg and Morrison[11] using an adiabatic calorimeter. The high temperature heat capacities, 325.25–711.75 K, are taken from Mustajoki.[12] These two sets of $C_p°$ data are joined smoothly at 298.15 K. The $C_p°$ values at temperatures, 720–1007 K, are extrapolated graphically, so that the derived enthalpy change $H°(1007\ K) - H°(298.15\ K) = 9.9$ kcal·mol^{-1} agrees with that determined by Dworkin.[13] The derived enthalpies at 700, 800 and 900 K are also in good agreement with those measured by Skuratov and Lapushkin.[14] The $C_p°$ values above 1007 K are obtained by graphical extrapolation.

The $S°(298.15\ K)$ is calculated from the adopted low temperature $C_p°$, based on $S°(2.9\ K) = 0.006276\ J \cdot K^{-1} \cdot mol^{-1}$.

The heat capacities of KBr(cr) were also measured by Nernst and Lindemann,[15] 78.7–89.2 K; Koref,[16] 137–234 K, and Clusius *et al.*[17] The enthalpies of KBr(cr) were determined by Magnus[18] and by Cooper.[19] The results are in reasonable agreement with the adopted functions except for those reported by Cooper.[14]

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The heats of sublimation to monomer and dimer are calculated as the enthalpy changes for the following two reactions KBr(cr) = KBr(g) and 2 KBr(cr) = K_2Br_2(g).

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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	−12.213	−386.674	−386.674	INFINITE
100	43.145	42.949	140.561	−9 761	−387.351	−385.394	201.309
200	49.873	75.509	100.634	−5.025	−387.660	−383.321	100.113
298.15	52.379	95.939	95.939	0.	−393.798	−380.431	66.650
300	52.300	96.263	95.940	0.097	−393.826	−380.348	66.224
400	53.806	111.525	98.011	5.406	−411.235	−372.297	48.617
500	55.250	123.669	101.968	10.850	−410.744	−362.615	37.882
600	56.358	133.837	106.456	16.429	−410 065	−353.050	30.736
700	58 084	142.647	111.010	22.146	−409.212	−343.612	25.641
800	60 417	150.546	115.466	28.064	−408.148	−334.311	21.828
900	63.687	157.840	119.773	34.260	−406.816	−325 158	18.872
1000	68.011	164 764	123.928	40.836	−405.141	−316.171	16.515
1007.000	68.367	165.240	124.214	41.313	--- CRYSTAL <---> LIQUID ---		
1100	73.053	171.491	127.948	47.897	−481.989	−302.762	14.377
1200	76.860	178.018	131.850	55.402	−478.460	−286.622	12.476
1300	79.622	184.283	135.644	63.231	−474.610	−270 790	10.880
1400	81.797	190.265	139.333	71.304	−470.520	−255.263	9.524
1500	83.680	195.974	142.921	79.580	−466.233	−240.036	8.359

PREVIOUS: December 1961 CURRENT: March 1967

$S°(298.15\ K)$ = [105.540] $J·K^{-1}·mol^{-1}$
T_{fus} = 1007 K

$\Delta_f H°(298.15\ K)$ = [−376.492] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 25.522 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1007\ K)–H°(298.15\ K)$, between the crystal and liquid.

Toguri *et al.*[1] studied the chemical equilibrium for the reaction KBr(l) + HCl(g) = KCl(l) + HBr(g). They obtained $\Delta_r G°(1073\ K)$ = 3.50 ± 0.08 and 3.54 $kcal·mol^{-1}$ from partial pressure data and emf data, respectively The corresponding value calculated from these tables is 3.78 $kcal·mol^{-1}$. Combination of the experimental results with JANAF auxiliary data leads to −89.70 and −89.74 $kcal·mol^{-1}$ for $\Delta_f H°(298.15\ K)$.

Heat Capacity and Entropy

The heat capacity of 16.7 $cal·K^{-1}·mol^{-1}$ (69.873 $J·K^{-1}·mol^{-1}$) was derived by Dworkin[2] from enthalpy data in the range 1010–1100 K. This $C_p°$ value is adopted here for the temperature range 298–2500 K.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The adopted T_{fus} = 1007 K and $\Delta_{fus}H°$ = 6.1 $kcal·mol^{-1}$ (25.522 $kJ·mol^{-1}$) were determined by Johnson and Bredig[3] and Dworkin and Bredig,[4] respectively.

Enthalpies of melting of 6.2 $kcal·mol^{-1}$ from phase diagram studies and 6.7 $kcal·mol^{-1}$ from calorimetric measurements were obtained by Aukrust *et al.*[5]

Vaporization Data

The boiling point, T_{vap} = 1671 K, is calculated as the temperature at which the sum of the partial pressures of KBr(g) and K_2Br_2(g) over KBr(l) equals one atmosphere. The value of $\Delta_{vap}H°$ is calculated as the enthalpy required to produce one mole of vapor mixture, which contains 19.5% dimer (K_2Br_2) and 80.5% monomer (KBr).

T_{vap} was reported to be 1648 and 1668 K by von Wartenberg and Albrecht[6] and Ruff and Mugdan,[7] respectively.

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	69.873	105.540	105.540	0.	−376.492	−365.987	64.119
300	69.873	105.972	105.541	0 129	−376.487	−365.922	63.713
400	69.873	126.073	108.282	7.117	−392.218	−359.099	46.894
500	69.873	141.665	113.457	14.104	−390.185	−351.053	36.674
600	69.873	154.404	119.252	21.091	−388.097	−343.422	29.898
700	69.873	165.175	125.063	28.078	−385.974	−336.144	25.083
800	69.873	174.505	130.673	35.066	−383.840	−329.171	21.493
900	69.873	182.735	136.010	42.053	−381.718	−322.465	18.715
1000	69.873	190.097	141.057	49.040	−379.630	−315.994	16.506
1100	69.873	196.757	145.823	56.027	−456.553	−305.119	14.489
1200	69.873	202.836	150.324	63.015	−453.541	−291 485	12.688
1300	69.873	208.429	154.581	70.002	−450.532	−278.103	11 174
1400	69.873	213.607	158.615	76.989	−447.529	−264.951	9.885
1500	69.873	218.428	162.444	83.977	−444.531	−252.015	8.776
1600	69.873	222.938	166.085	90.964	−441.539	−239.278	7.812
1700	69.873	227.174	169.555	97.951	−438.554	−226.728	6.967
1800	69.873	231 167	172.868	104.938	−435.579	−214.354	6.220
1900	69.873	234.945	176.037	111.926	−432.615	−202.144	5.557
2000	69.873	238.529	179.073	118.913	−429.665	−190.091	4.965
2100	69.873	241.938	181.986	125.900	−426.731	−178.184	4.432
2200	69.873	245.189	184.785	132.888	−423.816	−166.417	3.951
2300	69.873	248.295	187.480	139.875	−420.923	−154.782	3.515
2400	69.873	251.269	190.076	146.862	−418.055	−143.272	3.118
2500	69.873	254.121	192.581	153.849	−415.215	−131.881	2.756

PREVIOUS: December 1961 CURRENT: March 1967

0 to	1007 K	crystal
above	1007 K	liquid

Refer to the individual tables for details.

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

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
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	−12.213	−386.674	−386.674	INFINITE
100	43.145	42.949	140.561	−9.761	−387.351	−385.394	201.309
200	49.873	75.509	100.634	−5.025	−387.660	−383.321	100.113
298.15	52.379	95.939	95.939	0.	−393.798	−380.431	66.650
300	52.300	96.263	95.940	0.097	−393.826	−380.348	66.224
400	53.806	111.525	98.011	5.406	−411.235	−372.297	48.617
500	55.250	123.669	101.968	10.850	−410.744	−362.615	37.882
600	56.358	133.837	106.456	16.429	−410.065	−353.050	30.736
700	58.084	142.647	111.010	22.146	−409.212	−343.612	25.641
800	60.417	150.546	115.466	28.064	−408.148	−334.311	21.828
900	63.687	157.840	119.773	34.260	−406.816	−325.158	18.872
1000	68.011	164.764	123.928	40.836	−405.141	−316.171	16.515
1007.000	68.367	165.240	124.214	41.313	CRYSTAL <--> LIQUID		
1007.000	69.873	190.585	124.214	66.835	TRANSITION		
1100	69.873	196.757	130.090	73.333	−456.553	−305.119	14.489
1200	69.873	202.836	135.902	80.321	−453.541	−291.485	12.688
1300	69.873	208.429	141.269	87.308	−450.532	−278.103	11.174
1400	69.873	213.607	146.254	94.295	−447.529	−264.951	9.885
1500	69.873	218.428	150.906	101.283	−444.531	−252.015	8.776
1600	69.873	222.938	155.269	108.270	−441.539	−239.278	7.812
1700	69.873	227.174	159.375	115.257	−438.554	−226.728	6.967
1800	69.873	231.167	163.254	122.244	−435.579	−214.354	6.220
1900	69.873	234.945	166.929	129.232	−432.615	−202.144	5.557
2000	69.873	238.529	170.420	136.219	−429.665	−190.091	4.965
2100	69.873	241.938	173.745	143.206	−426.731	−178.184	4.432
2200	69.873	245.189	176.919	150.194	−423.816	−166.417	3.951
2300	69.873	248.295	179.955	157.181	−420.923	−154.782	3.515
2400	69.873	251.269	182.865	164.168	−418.055	−143.272	3.118
2500	69.873	254.121	185.659	171.155	−415.215	−131.881	2.756

PREVIOUS· CURRENT: March 1967

$S°(298.15) = 250.532\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -170.85 \pm 2.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -180.08 \pm 2.1\ kJ·mol^{-1}$

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

$\omega_e = 218.47\ cm^{-1}$ $\omega_e x_e = 0.7533\ cm^{-1}$ $\sigma = 1$
$B_e = 0.0807\ cm^{-1}$ $\alpha_e = 0.000401\ cm^{-1}$ $r_e = 2.821$ Å

Enthalpy of Formation

The enthalpy of formation is derived from the sublimation and vaporization data analyzed below. Numerous investigators have obtained total pressures by static methods or "apparent" pressures by effusion or transpiration. These pressures are converted to monomer pressures by use of functions [see $K_2Br_2(g)$ table] which are consistent with the dimer–monomer equilibrium data of Hagemark *et al.*[6] 2nd and 3rd law analyses of the monomer pressures show remarkable consistency over temperatures from 637 to 1668 K. The selected value of $\Delta_f H°(298\ K) = -43\ 04 \pm 0.5\ kcal·mol^{-1}$ ($-180.079 \pm 2.1\ kJ·mol^{-1}$) may be compared with $-43.8\ kcal\ mol^{-1}$ derived from $D_0° = 3.95$ eV [which is reported by Gaydon[14]] based on atomic fluorescence data.

Source	Reaction	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}
Wartenberg–Albrecht[1]	A	1368.15–1654.15	14	48.28 ± 0.31	46.70	−1.1 ± 0.2	−43.28
Ruff–Mugdan[2]	"	1361.15–1668.15	10	49.06 ± 0.56	47.16	−1.4 ± 0.4	−42.82
Fiock–Rodebush[3]	"	1179.15–1335.75	10	47.80 ± 0.05	46.95	−0.7 ± 0.1	−43.03
Hintz–Jellinek[4]	"	1523.15	1	–	47.34	–	−42.64
Murgulescu–Marta[5]	"	1373.15–1473.15	5	46.20 ± 1.15	47.69	1.1 ± 0.8	−42.29
Hagemark *et al.*[6]	"	1138.95–1416.02	26	47.15 ± 0.49	46.94	−0.2 ± 0.4	−43.04
Niwa[7]	B	823.15–923.15	6	48.04 ± 0.51	51.67	4.1 ± 0.6	−42.45
Mayer–Wintner[8]	"	884.90–929.40	6	56.15 ± 3.17	51.49	−5.2 ± 3.5	−42.63
Zimm–Mayer[9]	"	636.94–900.09	15	50.71 ± 0.21	50.58	−0.1 ± 0.2	−43.54

Reactions: (A) KBr(l) = KBr(g) (B) KBr(cr) = KBr(g)

Heat Capacity and Entropy

Rusk and Gordy[10] have investigated the pure rotational spectra of KBr in the 1.5 to 5.0 mm range of the microwave region by millimeter wave molecular beam spectroscopy. The reported values of ω_e, $\omega_e x_e$, B_e and r_e are adopted here and corrected to the average isotopic species. The value of α_e is obtained from Fabricand *et al.*[11] Molecular constants for KBr(g) have also been reported by Hertzberg[12] and Rice and Klemperer.[13] They are in good agreement with the values adopted. Herzberg[12] also lists an A state in 31770 cm^{-1} based on observed electronic spectra.

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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	−10.109	−170.852	−170.852	INFINITE
100	33 058	211.876	282.656	−7.078	−170.949	−185.884	97 096
200	36.056	235.946	253.888	−3.588	−172.505	−200.253	52.301
250	36.600	244.056	251.138	−1.771	−173.469	−207.082	43.267
298.15	36.922	250.532	250.532	0.	−180.079	−212.804	37.282
300	36.932	250.761	250.533	0.068	−180.136	−213.007	37.088
350	37 155	256.471	250.983	1.921	−198.500	−217.498	32.460
400	37.316	261.444	251.987	3.783	−199.139	−220.168	28.751
450	37.440	265 846	253.287	5.652	−199.755	−222.760	25.857
500	37.541	269.796	254.744	7.526	−200.349	−225.284	23.535
600	37.701	276.656	257.841	11.289	−201.486	−230.163	20.037
700	37 829	282.477	260.955	15.066	−202.575	−234.856	17.525
800	37 940	287.536	263.968	18.854	−203.639	−239.394	15.631
900	38.041	292.011	266.840	22.653	−204.705	−243.800	14.150
1000	38.136	296.024	269.562	26.462	−205.796	−248.086	12.959
1100	38.226	299.663	272.135	30.280	−285.888	−247.650	11.760
1200	38.314	302.992	274.570	34.107	−286.036	−244 167	10.628
1300	38.400	306.063	276.876	37.943	−286.179	−240.672	9.670
1400	38.484	308.911	279.063	41.787	−286.318	−237.167	8.849
1500	38.568	311.569	281.143	45.640	−286.455	−233.651	8.136
1600	38.650	314 061	283.123	49.501	−286.589	−230 126	7.513
1700	38.732	316.407	285.013	53.370	−286.723	−226.593	6.962
1800	38.814	318.623	286.819	57.247	−286.858	−223.052	6.473
1900	38.895	320 724	288.549	61.132	−286.996	−219.504	6.035
2000	38.975	322.721	290.208	65.026	−287.139	−215.948	5.640
2100	39 056	324.624	291.802	68.927	−287.291	−212.385	5.283
2200	39 136	326 443	293.335	72.837	−287.454	−208.814	4.958
2300	39 216	328.184	294.813	76.755	−287.631	−205.236	4.661
2400	39 296	329.855	296.238	80.680	−287.824	−201.649	4.389
2500	39.376	331.461	297.615	84.614	−288.037	−198 054	4.138
2600	39 456	333.007	298.947	88.556	−288.273	−194 450	3.907
2700	39.535	334.497	300.236	92.505	−288.533	−190 837	3.692
2800	39.615	335.937	301.486	96.463	−288.822	−187.213	3.493
2900	39.694	337.328	302.698	100.428	−289.140	−183.579	3.307
3000	39.774	338.675	303.875	104 401	−289.491	−179.933	3.133
3100	39.853	339.981	305 018	108.383	−289.877	−176.275	2.970
3200	39.932	341.247	306.131	112.372	−290.301	−172.603	2.817
3300	40.012	342.477	307.214	116.369	−290.757	−168.919	2.674
3400	40.091	343.673	308.269	120.374	−291.260	−165.219	2.538
3500	40.170	344.836	309.297	124.387	−291.806	−161.505	2.410
3600	40.249	345.969	310.300	128.408	−292.401	−157.773	2.289
3700	40.328	347.073	311.279	132.437	−293.047	−154.025	2.174
3800	40.408	348.149	312.235	136 474	−293 747	−150.259	2.065
3900	40.487	349.200	313.169	140.519	−294.504	−146.473	1.962
4000	40.566	350.226	314.083	144.571	−295.315	−142.667	1.863
4100	40 645	351.229	314.977	148.632	−296.192	−138.841	1.769
4200	40.724	352.209	315.852	152.700	−297.140	−134.992	1.679
4300	40.803	353.168	316.708	156.777	−298 160	−131.119	1.593
4400	40.882	354.107	317.548	160.861	−298.978	−127.249	1.511
4500	40.961	355.027	318.370	164.953	−300.084	−123.334	1.432
4600	41.040	355.928	319.177	169.053	−301.262	−119.393	1.356
4700	41.119	356.811	319.969	173.161	−302.492	−115.428	1.283
4800	41.198	357.678	320.745	177.277	−303.687	−111.448	1.213
4900	41.277	358.528	321.508	181.401	−305.060	−107.429	1.145
5000	41.356	359.363	322.256	185.532	−306.507	−103.381	1.080
5100	41.435	360.183	322.992	189.672	−308.031	−99.304	1.017
5200	41.514	360.988	323.715	193.819	−309.630	−95.196	0.956
5300	41.593	361.779	324.426	197.975	−311.305	−91.056	0.897
5400	41.672	362.558	325.125	202 138	−313 057	−86.884	0.840
5500	41.751	363.323	325.812	206.309	−314.885	−82.679	0.785
5600	41.830	364.076	326.489	210.488	−316.787	−78.440	0.732
5700	41.909	364.817	327.155	214.675	−318.418	−74.214	0.680
5800	41.988	365.547	327.810	218.870	−320.421	−69.913	0.630
5900	42.067	366.265	328.456	223.073	−322.491	−65.576	0.581
6000	42.146	366.973	329.092	227.283	−324.625	−61.204	0.533

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

$S°(298.15\ K)$ = [74 06] $J·K^{-1}·mol^{-1}$
T_{fus} = 823 K

$\Delta_f H°(0\ K)$ = unknown
$\Delta_f H°(298.15\ K) = -350.9 \pm 0.4$ $kJ·mol^{-1}$
$\Delta_{fus} H° = 17.656$ $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(LiBr, cr, 298.15 K) = −83 87 $kcal·mol^{-1}$(−350.912 $kJ·mol^{-1}$) was calculated from the enthalpy of solution of lithium bromide (cr) at infinite dilution and the ionic enthalpies of formation of Li^+(aq,∞) and Br^-(aq, ∞).

Parker[1] reviewed the enthalpy of solution data in the literature and gave the "best" value, $\Delta_{sol} H^∞ = -11{,}670 \pm 50$ $cal·mol^{-1}$ for LiBr(cr) → LiBr(aq,∞) at 298.15 K. The ionic enthalpy of formation, $\Delta_f H°(Li^+, aq, ∞\ 298.15\ K) = -66.49$ $kcal·mol^{-1}$, was calculated from $\Delta_f H°$(LiOH, aq, ∞ 298.15 K) = −121.46 $kcal·mol^{-1}$ [2] with $\Delta_f H°(OH^-, aq, ∞\ 298.15\ K) = -54.97$ $kcal·mol^{-1}$.[3] The $v\Delta_f H°$(Br, aq, ∞, 298.15 K) = −29.05 $kcal·mol^{-1}$ was also obtained from.[3] Combination of the ionic enthalpies of formation of Li^+(aq, ∞) and Br^-(aq, ∞) gives the enthalpy of formation of LiBr(aq, ∞), $\Delta_f H°(298.15\ K) = -95.54$ $kcal·mol^{-1}$.

Heat Capacity and Entropy

Dworkin[4] has measured the enthalpy changes by the drop method (723–883 K), yielding $H°(823;298) = 7.0$ $kcal·mol^{-1}$ for the crystal at the melting point. Heat capacities derived from his data were $C_p°(773\ K) = 15.1$ and $C_p°(853\ K) = 15.6$ $cal·K^{-1}·mol^{-1}$ for the crystal and liquid, respectively. The tabulated heat capacities were estimated based on these values and on the heat capacities of LiCl(cr), NaCl(cr) and NaBr(cr).

$S°(298.15\ K) = 17.7$ $cal·K^{-1}·mol^{-1}$(74.06 $J·K^{-1}·mol^{-1}$) was estimated by adding the entropy difference between NaBr(cr) and NaCl(cr) to the entropy of lithium chloride (cr) at 298.15 K. Comparisons with other alkali halides give results within ± 0.5 $cal·K^{-1}·mol^{-1}$ of this value. Kelley[5] has estimated $C_p° = 11.50 + 3.02 \times 10^{-3}$ T $cal·K^{-1}·mol^{-1}$ and $S°(298.15\ K) = 16.0 \pm 0.5$ $cal·K^{-1}mol^{-1}$.

Fusion Data

The selected enthalpy of fusion, $\Delta_{fus} H°(823\ K) = 4.22$ $kcal·mol^{-1}$(17.656 $kJ·mol^{-1}$), was obtained from enthalpy measurements in a drop calorimeter by Dworkin and Bredig.[6]

Kelley[7] reviewed some phase diagram studies of the lithium bromide system in the literature, and gave the enthalpy of fusion $\Delta_{fus} H°(825\ K) = 2.90$ $kcal·mol^{-1}$. Blanc[8] reported the enthalpy of fusion $\Delta_{fus} H°(819\ K) = 3.095$ $kcal·mol^{-1}$ by a cryoscopic method. Both values are too low.

References

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[8]M. Blanc, Compt. rend. 246, 570 (1958).

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	48.919	74.057	74.057	0.	−350.912	−341.630	59.852
300	48.995	74.360	74 058	0.091	−350.937	−341.573	59.473
400	51.233	88.767	76.007	5.104	−365.764	−335.373	43.795
500	53.430	100.430	79.760	10.335	−368.312	−327.524	34.216
600	56.087	110.394	84.054	15.804	−367.686	−319.419	27.808
700	59.768	119.300	88.463	21.586	−366.698	−311.447	23.240
800	64.455	127.583	92.840	27 794	−365.263	−303.647	19.826
823.000	65.333	129.422	93.837	29.287	--- CRYSTAL <--> LIQUID ---		
900	68.471	135.414	97.139	34.447	−363.383	−296.053	17 182
1000	71.379	142.787	101.339	41.448	−361.155	−288.689	15.080
1100	73.555	149.695	105.425	48.698	−358.678	−281.560	13.370
1200	75.228	156.172	109.387	56.142	−356.005	−274.666	11.956
1300	76.442	162.244	113.222	63.730	−353.191	−268.001	10.768
1400	77.278	167.942	116.929	71 418	−350.273	−261.557	9.759
1500	77.822	173.293	120.510	79.175	−347.283	−255.325	8.891
1600	78.199	178.329	123.968	86.977	−344.245	−249.293	8.139
1700	78.408	183.076	127.307	94.808	−486.412	−236.276	7.260
1800	78.576	187.563	130.531	102.658	−482.570	−221.673	6.433
1900	78.701	191.815	133.645	110.522	−478.721	−207.284	5.699
2000	78.743	195.853	136.655	118.395	−474.875	−193.097	5.043

PREVIOUS: September 1961 CURRENT: June 1966

$S°(298.15\ K) = [84.603]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 823\ K$

$\Delta_f H°(298.15\ K) = [-338.226]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 17.656\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding the $\Delta_{fus} H°$ and the difference in enthalpy, $H°(823\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Dworkin[1] has derived the heat capacity $C_p = 15.6\ cal \cdot K^{-1}\ mol^{-1}$ from enthalpy measurements (823–883 K) by the drop method. The liquid heat capacity was assumed to be constant as $15.6\ cal \cdot K^{-1} \cdot mol^{-1}$. $S°(298.15\ K)$ is obtained 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}(l→monomer) is taken as the temperature at which the calculated Gibbs energy change is zero for LiBr(l) → LiBr(g), while $\Delta_{vap} H°$(l→monomer) is the corresponding enthalpy of vaporization.

T_{vap}(l→equilibrium mixture) is taken as the temperature at which the sum of the calculated partial vapor pressures of LiBr(g) and Li_2Br_2(g) reaches one bar (trimer and higher polymers have been neglected in calculation). This value (1562 K) is in good agreement with the boiling point (at 1 atm) of 1583 K obtained from total vapor pressure measurements by von Wartenberg and Schulz[2] and also the boiling point of 1538 K by Ruff and Mugdan.[3] $\Delta_{vap} H°$(l→equilibrium mixture) at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 29.23 mole percent of dimer. For detailed information see LiBr(g) and Li_2Br_2(g) tables.

References

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[3]O. Ruff and S. Mugdan, Z. Anorg. Chem. **117**, 147 (1921).

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.							
100							
200							
298.15	65.270	84.603	84.603	0.	−338.226	−332.088	58.181
300	65.270	85.007	84.605	0.121	−338.221	−332.050	57.815
400	65.270	103.784	87.165	6.648	−351.534	−327.150	42.721
500	65.270	118.349	91.999	13.175	−352.786	−320.957	33.530
600	65.270	130.249	97.413	19.702	−351.102	−314.748	27.401
700	65.270	140.311	102.841	26.229	−349.369	−308.825	23.045
800	65.270	149.026	108 081	32.756	−347.614	−303.153	19.794
900	65.270	156.714	113.066	39.283	−345.861	−297.701	17.278
1000	65.270	163.591	117.781	45.810	−344.107	−292.444	15.276
1100	65.270	169.812	122.233	52.337	−342.352	−287.363	13.646
1200	65.270	175.491	126.438	58.864	−340.597	−282.441	12.294
1300	65.270	180.715	130.415	65.391	−338.843	−277.666	11.157
1400	65.270	185.552	134.182	71.918	−337.086	−273.026	10.187
1500	65.270	190.056	137.759	78.445	−335.326	−268.511	9.350
1600	65.270	194.268	141.160	84.972	−333.563	−264.115	8.622
1700	65.270	198.225	144.402	91.499	−477.034	−252.652	7.763
1800	65.270	201.956	147.497	98.026	−474.514	−239.526	6.951
1900	65.270	205.485	150.457	104.553	−472.004	−226.539	6.228
2000	65.270	208.833	153.293	111.080	−469.503	−213.685	5.581

PREVIOUS: September 1961 CURRENT: June 1966

298.15 to 823 K crystal
above 823 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°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0.							
100.							
200.						1	1
298.15	48.919	74.057	74.057	0.	−350.912	−341.630	59.852
300	48.995	74.360	74.058	0.091	−350.937	−341.573	59.473
400	51.233	88.767	76.007	5.104	−365.764	−335.373	43.795
500	53.430	100.430	79.760	10.335	−368.312	−327.524	34.216
600	56.087	110.394	84.054	15.804	−367.686	−319.419	27.808
700	59.768	119.300	88.463	21.586	−366.698	−311.447	23.240
800	64.455	127.583	92.840	27.794	−365.263	−303.647	19.826
823.000	65.333	129.422	93.837	29.287	CRYSTAL <--> LIQUID		
823.000	65.270	150.876	93.837	46.944	TRANSITION		
900	65.270	156.714	98.970	51.969	−345.861	−297.701	17.278
1000	65.270	163.591	105.094	58.496	−344.107	−292.444	15.276
1100	65.270	169.812	110.700	65.023	−342.352	−287.363	13.646
1200	65.270	175.491	115.866	71.550	−340.597	−282.441	12.294
1300	65.270	180.715	120.656	78.078	−338.843	−277.666	11.157
1400	65.270	185.552	125.121	84.605	−337.086	−273.026	10.187
1500	65.270	190.056	129.301	91.132	−335.326	−268.511	9.350
1600	65.270	194.268	133.231	97.659	−333.563	−264.115	8.622
1700	65.270	198.225	136.939	104.186	−477.034	−252.652	7.763
1800	65.270	201.956	140.449	110.713	−474.514	−239.526	6.951
1900	65.270	205.485	143.780	117.240	−472.004	−226.539	6.228
2000	65.270	208.833	146.949	123.767	−469.503	−213.685	5.581

PREVIOUS: CURRENT: June 1966

$S°(298.15\ K) = 224.345\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -146.3 \pm 13\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -154.0 \pm 13\ kJ·mol^{-1}$

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

$\omega_e = 563.16\ cm^{-1}$ $\omega_e x_e = 3.53\ cm^{-1}$ $\sigma = 1$
$B_e = 0.56112\ cm^{-1}$ $\alpha_e = 0.00573\ cm^{-1}$ $r_e = 2.1704$ Å

Enthalpy of Formation

$\Delta_f H°$(LiBr, g, 298.15 K) = −36.8 ± 3 kcal·mol^{-1} (−153.971 ± 13 kJ·mol^{-1}) is calculated from the selected enthalpy of vaporization and the enthalpy of formation for lithium bromide (l) Lithium bromide vaporizes to a mixture of monomeric and dimeric gases. (Higher polymers have been neglected in the calculation.) The enthalpies of vaporization to monomer and to dimer were chosen to satisfy (1) the total vapor pressure data measured by von Wartenberg and Schulz[1] and by Ruff and Mugdan,[2] the partial vapor pressures of monomer and dimer derived from Miller and Kusch[3] in an analysis of the velocity distribution of molecules in alkali halide vapor. The selected enthalpies of vaporization are $\Delta_{vap}H°$(larwrtlmonomer, 298 15 K) = 44.0 ± 3 kcal·mol^{-1} and $\Delta_{vap}H°$(l→dimer, 298.15 K) = 42.0 ± 5 kcal·mol^{-1} which combine with the enthalpy of formation of lithium bromide (l), $\Delta_f H°(298.15\ K) = -80.84$ kcal·mol^{-1}, to give the standard enthaply of formation of LiBr(g) and $Li_2Br_2(g)$ − 36.8 and −119.7 kcal mol^{-1} (−153.971 and −500.825 kJ·mol^{-1}), respectively. The derived enthaply of dissociation is $\Delta_d H°$(298 15 K) = 46.0 kcal·mol^{-1} for $Li_2Br_2(g) \rightarrow 2LiBr(g)$.

Berkowitz *et al.*[4] have measured mass-spectrometrically the enthaply of dissociation $\Delta_r H°(850\ K) = 45.9$ kcal·mol^{-1}($\Delta_r H°(298.15\ K) = 46.9$ kcal·mol^{-1}) for $Li_2Br_2(g) \rightarrow 2LiBr(g)$ in a double oven apparatus by the 2nd law method. Hildenbrand *et al.*[5] have determined mass-spectrometrically the enthaply of sublimation of lithium bromide by the 2nd law method as $\Delta_{sub}H°$(cr → monomer, 740 K) = 46.9 and $\Delta_{sub}H°$(cr → dimer, 740 K) = 45 0 kcal·mol^{-1} (equivalent to $\Delta_{vap}H°$(l → monomer, 298.15 K) = 45.82 kcal·mol^{-1} and $\Delta_{vap}H°$(l → dimer, 298.15 K) = 41.93 kcal·mol^{-1}) These values are in reasonable agreement with those selected in the tabulation.

Heat Capacity and Entropy

The bond distance (r_e) was obtained from the microwave studies by Honig *et al.*[6] The vibrational constants (ω_e and $\omega_e x_e$) were determined from the infrared spectrum by Klemperer *et al.*[7] The rotational constants which have been corrected to the average isotopic species were obtained by Herbert *et al.*[8] using microwave spectra. Their data are in good agreement with those reported by Honig *et al.*[6] and Rusk and Gordy.[9]

The tabulated thermodynamic functions are in reasonable agreement with those calculated by Wilkins[10] who used slightly different molecular constants.

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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	−9.177	−146.271	−146.271	INFINITE
100	29.297	190.290	252.948	−6.266	−145.252	−160.854	84.022
200	31.695	211.235	227.385	−3.230	−146.508	−176.048	45.979
250	32.974	218.450	224.899	−1.612	−147.426	−183.330	38.305
298.15	33.952	224.345	224.345	0.	−153.971	−189.498	33.199
300	33.985	224.555	224.345	0.063	−154.024	−189.718	33.033
350	34.753	229.854	224.762	1.782	−169.893	−194.785	29.070
400	35.336	234.534	225.697	3.535	−170.392	−198.308	25.896
450	35.785	238.724	226.916	5.314	−170.958	−201.764	23.420
500	36.136	242.513	228.289	7.112	−174.594	−204.847	21.400
600	36.646	249.149	231.228	10 753	−175.796	−210.783	18.350
700	36.995	254.826	234.204	14 436	−176.908	−216.525	16.157
800	37.252	259.784	237.098	18.149	−177.967	−222.112	14.502
900	37.451	264.183	239.867	21.884	−179.005	−227.568	13.208
1000	37.614	268.138	242.500	25.638	−180.024	−232.909	12.166
1100	37.752	271.729	244.996	29.406	−181.029	−238.148	11.309
1200	37.873	275.020	247.363	33.188	−182 019	−243.297	10.590
1300	37.981	278.055	249.609	36.980	−182.999	−248.364	9.979
1400	38.081	280.874	251.743	40.784	−183.966	−253.356	9.453
1500	38.174	283.504	253.773	44.596	−184.921	−258.279	8.994
1600	38.261	285.971	255 709	48.418	−185.863	−263.139	8.591
1700	38.345	288.293	257.559	52.248	−332.030	−260.764	8.012
1800	38.425	290.487	259.327	56 087	−332.199	−256.567	7.445
1900	38.503	292.567	261 023	59 933	−332.369	−252.360	6.938
2000	38.579	294.543	262.650	63.788	−332.541	−248.145	6.481
2100	38.653	296.428	264 214	67 649	−332.718	−243.920	6.067
2200	38.726	298.227	265 719	71.518	−332 901	−239 688	5.691
2300	38 798	299.950	267 170	75.394	−333.093	−235.447	5.347
2400	38.869	301.603	268.571	79.278	−333.295	−231.197	5.032
2500	38.939	303.191	269 924	83.168	−333.508	−226.938	4.742
2600	39.008	304.720	271.233	87.065	−333.736	−222.671	4.474
2700	39.077	306.193	272.501	90 970	−333.978	−218.395	4.225
2800	39 145	307.616	273 730	94.881	−334.236	−214 109	3.994
2900	39.213	308.990	274 922	98.799	−334.512	−209.814	3.779
3000	39.280	310.321	276 080	102.723	−334.806	−205.509	3.578
3100	39.347	311.610	277.205	106.655	−335.119	−201.194	3.390
3200	39 414	312.860	278.300	110.593	−335.451	−196.869	3.214
3300	39.480	314.074	279.366	114.537	−335.803	−192.533	3.048
3400	39.546	315.254	280.404	118.489	−336.175	−188.186	2.891
3500	39.612	316.401	281.416	122.447	−336.568	−183.828	2.743
3600	39.678	317.518	282.404	126.411	−336.981	−179.458	2.604
3700	39.744	318.606	283.367	130.382	−337.415	−175.076	2.472
3800	39.810	319.667	284.309	134.360	−337.870	−170.683	2.346
3900	39.875	320.702	285.229	138.344	−338.346	−166.277	2.227
4000	39.940	321.712	286.128	142.335	−338.843	−161.858	2.114
4100	40.005	322.699	287.008	146.332	−339.363	−157.427	2.006
4200	40.071	323.664	287.870	150.336	−339.905	−152.983	1.903
4300	40.136	324.607	288 713	154.346	−340.470	−148.526	1.804
4400	40.201	325.531	289.539	158.363	−341.038	−144.057	1.710
4500	40.265	326.435	290.349	162.386	−341.641	−139.574	1.620
4600	40.330	327.321	291.143	166.416	−342.270	−135.077	1.534
4700	40.395	328.189	291.922	170.452	−342.925	−130.566	1.451
4800	40.460	329.040	292.687	174.495	−343.605	−126.040	1.372
4900	40.524	329.875	293.437	178.544	−344.311	−121.500	1.295
5000	40.589	330.694	294.174	182.600	−345.046	−116.946	1.222
5100	40.653	331.499	294.898	186.662	−345.805	−112.377	1.151
5200	40.718	332.289	295.610	190.731	−346.598	−107.792	1.083
5300	40.782	333.065	296.309	194.806	−347.424	−103.192	1.017
5400	40.847	333.828	296.997	198.887	−348.283	−98.575	0.954
5500	40.911	334.578	297.673	202.975	−349.177	−93.943	0.892
5600	40.976	335.316	298.339	207.069	−350.108	−89.294	0.833
5700	41.040	336.041	298.994	211 170	−351.077	−84.628	0.776
5800	41.104	336.756	299.639	215.277	−352.086	−79.945	0.720
5900	41.169	337.459	300.274	219.391	−353.137	−75.244	0.666
6000	41.233	338.151	300.900	223.511	−354.231	−70.525	0.614

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

$S°(298.15\ K) = 244.95 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -27.7 \pm 41.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -35.3 \pm 41.8\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A_1{}^2\Pi_{1/2}$	25765.2	2
$A_2{}^2\Pi_{3/2}$	25876.3	2
$B[^2\Sigma]$	[26500]	2
$C[^2\Sigma]$	39285.9	2

$\omega_e = 373.2\ cm^{-1}$ $\omega_e x_e = 1.34\ cm^{-1}$ $\sigma = 1$
$B_e = 0.16241\ cm^{-1}$ $\alpha_e = [0.00079]\ cm^{-1}$ $r_e = 2.36 \pm 0.10$ Å

Enthaply of Formation

No thermochemical measurement of the enthaply of formation has been made. The selected value, $\Delta_f H°$(MgBr, g, 0 K) = -6.611 ± 10.0 kcal·mol^{-1} (-27.660 kJ·mol^{-1}), is based on an analysis of spectroscopic data. Herzberg[1] obtained the value $D_0° \leq 3.35$ eV from predissociation which sets in above ν_3 = of A Π^2 state. Gaydon[2] recommended $D_0° = 3.2 \pm 1.0$ eV which was obtained from a linear Birge–Sponer extrapolation of the ground state vibrational levels (ν, 0–6). Our adopted vibrational constants give this same value by a similar extrapolation. The linear Birge–Sponer $D_0°$ value adjusts to 3.03 eV (69.79 kcal·mol^{-1}) when corrected for the ionic character of the Mg–Br bond by the method suggested by Hildenbrand.[3] This adjusted $D_0°$ value is adopted and corresponds to $\Delta_f H°(298.15\ K)$ of -35.3 kJ·mol^{-1}.

Two lower values of $D_0°$ have been reported from results of ionic model calculations.[4,5] Margrave[4] calculated an ionic binding energy of 135 kcal·mol^{-1} which gives $D_0° = 1.75$ eV. Krasnov and Karaseva,[5] using a Rittner potential function[6], found $D_0° = 2.39$ eV which probably represents a minimum value. In addition, we find $D_0°$(MgBr, g, 298.15 K)/$\Delta_{at}H°(MgBr_2, g, 298.15\ K) = 0.44$ which is quite consistent with values of this ratio for other alkaline–earth halides.[7] This consistency provides further support for our adopted results. An estimated uncertainty of ± 10.0 kcal·mol^{-1} (41.8 kJ·mol^{-1}) is believed to be realistic.

Heat Capacity and Entropy

Values for the ground state vibrational constants and bond length are taken from the tabulation of Rosen.[8] The adopted value of r_e which was obtained from a rotational analysis of the (0,0) bands of the $A^2\Pi$–$X^2\Sigma$ system by Patel and Patel[9,10] gives $r_e(MgBr)/r_e(MgBr_2) = 1.01$. Comparison of values for this ratio for several alkaline–earth halides[7] shows that $r_e(MX)/r_e(MX_2)$ is generally slightly less than one (~0.96). This suggests that the uncertainty in r_e(MgBr) may be as high as 0.1 Å, assuming r_e for $MgBr_2$ is correct.[7] The value of B_e is calculated from r_e. α_e is obtained from the other constants assuming a Morse potential function.

The electronic levels except for the two uppe most states are from Rosen.[8] We estimate a $^2\Sigma$ state to lie at 26500 cm^{-1} by analogy with those observed for CaBr and SrBr.[7] The assignment o the level at 39285.9 cm^{-1} is rather uncertain. Rosen[8] has assigned this level as a $C^2\Pi$ state. Very recently, Reddy and Rao[11] observed that the bands were single–headed, and they attributed the system to a $C^2\Sigma$–$X^2\Sigma$ transition by analogy with that for MgF. Comparison of the observed spectra for MgCl, CaBr, SrBr, and BaBr[7] suggests yet another assignment. It appears likely that the observed level near 40000 cm^{-1} arises from a $D^2\Sigma$–$X^2\Sigma$ transition, and the $C^2\Pi$ state, estimated to lie near 30000 cm^{-1}, has gone unobserved. We tentatively adopt the assignment of Reddy and Rao.[11] However, thermodynamic functions based on the alternate assignments are not significantly different from those adopted, below 4500 K.

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^{-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	−9.580	−27.670	−27.670	INFINITE
100	30.272	208.838	275.326	−6.649	−26.777	−44.018	22.993
200	33.916	231.036	248.160	−3.425	−28.011	−60.847	15.892
250	34.967	238.726	245.529	−1.701	−28.865	−68.960	14.408
298.15	35.639	244.946	244.946	0.	−35.342	−75.942	13.305
300	35.660	245.166	244.947	0.066	−35.392	−76.194	13.266
350	36.132	250.701	245.383	1.861	−51.184	−82.118	12.255
400	36.467	255.549	246.357	3.677	−51.577	−86.511	11.297
450	36.715	259.859	247.622	5.507	−51.988	−90.853	10.546
500	36.904	263.738	249.043	7.347	−52.418	−95.148	9.940
600	37.173	270.491	252.071	11.052	−53.341	−103.609	9.020
700	37.359	276.236	255.123	14.779	−54.355	−111.908	8.351
800	37.498	281.235	258.081	18.522	−55.476	−120.055	7.839
900	37.609	285.658	260.904	22.278	−56.721	−128.054	7.432
1000	37.703	289.625	263.582	26.044	−66.699	−135.195	7.062
1100	37.785	293.223	266.115	29.818	−68.247	−141.969	6.742
1200	37.860	296.514	268.513	33.601	−69.791	−148.603	6.469
1300	37.928	299.547	270.785	37.390	−71.333	−155.108	6.232
1400	37.993	302.360	272.941	41.186	−200.282	−158.328	5.907
1500	38.054	304.983	274.991	44.989	−200.467	−155.324	5.409
1600	38.113	307.441	276.943	48.797	−200.652	−152.309	4.972
1700	38.171	309.754	278.806	52.611	−200.837	−149.282	4.587
1800	38.227	311 937	280.586	56.431	−201.023	−146.244	4.244
1900	38.281	314 005	282.291	60.256	−201.210	−143.195	3.937
2000	38.335	315.970	283.927	64.087	−201.401	−140.137	3.660
2100	38.389	317.842	285.497	67.923	−201.596	−137.069	3.409
2200	38.441	319.629	287.009	71.765	−201.796	−133.992	3.181
2300	38.493	321.339	288.464	75.612	−202.001	−130.905	2.973
2400	38.545	322.978	289.868	79.464	−202.214	−127.809	2.782
2500	38.597	324.553	291.225	83.321	−202.434	−124.705	2.606
2600	38.649	326.068	292.536	87.183	−202.662	−121.591	2.443
2700	38.702	327.527	293.805	91.051	−202.898	−118.468	2.292
2800	38.755	328.936	295.034	94.924	−203.142	−115.337	2.152
2900	38.808	330.297	296.227	98.802	−203.396	−112.197	2.021
3000	38.863	331.613	297.385	102.685	−203.658	−109.047	1.899
3100	38.919	332.888	298.510	106.574	−203.930	−105.889	1.784
3200	38.976	334.125	299.603	110.469	−204.211	−102.722	1.677
3300	39.035	335.325	300.668	114.370	−204.501	−99.546	1.576
3400	39.097	336.491	301.704	118.276	−204.801	−96.361	1.480
3500	39.161	337.626	302.715	122.189	−205.111	−93.168	1.390
3600	39.228	338.730	303.700	126.108	−205.431	−89.965	1.305
3700	39.298	339.806	304.661	130.035	−205.761	−86.753	1.225
3800	39.372	340.855	305.600	133.968	−206.103	−83.532	1.148
3900	39.450	341.878	306.517	137.909	−206.457	−80.302	1.076
4000	39.531	342.878	307.413	141.858	−206.823	−77.062	1.006
4100	39.618	343.855	308.290	145.816	−207.203	−73.813	0.940
4200	39.708	344.811	309.149	149.782	−207.597	−70.555	0.877
4300	39.804	345.746	309.989	153.757	−208.006	−67.288	0.817
4400	39.905	346 663	310.812	157.743	−208.432	−64.010	0.760
4500	40.011	347.561	311.619	161.739	−208.874	−60.723	0.705
4600	40.123	348.441	312.410	165.745	−209.334	−57.426	0.652
4700	40.239	349.305	313.186	169.763	−209.814	−54.118	0.601
4800	40.362	350 154	313.947	173.793	−210.314	−50.800	0.553
4900	40.490	350.987	314.694	177.836	−210.835	−47.472	0.506
5000	40.623	351.807	315.428	181.891	−211.379	−44.132	0.461
5100	40.762	352.612	316.150	185.961	−211.946	−40.782	0.418
5200	40.907	353.405	316.858	190.044	−212.538	−37.420	0.376
5300	41.056	354.186	317.555	194.142	−213.155	−34.046	0.336
5400	41.212	354.955	318.241	198.256	−213.799	−30.661	0.297
5500	41.372	355.713	318.915	202.385	−214.470	−27.263	0.259
5600	41.537	356.459	319.579	206.530	−215.170	−23.853	0.222
5700	41 707	357 196	320.233	210.692	−215.899	−20.430	0.187
5800	41.882	357.923	320.876	214.872	−216.659	−16.995	0.153
5900	42.062	358.641	321.510	219.069	−217.450	−13.546	0.120
6000	42.245	359.349	322.135	223.284	−218.273	−10.083	0.088

PREVIOUS: June 1975 (1 atm) CURRENT: June 1975 (1 bar)

$S°(298.15)$ = [269.52 ± 8] J·K^{-1}·mol^{-1}

$\Delta_f H°(0\ K)$ = [464.4 ± 42] kJ·mol^{-1}
$\Delta_f H°(298.15)$ = [457.3 ± 42] kJ·mol^{-1}

Electronic Levels and Quantum Weights					
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[6]	[15199]	[6]	[15890]	[2]
[11783]	[2]	[15331]	[8]	[16796]	[2]
[12034]	[4]	[15428]	[10]	[16947]	[8]
[12417]	[6]	[15447]	[12]	[17174]	[4]
[12900]	[8]	[15691]	[6]	[17344]	[6]
[13461]	[10]	[15699]	[4]		

ω_e = [300] cm^{-1} $\omega_e x_e$ = [0.7] cm^{-1} σ = 1
B_e = [0.066] cm^{-1} α_e = [0.0002] cm^{-1} r_e = [2.42] Å

Enthaply of Formation

The adopted value of $\Delta_f H°(298.15\ K)$ is that estimated by Brewer[1] using bonding models. The value of $\Delta_f H°(0\ K)$ combined with JANAF data[2] for Mo(g) and Br(g) gives $D°_0$(Mo–Br) = 310.87 ± 42 kJ·mol^{-1}. This value of the bond dissociation energy agrees favorably with the mean Mo–Br bond energy $\Delta_{at} H°(MoBr_4, g, 0\ K)/4$ = 317.98 kJ·mol^{-1}.[2]

Enthaply Capacity and Entropy

The Mo–Br bond length of 2.42 Å and the ground state vibrational frequency of 300 cm^{-1} are estimates from Brewer.[1] The electronic contributions are assumed to be the same as those of the free gaseous ion, Mo^+, as suggested by Brewer.[1] All states up to 17,344 cm^{-1} as listed by Moore[3] are included in the calculation. Our thermodynamic functions differ slightly from those reported by Brewer[1] due to the use of non–zero values for $\omega_e x_e$ and α_e. Estimates for α_e and $\omega_e x_e$ are based on the empirical correlations of Calder and Ruedenberg.[4]

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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})	$S°-[G°-H°(T_r)]/T$ (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	−9.796	464.355	464.355	INFINITE
100	31.264	232.325	300.685	−6.836	465.427	445.589	−232.752
200	34.897	255.303	272.802	−3.500	464.470	426.047	−111.272
250	35.718	263.186	270.117	−1.733	463.711	416.526	−87.028
298.15	36.214	269.523	269.523	0.	457.311	408.172	−71.510
300	36.229	269.747	269.524	0.067	457.264	407.867	−71.016
350	36.566	275.359	269.966	1.887	441.545	400.504	−59.772
400	36.800	280.258	270.953	3.722	441.223	394.663	−51.538
450	36.971	284.603	272.233	5.566	440.882	388.863	−45 138
500	37.101	288.505	273.668	7.418	440.525	383.102	−40 022
600	37.285	295.287	276.723	11.138	439.769	371.687	−32.358
700	37.413	301.044	279.796	14.874	438.962	360.404	−26.894
800	37.509	306.047	282.772	18.620	438.111	349.239	−22.803
900	37.587	310.469	285.608	22.375	437.217	338.183	−19.628
1000	37.653	314.433	288.296	26.137	436.280	327.229	−17.093
1100	37.712	318.024	290.838	29.905	435.294	316.371	−15.023
1200	37.768	321.308	293.242	33.679	434.254	305.605	−13.303
1300	37.822	324.333	295.519	37.459	433.152	294.929	−11.850
1400	37.880	327.138	297.679	41.244	431.982	284.340	−10 609
1500	37.945	329.754	299.731	45 035	430.739	273.837	−9.536
1600	38.024	332.205	301.685	48.833	429.415	263.419	−8.600
1700	38.123	334.513	303.549	52.640	428.007	253.087	−7.776
1800	38.251	336 696	305.330	56.459	426.507	242.841	−7.047
1900	38.416	338 768	307.036	60.292	424.911	232.680	−6.397
2000	38.627	340 744	308.672	64.144	423.213	222.606	−5.814
2100	38.891	342.635	310.245	68.019	421.410	212.620	−5.289
2200	39.216	344.451	311.759	71.924	419.497	202.722	−4.813
2300	39.610	346.203	313.218	75.864	417.471	192.913	−4.381
2400	40.075	347.898	314.628	79.848	415.328	183.195	−3.987
2500	40.617	349.545	315.992	83.882	413.063	173.569	−3.627
2600	41.236	351.150	317.313	87.974	410.663	164.036	−3.296
2700	41.931	352.719	318.596	92.132	408.096	154.599	−2.991
2800	42.701	354.257	319.842	96.363	405.307	145.260	−2.710
2900	43.541	355.770	321.055	100.674	366.340	136.076	−2.451
3000	44 445	357.261	322.237	105.073	364.925	128.160	−2.231
3100	45.406	358.734	323.391	109.565	363.596	120.290	−2.027
3200	46.414	360.192	324.518	114.156	362.358	112.461	−1.836
3300	47.460	361.636	325.621	118.849	361.217	104.670	−1.657
3400	48.534	363.069	326.701	123.649	360.178	96.912	−1.489
3500	49.623	364.491	327.761	128.557	359.244	89.182	−1.331
3600	50.717	365.904	328.801	133.574	358.418	81.478	−1.182
3700	51.805	367.309	329.822	138.700	357.700	73.796	−1.042
3800	52.875	368.705	330.827	143.934	357.091	66.131	−0.909
3900	53.916	370.092	331.816	149.274	356.590	58.481	−0.783
4000	54.920	371.469	332.790	154.716	356.194	50.842	−0.664
4100	55.877	372.837	333.751	160.256	355.901	43.212	−0.551
4200	56.781	374.195	334.697	165.890	355.707	35.588	−0.443
4300	57.624	375.541	335.632	171.611	355.606	27.968	−0.340
4400	58.401	376.875	336.554	177.412	355.593	20.349	−0.242
4500	59.109	378.195	337.465	183.289	355.662	12.729	−0.148
4600	59.744	379.502	338.364	189.232	355.807	5.107	−0.058
4700	60.306	380.793	339.253	195.235	356.020	−2.520	0.028
4800	60.793	382.067	340.132	201.290	356.296	−10.151	0.110
4900	61.205	383.325	341.001	207.391	356.626	−17.788	0.190
5000	61.545	384.565	341.860	213.529	−234.380	−19.702	0.206
5100	61.815	385.787	342.709	219.698	−235.641	−15.396	0.158
5200	62.016	386.989	343.549	225.890	−237.013	−11.064	0.111
5300	62.153	388.172	344.380	232.099	−238.501	−6.705	0 066
5400	62.229	389.335	345.202	238.318	−240.111	−2.317	0.022
5500	62.248	390.477	346.014	244.543	−241.844	2.102	−0.020
5600	62.214	391.598	346.818	250.766	−243.706	6.554	−0.061
5700	62.131	392.699	347.614	256.984	−245.697	11.041	−0.101
5800	62.004	393.778	348.400	263.191	−247.820	15.563	−0.140
5900	61.837	394.837	349.178	269.383	−250.074	20.123	−0.178
6000	61.634	395.874	349.948	275.557	−252.464	24.722	−0.215

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

$S°(298.15\ K) = 235.48 \pm 0.4\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 308.4 \pm 21\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 300.8 \pm 21\ kJ·mol^{-1}$

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

$\omega_e = 699.1\ cm^{-1}$ $\omega_e x_e = 4.7\ cm^{-1}$ $\sigma = 1$
$B_e = 0.443\ cm^{-1}$ $\alpha_e = 0.00399\ cm^{-1}$ $r_e = 1.79$ Å

Enthaply of Formation

Miller and Dunford[1] have extrapolated the ground state vibrational levels and obtain $D_0^o = 67 \pm 5$ kcal·mol^{-1} or $\Delta_f H°(0\ K) = 73.7 \pm 5$ kcal·mol^{-1} (308.361 ± 21 kJ·mol^{-1}).

Heat Capacity and Entropy

Miller and Dunford[1] give all the vibrational and rotational constants, which have been adjusted to the normally occurring isotopic mixture for bromine.

Reference

[1]R. V. Miller and H. B. Dunford, J. Chem. Phys. 35, 1202 (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	−8.989	308.359	308.359	INFINITE
100	29.149	202.331	263.129	−6.080	308.421	298.871	−156.114
200	30.586	222.859	238.409	−3.110	307.484	289.653	−75.650
250	31.724	229.806	236.015	−1.552	306.907	285.261	−59.602
298.15	32.730	235.482	235.482	0.	300.758	281.804	−49.371
300	32.766	235.685	235.483	0.061	300.722	281.686	−49.046
350	33.634	240.803	235.885	1.721	285.329	279.359	−41.692
400	34.334	245.342	236.789	3.421	285.384	278.502	−36.369
450	34.892	249.419	237.969	5.152	285.462	277.638	−32.227
500	35.339	253.119	239.302	6.909	285.556	276.763	−28.913
600	35.997	259.625	242.162	10.478	285.774	274.985	−23.940
700	36.449	265.209	245.065	14.101	286.007	273.168	−20.384
800	36.774	270.099	247.895	17.763	286.237	271.318	−17.715
900	37.019	274.445	250.608	21.453	286.457	269.440	−15.638
1000	37.211	278.356	253.190	25.165	286.662	267.538	−13.975
1100	37.368	281.910	255.642	28.894	286.851	265.617	−12.613
1200	37.499	285.167	257.969	32.638	287.024	263.678	−11.478
1300	37.613	288.173	260.178	36.394	287.183	261.726	−10.516
1400	37.713	290.964	262.279	40.160	287.328	259.763	−9.692
1500	37.803	293.569	264.279	43.936	287.460	257.789	−8.977
1600	37.885	296.012	266.187	47.720	287.580	255.807	−8.351
1700	37.961	298.311	268.009	51.513	287.690	253.818	−7.799
1800	38.032	300.483	269.754	55.312	287.788	251.822	−7.308
1900	38.100	302.541	271.425	59.119	287.875	249.822	−6.868
2000	38.165	304.497	273.031	62.932	287.951	247.817	−6.472
2100	38.226	306.360	274.574	66.752	288.016	245.809	−6.114
2200	38.286	308.140	276.059	70.577	288.070	243.798	−5.788
2300	38.345	309.843	277.491	74.409	288.112	241.784	−5.491
2400	38.401	311.476	278.874	78.246	288.143	239.769	−5.218
2500	38.457	313.045	280.209	82.089	288.163	237.753	−4.968
2600	38.511	314.554	281.501	85.938	288.171	235.737	−4.736
2700	38.565	316.009	282.753	89.791	288.170	233.720	−4.522
2800	38.617	317.412	283.966	93.651	288.158	231.703	−4.322
2900	38.670	318.768	285.142	97.515	288.138	229.688	−4.137
3000	38.721	320.080	286.285	101.384	288.110	227.672	−3.964
3100	38.772	321.351	287.396	105.259	288.076	225.658	−3.802
3200	38.823	322.582	288.476	109.139	288.036	223.646	−3.651
3300	38.873	323.778	289.528	113.024	287.993	221.634	−3.508
3400	38.923	324.939	290.553	116.913	287.948	219.624	−3.374
3500	38.972	326.068	291.551	120.808	287.901	217.615	−3.248
3600	39.021	327.167	292.525	124.708	287.856	215.607	−3.128
3700	39.070	328.236	293.476	128.612	287.812	213.601	−3.016
3800	39.119	329.279	294.405	132.522	287.772	211.596	−2.909
3900	39.168	330.296	295.312	136.436	287.737	209.592	−2.807
4000	39.216	331.288	296.199	140.355	287.707	207.589	−2.711
4100	39.264	332.257	297.067	144.279	287.685	205.586	−2.619
4200	39.312	333.204	297.916	148.208	287.671	203.584	−2.532
4300	39.360	334.129	298.747	152.142	287.666	201.582	−2.449
4400	39.408	335.035	299.562	156.080	287.671	199.580	−2.369
4500	39.456	335.921	300.360	160.023	287.687	197.577	−2.293
4600	39.503	336.789	301.143	163.971	287.714	195.575	−2.221
4700	39.551	337.639	301.910	167.924	287.753	193.571	−2.151
4800	39.598	338.472	302.663	171.882	287.805	191.567	−2.085
4900	39.646	339.289	303.402	175.844	287.870	189.561	−2.021
5000	39.693	340.090	304.128	179.811	287.948	187.554	−1.959
5100	39.740	340.877	304.841	183.782	288.039	185.546	−1.900
5200	39.787	341.649	305.541	187.759	288.144	183.535	−1.844
5300	39.834	342.407	306.230	191.740	288.263	181.522	−1.789
5400	39.881	343.152	306.907	195.726	288.396	179.507	−1.736
5500	39.928	343.884	307.572	199.716	288.543	177.489	−1.686
5600	39.975	344.604	308.227	203.711	288.704	175.468	−1.637
5700	40.022	345.312	308.872	207.711	288.879	173.445	−1.589
5800	40.069	346.009	309.506	211.716	289.067	171.418	−1.544
5900	40.116	346.694	310.130	215.725	289.268	169.388	−1.500
6000	40.163	347.369	310.746	219.739	289.483	167.354	−1.457

PREVIOUS December 1962 (1 atm) CURRENT December 1962 (1 bar)

$S°(298\ 15\ K) = 273.52\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 91.41 \pm 0.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 82.13 \pm 0.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1801(1)
542 (1)
[265](1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: C_s
Bond Distances: O–N = 1.15 ± 0.04 Å; N–Br = 2.14 ± 0.02 Å
Bond Angle: O–N–Br = 117 ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = 5.16414 \times 10^{-115}\ g^3·cm^6$

Enthaply of Formation

The chemical equilibrium of the reaction $2NO(g) + Br_2(g) = 2NOBr(g)$ has been studied by Trautz and Dalal,[1] Blair *et al.*,[2] and Krauss.[3] Using the reported equilibrium constants, the enthalpy changes $\Delta_r H°(298.15\ K)$, of this reaction are evaluated by both the 2nd and 3rd law methods. Based on the 3rd law $\Delta_r H°(298.15\ K)$ values, the enthaplies of formation for NOBr(g) are derived. The results obtained are presented in the table below. The value of $\Delta_f H°$(NOBr, g, 298 15 K) adopted is 19.63 ± 0.2 kcal·mol^{-1} (82.132 ± 0.8 kJ·mol^{-1}).

Source	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}
Trautz and Dalal[1]	*	258.2 – 603.2	−11.11	−11.30	−0.4	19.62
Blair *et al.*[2]	30	296.9 – 502.9	−11.74 + 0.07	−11.26	1.3 ± 0.2	19.64
Krauss[3]	23	264.0 – 290.1	−13.46 + 0.30	−9.62	−13.7 ± 1.1	20.46

*The data points employed for evaluation are calculated from a given equation.

Heat Capacity and Entropy

The molecular structure of NOBr(g) has been determined by electron diffraction by Ketelaar and Palmer.[4] The results were confirmed later by Weatherly and Williams,[5] who studied the microwave spectrum of NOBr(g) in the region 20000–40000 Mc/sec and analyzed the J = 2 → 3 transition. The values of bond length and angle adopted are obtained from Ketelaar and Palmer.[4] The infrared absorption spectrum of NOBr(g) has been examined from 400 to 5303 cm^{-1} by Burns and Bernstein.[6] The authors observed the first two fundamental vibrational frequencies and obtained the third from combination and overtones. These assignments are adopted. The principal moments of inertia are: $I_A = 0.9405 \times 10^{-39}$, $I_B = 22.9668 \times 10^{-39}$, and $I_C = 23.9093 \times 10^{-39}$ g·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^{-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	−11.654	91.410	91.410	INFINITE
100	36.257	228.950	311.488	−8.254	90.510	86.963	−45.425
200	42.124	256.017	277.590	−4.315	89.087	83.973	−21.931
250	44.073	265.637	274.266	−2.157	88.380	82.775	−17.295
298.15	45.473	273.525	273.525	0.	82.132	82.417	−14 439
300	45.520	273.806	273.526	0.084	82.092	82.419	−14.350
350	46.660	280.912	274.084	2.390	66.605	83.326	−12.436
400	47.623	287.207	275.339	4.747	66.571	85.717	−11.194
450	48.480	292.866	276.977	7.150	66.562	88.111	−10.228
500	49.264	298.015	278.827	9.594	66.573	90.505	−9.455
600	50.656	307.124	282.804	14.592	66.639	95.286	−8.295
700	51.831	315.023	286.855	19.718	66.748	100.053	−7.466
800	52.807	322.010	290.821	24.951	66.881	104.802	−6.843
900	53.609	328.278	294.640	30.274	67.031	109.533	−6.357
1000	54.266	333.961	298.293	35.668	67.187	114.247	−5.968
1100	54.804	339.159	301.775	41.123	67.347	118.945	−5.648
1200	55.248	343.947	305.092	46.626	67.506	123.629	−5.381
1300	55.615	348.385	308.254	52.170	67.660	128.300	−5.155
1400	55.922	352.518	311.270	57.747	67.809	132.959	−4.961
1500	56.179	356.385	314.150	63.352	67.951	137.607	−4.792
1600	56.397	360.018	316.904	68.982	68.082	142.247	−4.644
1700	56.583	363.443	319.542	74.631	68.202	146.878	−4.513
1800	56.742	366.681	322.072	80.297	68.309	151.503	−4.396
1900	56.880	369.753	324.501	85.979	68.402	156.122	−4.292
2000	57.000	372.674	326.837	91.673	68.477	160.737	−4.198
2100	57 104	375.457	329.087	97.378	68.535	165.349	−4.113
2200	57.196	378.116	331.255	103.093	68.575	169.958	−4.035
2300	57.276	380.660	333.349	108.817	68.594	174.566	−3.965
2400	57.348	383.099	335.371	114.548	68.592	179.173	−3.900
2500	57.412	385.442	337.327	120.286	68.569	183.781	−3.840
2600	57.469	387.695	339.222	126.030	68.525	188.390	−3.785
2700	57.520	389.864	341.057	131.780	68.461	193.002	−3.734
2800	57.566	391.957	342.838	137.534	68.375	197.616	−3.687
2900	57.607	393.978	344.567	143.293	68.271	202.233	−3.643
3000	57.645	395.932	346.247	149.055	68.147	206.855	−3.602
3100	57.679	397.822	347.880	154.821	68.007	211.481	−3.563
3200	57.710	399.654	349.469	160.591	67.850	216.111	−3.528
3300	57.739	401.430	351.017	166.363	67.679	220.747	−3.494
3400	57.765	403.154	352.525	172.139	67.495	225.388	−3.463
3500	57.789	404.829	353.996	177.916	67.300	230.034	−3.433
3600	57.811	406.457	355.431	183.696	67.095	234.687	−3.405
3700	57.831	408.042	356.831	189.478	66.882	239.345	−3.379
3800	57.850	409.584	358.199	195.262	66.662	244.010	−3.354
3900	57.867	411.087	359.536	201.048	66.437	248.680	−3.331
4000	57.884	412.552	360.843	206.836	66.208	253.355	−3.308
4100	57.899	413.982	362.122	212.625	65.977	258.037	−3.287
4200	57.913	415.377	363.374	218.416	65.744	262.724	−3.267
4300	57.926	416.740	364.599	224.207	65.510	267.417	−3.248
4400	57.938	418.072	365.799	230.001	65.277	272.115	−3.230
4500	57 949	419.374	366.975	235.795	65.045	276.818	−3.213
4600	57.960	420.648	368.128	241.590	64.815	281.527	−3.197
4700	57.970	421.895	369.259	247.387	64.587	286.240	−3.181
4800	57.979	423.115	370.368	253.184	64.361	290.959	−3.166
4900	57.988	424.311	371.457	258.983	64.138	295.682	−3.152
5000	57.996	425.482	372.526	264.782	63.918	300.410	−3.138
5100	58.004	426.631	373.576	270.582	63.701	305.142	−3.125
5200	58.012	427.757	374.607	276.383	63.486	309.878	−3.113
5300	58.019	428.862	375.620	282.184	63.274	314.619	−3.101
5400	58.025	429.947	376.616	287.986	63.064	319.363	−3.089
5500	58.032	431.012	377.595	293.789	62.856	324.111	−3.078
5600	58.037	432.057	378.559	299.593	62.650	328.863	−3.068
5700	58.043	433.085	379.506	305.397	62.444	333.618	−3.057
5800	58.048	434.094	380.439	311.201	62.238	338.378	−3.047
5900	58.054	435.086	381.357	317.006	62.032	343.140	−3.038
6000	58.058	436.062	382.260	322.812	61.825	347.907	−3.029

PREVIOUS. December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°(298.15\ K) = 86.82 \pm 0.25\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1020\ K$

$\Delta_fH°(0\ K) = -354.30 \pm 0.42\ kJ·mol^{-1}$
$\Delta_fH°(298.15\ K) = -361.41 \pm 0.42\ kJ·mol^{-1}$
$\Delta_{fus}H° = 26.108\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of solution of NaBr(cr) in water has been measured by Askew *et al.*[1] and Wallace[2] to be +0.01 and −0.144 kcal·mol^{-1}, respectively Using $\Delta_fH°$(Na$^+$, aq, 298.15 K) = −57.39 and $\Delta_fH°$(Br$^-$, aq, 298.15 K) = −29.05 kcal·mol^{-1}, from Wagman,[3] the respective value of $\Delta_fH°$(298.15 K) for NaBr(cr) was found to be −86.3 and −86.45 kcal·mol^{-1}. The adopted value is the average of these two.

Heat Capacity and Entropy

The low temperature heat capacities (7.21–301.73 K) were measured by Gardner and Taylor.[4] The high temperature enthalpy changes (290–645, 290–816 K) were determined by Magnus.[5] Based upon the latter data, the high temperature heat capacities were derived. The two sets of $C_p°$ data were joined smoothly at 298.15 K by graphical method. $S°$(298.15 K) was obtained from Gardner and Taylor[4] using $S°(10\ K) = 0.034\ cal·K^{-1}·mol^{-1}$.

Fusion Data

T_{fus} and $\Delta_{fus}H°$ were reported by Dworkin and Bredig[6] The values, T_{fus} = 1014 K and $\Delta_{fus}H°$ = 5.52 kcal·mol^{-1}, reported by Blanc[7] were not used.

Sublimation Data

The value of $\Delta_{sub}H°$(298.15 K) was derived from six sets of vapor pressure data by both the 2nd and 3rd law methods. See 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^{-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	−11.590	−354.302	−354.302	INFINITE
100	40.166	35.606	130.332	−9.473	−354.921	−353.408	184.601
200	48.744	66.818	91.420	−4.920	−355.275	−351.758	91.870
298.15	51.400	86.818	86.818	0.	−361.414	−349.267	61.190
300	51.442	87.136	86.819	0.095	−361.441	−349.192	60.800
400	53.451	102.226	88.863	5.345	−379.052	−341.804	44.635
500	54.852	114.311	92.784	10.764	−378.581	−332.542	34.740
600	56.066	124.419	97.236	16.310	−377.911	−323.394	28.154
700	57.321	133.156	101.757	21.979	−377.063	−314.372	23.459
800	58.576	140.892	106.175	27.774	−376.054	−305.484	19.946
900	59.831	147.864	110.426	33.694	−374.903	−296.730	17.222
1000	61.086	154.232	114.492	39.740	−373.631	−288.111	15.049
1020.000	61.337	155.445	115.284	40.964	--- CRYSTAL <---> LIQUID ---		
1100	62.342	160.113	118.376	45.911	−372.260	−279.625	13.278
1200	63.597	165.592	122.085	52.208	−467.569	−268.827	11.702
1300	64.852	170.732	125.631	58.631	−465.125	−252.364	10.140
1400	66.107	175.584	129.027	65.179	−462.561	−236.093	8.809
1500	67.345	180.187	132.286	71.851	−459.877	−220.010	7.661
1600	68.618	184.573	135.418	78.649	−457.072	−204.109	6.663
1700	69.925	188.772	138.434	85.576	−454.144	−188.388	5.788
1800	71.267	192.807	141.343	92.635	−451.091	−172.843	5.016
1900	72.645	196.697	144.155	99.830	−447.910	−157.471	4.329
2000	74.057	200.459	146.876	107.165	−444.598	−142.270	3.716

PREVIOUS: CURRENT: September 1964

$S°(298.15\ K)$ = [104.363] $J·K^{-1}·mol^{-1}$
T_{fus} = 1020 K

$\Delta_f H°(298.15\ K)$ = [−339.343] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 26.108 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1020\ K)-H°(298.15\ K)$, between the crystal and liquid. The equilibrium constant of the reaction NaBr(l) + HCl(g) = NaCl(l) + HBr(g) has been determined by Toguri *et al* [1] From the reported data, ln K(800°C) = −1.19 ± 0.01, the enthalpy of reaction ($\Delta_r H°(298.15\ K)$) was derived to be 2.11 $kcal·mol^{-1}$. Using $\Delta_f H°$(HCl, g, 298.15 K) = −22 062, $\Delta_f H°$(NaCl, l, 298.15 K) = −92.24 and $\Delta_f H°$(HBr, g, 298.15 K) = 8.70 $kcal·mol^{-1}$, the value of $\Delta_f H°(298.15\ K)$ for NaBr(l) was evaluated to be −81.0 ± 0.5 $kcal·mol^{-1}$ which is in reasonable agreement with the value adopted. The values of $\Delta_f H°(298.15\ K)$ for HCl(g) and HBr(g) were obtained from Wagman.[2]

Heat Capacity and Entropy

Heat capacity for NaBr(l) is estimated by comparison with those for NaCl(cr), NaCl(l), AgCl(cr), and AgCl(l). The entropy 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 Dworkin and Bredig.[3] The values, T_{fus} = 1014 K and $\Delta_{fus}H°$ = 5.52 $kcal·mol^{-1}$, reported by Blanc,[4] were not used.

Vaporization Data

The boiling point, T_{vap}(l → monomer), is calculated as the temperature at which the value of $\Delta_r G° = 0$ for the reaction NaBr(l) → NaBr(g). The difference between $\Delta_f H°$ for NaBr(l) and NaBr(g) at T_{vap}(l → monomer) is the enthalpy of vaporization, $\Delta_{vap}H°$(l → monomer).

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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							
100							
200.							
298.15	62.342	104.363	104.363	0.	−339.343	−332.427	58.240
300	62.342	104 749	104.364	0.115	−339.350	−332.384	57.873
400	62.342	122.683	106.810	6.349	−355.977	−326.912	42.690
500	62.342	136.594	111.427	12.584	−354.690	−319.792	33.408
600	62.342	147 961	116.598	18.818	−353.332	−312.939	27.244
700	62.342	157.571	121.782	25.052	−351.919	−306.318	22.858
800	62.342	165.895	126 787	31.286	−350.470	−299.903	19.582
900	62.342	173.238	131.549	37.520	−349.005	−293.670	17 044
1000	62.342	179.806	136.052	43.754	−347.545	−287.600	15.023
1100	62.342	185.748	140.304	49.989	−346.111	−281.675	13.376
1200	62.342	191.172	144.320	56.223	−441.483	−273.439	11 902
1300	62.342	196.162	148.119	62.457	−439.228	−259.526	10.428
1400	62.342	200.782	151 717	68.691	−436.977	−245.788	9.170
1500	62.342	205 084	155.133	74.925	−434.731	−232.210	8.086
1600	62.342	209.107	158.382	81.159	−432.490	−218.781	7.142
1700	62.342	212.886	161.478	87.394	−430.256	−205.493	6.314
1800	62.342	216.450	164.434	93.628	−428.027	−192.336	5.581
1900	62.342	219.820	167.262	99.862	−425.807	−179.303	4.929
2000	62.342	223.018	169.970	106.096	−423.596	−166.386	4.346
2100	62.342	226.060	172.569	112.330	−421.395	−153.580	3.820
2200	62.342	228.960	175.067	118.564	−419.205	−140.878	3.345
2300	62.342	231.731	177.471	124 799	−417.028	−128.276	2.913
2400	62.342	234.384	179.787	131.033	−414.864	−115 768	2.520
2500	62.342	236.929	182.023	137.267	−412.716	−103.349	2.159

PREVIOUS: CURRENT September 1964

0	to	1020	K	crystal
above		1020	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°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−11.590	−354.302	−354.302	INFINITE
100	40.166	35.606	130.332	−9.473	−354.921	−353.408	184.601
200	48.744	66.818	91.420	−4.920	−355.275	−351.758	91.870
298.15	51.400	86.818	86.818	0.	−361.414	−349.267	61.190
300	51.442	87.136	86.819	0.095	−361.441	−349.192	60.800
400	53.451	102.226	88.863	5.345	−379.052	−341.804	44.635
500	54.852	114.311	92.784	10.764	−378.581	−332.542	34.740
600	56.066	124.419	97.236	16.310	−377.911	−323.394	28.154
700	57.321	133.156	101.757	21.979	−377.063	−314.372	23.459
800	58.576	140.892	106.175	27.774	−376.054	−305.484	19.946
900	59.831	147.864	110.426	33.694	−374.903	−296.730	17.222
1000	61.086	154.232	114.492	39.740	−373.631	−288.111	15.049
1020.000	61.337	155.445	115.284	40.964	CRYSTAL <--> LIQUID		
1020.000	62.342	181.041	115.284	67.072	TRANSITION		
1100	62.342	185.748	120.239	72.060	−346.111	−281.675	13.376
1200	62.342	191.172	125.928	78.294	−441.483	−273.439	11.902
1300	62.342	196.162	131.141	84.528	−439.228	−259.526	10.428
1400	62.342	200.782	135.952	90.762	−436.977	−245.788	9.170
1500	62.342	205.084	140.419	96.996	−434.731	−232.210	8.086
1600	62.342	209.107	144.588	103.230	−432.490	−218.781	7.142
1700	62.342	212.886	148.496	109.465	−430.256	−205.493	6.314
1800	62.342	216.450	152.173	115.699	−428.027	−192.336	5.581
1900	62.342	219.820	155.645	121.933	−425.807	−179.303	4.929
2000	62.342	223.018	158.935	128.167	−423.596	−166.386	4.346
2100	62.342	226.060	162.059	134.401	−421.395	−153.580	3.820
2200	62.342	228.960	165.035	140.635	−419.205	−140.878	3.345
2300	62.342	231.731	167.875	146.870	−417.028	−128.276	2.913
2400	62.342	234.384	170.591	153.104	−414.864	−115.768	2.520
2500	62.342	236.929	173.194	159.338	−412.716	−103.349	2.159

PREVIOUS: CURRENT: September 1964

$S°(298.15\ K) = 241.218\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -135.04 \pm 2.09\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -143.93 \pm 2.09\ kJ·mol^{-1}$

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

$\omega_e = 302.1 \pm 4\ cm^{-1}$ $\omega_e x_e = 1.50\ cm^{-1}$ $\sigma = 1$
$B_e = 0.1495\ cm^{-1}$ $\alpha_e = 0.000939\ cm^{-1}$ $r_e = 2.5020 \pm 0.0001$ Å

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was calculated from $\Delta_f H°(298.15\ K)$ and $\Delta_{sub} H°(298.15\ K)$ for NaBr(cr). The latter was derived by both the 2nd and 3rd law methods from six sets of vapor pressure data, corrected for the presence of dimer species in the vapor. The results are listed as follows.

Source	Reaction	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)^a$ kcal·mol^{-1}
Niwa[1]	NaBr(cr) → NaBr(g)	50.31	51.97	−35.24
Cogin and Kimball[2]	NaBr(cr) → NaBr(g)	52.14	52.26	−34.18
Mayer and Wintner[3]	NaBr(cr) → NaBr(g)	65.30	52.59	−33.79[b]
Ruff and Mugdan[4]	NaBr(l) → NaBr(g)	47.48	46.43	−34.15
Wartenberg and Albrecht[5]	NaBr(l) → NaBr(g)	47.54	46.38	−34.15
Bloom *et al.*[6]	NaBr(l) → NaBr(g)	51.53	46.23	−34.88[b]

[a]Based on the average of the 2nd and 3rd law values.
[b]Only the 3rd law value being used.

The value of $\Delta_f H°$(NaBr, g, 298.15 K) = −34.40 ± 0.50 kcal·mol^{-1} (−143.930 kJ·mol^{-1}) adopted is the average value of the six $\Delta_f H°(298.15\ K)$ values listed in the above table The dissociation energy was calculated to be 86.28 kcal·mol^{-1} or 3.74 eV which is in good agreement with the values, 3.84 ± 1 and 3.85 eV, reported by Gaydon[7] and Herzberg,[8] respectively. According to Brewer,[9] Gaydon's original reported value, D_0^0 = 3 8, is an average of the value of 3.84 eV from atomic fluorescence and the value of 3.75 eV calculated for Gaydon by Brewer from pressure data available at that time.

Heat Capacity and Entropy

The values of ω_e, $\omega_e x_e$, B_e and α_e were taken from Rice and Klemperer.[10] The adopted bond distance (r_e) reported by Honing *et al.*[11] was derived from microwave spectrum. By electron–diffraction method, the Na–Br bond distance was determined as 2.64 ± 0.01 Å by Maxwell *et al.*[12] The discrepancy may be due to the presence of a large proportion of dimer at the higher pressures used in the electron–diffraction determination. The ground state configuration was reported by G. Herzberg.[8]

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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	−9.807	−135.035	−135.035	INFINITE
100	31.273	203.967	272.441	−6.847	−134.812	−150.135	78.422
200	34.956	226.965	244.505	−3.508	−136.379	−164.890	43.065
250	35.803	234.864	241.813	−1.737	−137.340	−171.910	35.919
298.15	36.323	241.218	241.218	0.	−143.930	−177.817	31.153
300	36.339	241.443	241.219	0.067	−143.984	−178.027	30.997
350	36.699	247.073	241.663	1.894	−159.936	−182.814	27.283
400	36.957	251.991	242.653	3.735	−163.178	−185.836	24.268
450	37.150	256.356	243.937	5.588	−163.808	−188.630	21.896
500	37.301	260.278	245.379	7.450	−164.411	−191.355	19.991
600	37.529	267.100	248.447	11.192	−165.545	−196.636	17.119
700	37.699	272.899	251.536	14.954	−166.604	−201.733	15.054
800	37.837	277.942	254.529	18.731	−167.612	−206.682	13.495
900	37 957	282.405	257.383	22.520	−168.592	−211.507	12.276
1000	38.065	286.410	260.089	26.322	−169.565	−216.223	11.294
1100	38.165	290.043	262.649	30.133	−170.553	−220.841	10.487
1200	38.260	293.368	265.073	33.954	−268.339	−222.928	9.704
1300	38.351	296.434	267.369	37 785	−268.487	−219.138	8.805
1400	38.440	299.279	269.547	41.625	−268.631	−215.337	8.034
1500	38.526	301.934	271.619	45.473	−268.770	−211.525	7.366
1600	38.611	304.423	273.592	49.330	−268.907	−207.704	6.781
1700	38.695	306.767	275.476	53.195	−269.041	−203.875	6.264
1800	38 778	308.981	277.276	57.069	−269.173	−200.038	5.805
1900	38.860	311.080	279.000	60.950	−269.305	−196.193	5.394
2000	38.941	313.075	280.655	64.840	−269.438	−192.342	5.023
2100	39.022	314.977	282.244	68.739	−269.573	−188.484	4.688
2200	39 103	316.794	283.774	72.645	−269.711	−184.619	4.383
2300	39.183	318.534	285.247	76.559	−269.854	−180.748	4.105
2400	39.263	320.203	286 669	80.481	−270 002	−176.871	3.849
2500	39.342	321.808	288.043	84.412	−270.158	−172.987	3.614
2600	39.422	323.352	289.371	88.350	−270.321	−169.097	3.397
2700	39.501	324.841	290 658	92.296	−270.492	−165.201	3.196
2800	39.580	326.279	291.904	96.250	−270.674	−161.298	3.009
2900	39 660	327.670	293.114	100.212	−270.865	−157.388	2.835
3000	39.739	329.016	294.288	104.182	−271.066	−153.472	2.672
3100	39.817	330.320	295.430	108.160	−271.279	−149.548	2.520
3200	39.896	331.585	296.540	112.146	−271.502	−145.618	2.377
3300	39.975	332.814	297.621	116.139	−271.737	−141 681	2.243
3400	40.054	334.009	298 673	120.141	−271.985	−137.736	2.116
3500	40 132	335.171	299.700	124.150	−272.246	−133.784	1.997
3600	40.211	336.303	300.701	128.167	−272.519	−129.824	1 884
3700	40.289	337.405	301.678	132.192	−272.807	−125.856	1.777
3800	40.368	338.481	302.632	136.225	−273.110	−121.880	1.675
3900	40 446	339.530	303.565	140.265	−273.429	−117.897	1.579
4000	40.524	340.555	304 477	144.314	−273.766	−113.904	1.487
4100	40.603	341.557	305.369	148.370	−274.121	−109.903	1.400
4200	40.681	342.536	306.243	152.434	−274.494	−105.894	1.317
4300	40 759	343.495	307.098	156.506	−274.892	−101.875	1.238
4400	40.837	344 433	307.936	160.586	−275.271	−97 850	1.162
4500	40.916	345.351	308.757	164.674	−275.695	−93.813	1.089
4600	40 994	346.251	309.562	168.769	−276.153	−89.767	1.019
4700	41.072	347.134	310.352	172.873	−276.638	−85.710	0.953
4800	41.150	347.999	311.128	176.984	−277.153	−81.642	0.888
4900	41.228	348.849	311.889	181.103	−277.700	−77.563	0.827
5000	41.307	349.682	312.636	185.230	−278.273	−73.474	0.768
5100	41.385	350.501	313.371	189.364	−278.888	−69.371	0.711
5200	41.463	351.305	314.093	193.506	−279.543	−65.257	0.656
5300	41.541	352.096	314.802	197.657	−280.239	−61.129	0.602
5400	41.619	352.873	315.500	201.815	−280.979	−56.988	0.551
5500	41.697	353.638	316.187	205.981	−281.766	−52.833	0.502
5600	41.775	354.390	316.862	210.154	−282.601	−48.664	0.454
5700	41.853	355.130	317.527	214.336	−283.488	−44.478	0.408
5800	41.931	355.858	318.182	218.525	−284.428	−40.277	0.363
5900	42.010	356.576	318.826	222.722	−285.424	−36.059	0.319
6000	42.088	357.282	319.461	226.927	−286.319	−31.842	0.277

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

$D_0^\circ = 19332 \pm 200$ cm^{-1}
$S°(298.15\ K) = 232.97 \pm 0.1$ J·K^{-1}·mol^{-1}

$\Delta_f H°(0\ K) = 133.3 \pm 2.4$ kJ·mol^{-1}
$\Delta_f H°(298.15\ K) = 125.8 \pm 2.4$ kJ·mol^{-1}

Electronic Levels and Molecular Constants ($^{79}Br^{16}O$), cm^{-1}

State	T_e	g_i	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	$D_e \cdot 10^6$	r_e/Å
$X^2\Pi_{3/2}$	0	2	727.05	4.932	–	0.4299	0.003639	0.594	1.717
$X^2\Pi_{1/2}$	968	2	727.05	4.932	–	0.4299	0.003639	0.594	1.717
$A^2\Pi_{3/2}$	27871	2	511.3	4.83	−0.074	0.314	0.0034	0.474	1.95
$A^2\Pi_{1/2}$	[29321]	2	511.3	4.8	−0.074	0.314	0.0034	0.474	1.95

Point Group: $C_{\infty v}$ σ=1

Enthalpy of Formation

The two existing spectroscopic studies by Coleman and Gaydon[1] and Durie and Ramsay[2] yield dissociation energy values for BrO(g). One should note, with respect to those studies, that the first bound excited state $A^2\Pi$ of BrO(g) dissociates to $Br(^2P_{3/2}) + O(^1D_2)$. A linear Birge–Sponer extrapolation of the Coleman and Gaydon[1] data gave 17800 cm^{-1} or 213.2 kJ·mol^{-1} for the ground state dissociation energy. Assuming the extrapolation was high by up to 20%, they recommended 1.75 ± 0.3 eV or 170 ± 29 kJ·mol^{-1} Durie and Ramsay,[2] from a graphical Birge–Sponer extrapolation, calculated a dissociation energy of $D_0^\circ = 19332 \pm 200$ cm^{-1} or 231.6 ± 2.4 kJ·mol^{-1}. The latter value leads to the present adopted value for $\Delta_f H°(298.15\ K)$ for BrO(g) of 125.8 ± 2.4 kJ·mol^{-1}. Additional data needed for the calculations presented here, e.g. thermal functions for the Br(g), and Br_2(ref), O(g), and O_2(ref), are taken from the JANAF Thermochemical Tables.[3]

Heat Capacity and Entropy

The spectroscopic results tabulated above are for the $^{79}Br^{16}O$ *isotopomer. Isotopic relationships*[4] are used to convert the above constants to those for the normally occurring, 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.

Values of ω_e and $\omega_e x_e$ given in the table above for the ground state are from Butler *et al.*,[5] while those for the first excited state are from Barnett *et al.*[6] These values in fact described an average $^2\Pi$ state; there are differences in the vibrational constants for the $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$ states but they are not considered in this calculation. The B_e value for the ground state is from Amano *et al.*[7] The internuclear distance and value for B_e for the A state are from Barnett *et al.*[6] The value of D_e for the excited state was estimated.[4] Barnett *et al.*[6] gave a dissociation energy of 8960 cm^{-1} for the A state which is used in conjunction with T_e to provide an energy cutoff from the sum–over–states calculation on the excited state.

Previously, the value of the spin orbit constant, A_o, for the inverted doublet $X^2\Pi$ ground state adopted by Huber and Herzberg[8] was an average based on two values derived from the EPR spectra studies: $A_o = -815$ cm^{-1} of Carrington *et al.*[9] and $A_o = -980$ cm^{-1} of Brown *et al.*[10] The recent measured value of McKellar,[11] $A_o = -968$ cm^{-1}, for the spin–orbit splitting of the ground state is adopted here. For ClO the spin–orbit splitting of the A state is approximately 1.5 times the value found for the ground state.[12] Using the same factor of 1.5, the spin–orbit splitting for the A state in BrO is estimated to be 1450 cm^{-1}.

Numerous excited states have been estimated by Monks *et al.*[13] and observed by Duignan and Hudgens.[14] These states are not fully characterized in terms of vibrational and rotational constants and do not contribute significantly to the thermal functions below 6000 K.

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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	0.0	INFINITE	−9.061	133.305	133.305	INFINITE
50	29.103	179.334	331.631	−7.615	133.611	129.149	−134.918
100	29.139	199.511	261.104	−6.159	133.358	124.765	−65.169
150	29.592	211.388	242.681	−4.694	132.932	120.555	−41.980
200	30.805	220.050	235.985	−3.187	132.424	116.505	−30.427
250	32.493	227.101	233.523	−1.606	131.869	112.588	−23.523
298.15	34.182	232.970	232.970	0.000	125.770	109.582	−19.198
300	34.244	233.182	232.971	0.063	125.736	109.482	−19.062
400	37.062	243.447	234.351	3.638	110.586	107.200	−13.999
500	38.719	251.915	237.042	7.436	111.008	106.307	−11.105
600	39.525	259.055	240.132	11.354	111.486	105.321	−9.169
700	39.839	265.176	243.283	15.325	111.960	104.256	−7.780
800	39.901	270.502	246.360	19.313	112.405	103.125	−6.733
900	39.846	275.199	249.308	23.301	112.808	101.940	−5.916
1000	39.746	279.392	252.111	27.281	113.170	100.713	−5.261
1100	39.634	283.175	254.766	31.250	113.493	99.451	−4.722
1200	39.528	286.619	257.279	35.208	113.780	98.162	−4.273
1300	39.437	289.779	259.659	39.156	114.036	96.850	−3.891
1400	39.361	292.699	261.916	43.096	114.265	95.519	−3.564
1500	39.301	295.412	264.060	47.029	114.467	94.173	−3.279
1600	39.256	297.947	266.099	50.957	114.647	92.814	−3.030
1700	39.225	300.326	268.043	54.881	114.805	91.445	−2.810
1800	39.205	302.568	269.900	58.802	114.942	90.066	−2.614
1900	39.194	304.687	271.675	62.722	115.057	88.681	−2.438
2000	39.189	306.697	273.377	66.641	115.153	87.291	−2.280
2100	39.189	308.609	275.009	70.560	115.226	85.895	−2.136
2200	39.189	310.432	276.578	74.479	115.279	84.497	−2.006
2300	39.188	312.174	278.088	78.398	115.310	83.098	−1.887
2400	39.182	313.842	279.544	82.316	115.318	81.697	−1.778
2500	39.168	315.441	280.948	86.234	115.303	80.296	−1.678
2600	39.145	316.977	282.304	90.150	115.264	78.897	−1.585
2700	39.110	318.454	283.616	94.062	115.201	77.498	−1.499
2800	39.061	319.875	284.886	97.971	115.112	76.103	−1.420
2900	38.996	321.245	286.116	101.874	114.998	74.711	−1.346
3000	38.915	322.566	287.309	105.770	114.858	73.325	−1.277
3100	38.817	323.840	288.467	109.656	114.690	71.945	−1.212
3200	38.701	325.071	289.592	113.532	114.496	70.568	−1.152
3300	38.568	326.260	290.685	117.396	114.276	69.198	−1.095
3400	38.418	327.409	291.748	121.245	114.028	67.836	−1.042
3500	38.251	328.520	292.783	125.079	113.755	66.483	−0.992
3600	38.068	329.595	293.791	128.895	113.453	65.136	−0.945
3700	37.871	330.635	294.773	132.692	113.124	63.796	−0.901
3800	37.661	331.643	295.730	136.469	112.769	62.471	−0.859
3900	37.439	332.618	296.663	140.224	112.389	61.150	−0.819
4000	37.205	333.563	297.574	143.956	111.980	59.840	−0.781
4100	36.963	334.479	298.463	147.665	111.547	58.545	−0.746
4200	36.712	335.366	299.331	151.349	111.088	57.255	−0.712
4300	36.454	336.227	300.179	155.007	110.603	55.980	−0.680
4400	36.191	337.062	301.008	158.639	110.093	54.717	−0.650
4500	35.924	337.873	301.818	162.245	109.559	53.463	−0.621
4600	35.654	338.659	302.611	165.824	108.999	52.222	−0.593
4700	35.382	339.423	303.386	169.376	108.416	50.994	−0.567
4800	35.108	340.165	304.144	172.900	107.809	49.780	−0.542
4900	34.835	340.886	304.887	176.397	107.177	48.579	−0.518
5000	34.562	341.587	305.614	179.867	106.523	47.388	−0.495
5100	34.291	342.269	306.326	183.310	105.844	46.213	−0.473
5200	34.021	342.932	307.024	186.725	105.143	45.048	−0.452
5300	33.755	343.578	307.707	190.114	104.418	43.900	−0.433
5400	33.491	344.206	308.377	193.476	103.669	42.765	−0.414
5500	33.232	344.818	309.034	196.813	102.898	41.646	−0.396
5600	32.976	345.415	309.679	200.123	102.103	40.537	−0.378
5700	32.724	345.996	310.311	203.408	101.285	39.445	−0.361
5800	32.477	346.563	310.931	206.668	100.444	38.367	−0.346
5900	32.235	347.116	311.540	209.903	99.579	37.305	−0.330
6000	31.998	347.656	312.137	213.115	98.690	36.256	−0.316

PREVIOUS CURRENT: March 1996 (1 bar)

Bromine Oxide (OBrO)

Ideal Gas

$M_r = 111.9028$

Bromine oxide (OBrO)

$Br_1O_2(g)$

$\Delta_a H°(0\ K) = [450 \pm 25]\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = 271.1 \pm 2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [161.5 \pm 25]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298\ 15\ K) = [152.0 \pm 25]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
X^2B_1	0.0	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
800 (1)
300 (1)
852 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Br–O = 1.649 Å
Bond Angle: O–Br–O = 114.4°
Product of the Moments of Inertia. $I_A I_B I_C = 409.0844 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

For the series OXO(g) [where X = F, Cl, Br, I], there is only reliable experimental data for OClO(g). Assuming that the values $\Delta_a H°$(OClO,g) and $D_0°$(ClO) are reasonable, we adopt the ratio of the numbers (~1.94) to apply for a similar relationship between BrO(g) and OBrO(g). Thus we calculate $\Delta_a H°$(OBrO, g, 0 K) = 1.94×$D_0°$ (BrO) = 450 ± 25 kJ·mol^{-1}.

Cottrell[1] reported D(O–BrO) ≥ 70 ± 10 kcal·mol^{-1}. This converts to $\Delta_f H°(0\ K) = 87\ kJ \cdot mol^{-1}$. This value was based on the enthalpy of formation of BrO_2(cr) reported by Pflugmacher *et al.*[2] and a $D_0°$(BrO) = 2.25 eV or 52 kcal·mol^{-1}. Cottrell expressed doubt as to the validity of this value based on comparison with ClO_2. The enthalpy of dissociation reported by Vedeneyev *et al.*[3] was ΔH(298 K) ≥ 70 kcal·mol^{-1} for the reaction $BrO_2 \rightarrow BrO + O$. This is an estimated value based on the work by Cottrell (1954) although a different temperature was given.

In contrast, Huie and Laszlo[4] have estimated the enthalpy of formation of OBrO(g) in the following manner. According to Stanbury,[5] the enthalpy of formation of OBrO in the gas phase can be estimated by assuming that the difference in the $\Delta_f G$ for Cl_2(g) and ClO_2(aq) also applies for the bromine species. Using a value of 2.9 kJ·mol^{-1} recommended by Wagman *et al.*[6] as this difference and $\Delta G(BrO_2, aq) = 144.0$ kJ·mol^{-1}, we obtain $\Delta G° = 146.9$ kJ·mol^{-1} for OBrO(g) and $\Delta_f H° = 122.5$ kJ mol^{-1}. In comparison $D_0°$(BrO) = 231.6 kJ·mol^{-1}.

Heat Capacity and Entropy

Mueller *et al.*[7] have measured the microwave spectra of OBrO(g). Preliminary analysis of the data suggested a bent structure (r_o = 1.649 Å and <(OBrO) = 114.4°). This structure is adopted and is consistent with the expected trends in the corresponding chlorine and iodine oxide molecules. The principal moments of inertia (in g·cm^2) are $I_A = 3.0275 \times 10^{-39}$, $I_B = 10.2087 \times 10^{-39}$, and $I_C = 13.2361 \times 10^{-39}$.

In support of this study, Byberg and Spanget-Larsen[8] used modified extended Huckel theory to calculate nuclear quadrupole coupling constants for a series of oxygen halogen compounds. The comparison of calculated values with observed values helped confirm the geometry of BrO_2: C_{2v} symmetry with a bond length of 1.625 Å and a bond angle of 117.6° This geometry was assumed to be similar to that of ClO_2, using a 0.15 Å difference between the covalent radii of the chlorine and bromine atoms.

Tevault *et al.*[9] observed the infrared spectra of BrO_2 in a solid argon matrix. Assuming the proper identification of the antisymmetric stretching ν_3 to be 852 cm^{-1}, the apex angle was calculated to be 110 ± 2°. This was close to the value observed for the analogous matrix isolated ClO_2.

The recommended vibrational frequency (ν_3) is that suggested by Jacox.[10] This data is based on the infrared spectra of the argon matrix isolated radical as studied by Tevault *et al.*[9] Preliminary microwave studies by Mueller *et al.*[7] suggested an approximate value for ν_2 (300 cm^{-1}). The unobserved vibrational frequency (ν_1) is estimated from those which describe the other halogen oxide molecules.[11] Maier and Bothur,[12] using flash photolysis, trapped OBrO in a matrix and measured ν_1 and ν_3 for two isotopes. Their values for ν_3 are within a few wave numbers of the values derived by Tevault *et al.*[9] ν_1 values are of the order of 791–799 cm^{-1}, depending on the concentration of the pyrolized mixture (Br_2/O_2/Ar).

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Continued on page 548

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	.000	.000	INFINITE	−11.395	161.500	161.500	INFINITE
50	33.368	204.239	398.861	−9.731	161.299	159.420	−166.544
100	35.399	227.876	308 078	−8.020	160.573	157.809	−82.431
150	37 993	242.726	283.956	−6.185	159.790	156.596	−54.531
200	40.539	254.003	275.111	−4.222	159.010	155.649	−40.651
250	43.088	263.324	271.846	−2.131	158.236	154.898	−32.364
298 15	45.364	271.112	271.112	.000	151.957	154.979	−27.152
300	45.446	271.393	271.113	.084	151.916	154.998	−26.988
400	49 171	285.010	272.944	4.826	136.447	159.211	−20.791
500	51 674	296.270	276.516	9.877	136.594	164.888	−17.226
600	53.335	305.848	280.626	15.133	136.830	170.525	−14.846
700	54 463	314.160	284.836	20.526	137.100	176.120	−13.142
800	55.253	321.487	288.969	26 015	137.375	181.675	−11.862
900	55.823	328.030	292.952	31.570	137.643	187.196	−10.865
1000	56.246	333.934	296.760	37.174	137.898	192.688	−10.065
1100	56.567	339.311	300.387	42.816	138.139	198.156	−9.410
1200	56 817	344.244	303.839	48.485	138.364	203.602	−8.863
1300	57.013	348.800	307.125	54.177	138.572	209.030	−8.399
1400	57.172	353.031	310.254	59.887	138.764	214.442	−8.001
1500	57.301	356.980	313.239	65.611	138.937	219.842	−7.656
1600	57.407	360.681	316.090	71.346	139.090	225.230	−7.353
1700	57 495	364.164	318.816	77.091	139.223	230.610	−7.086
1800	57.570	367.453	321.428	82.845	139.334	235.982	−6 848
1900	57.634	370.567	323.933	88.605	139.420	241.349	−6.635
2000	57.688	373.525	326.339	94.371	139.481	246.712	−6.443
2100	57.735	376.341	328.654	100.142	139.515	252.073	−6.270
2200	57.776	379.028	330.883	105.918	139.520	257.433	−6.112
2300	57.812	381.597	333.032	111.698	139.497	262.792	−5.968
2400	57.843	384.058	335.108	117.480	139.443	268.154	−5.836
2500	57.871	386.420	337.113	123.266	139.358	273.519	−5.715
2600	57 896	388.690	339.053	129.054	139.244	278.887	−5.603
2700	57.918	390.875	340.933	134.845	139.100	284.261	−5.499
2800	57.937	392.982	342.754	140.638	138.926	289 640	−5.403
2900	57.955	395.015	344.521	146.433	138.725	295.026	−5.314
3000	57.971	396.980	346.237	152.229	138.496	300.420	−5.231
3100	57.986	398.881	347.905	158.027	138.243	305.822	−5.153
3200	57 999	400.723	349.527	163.826	137.965	311.231	−5.080
3300	58.011	402.508	351.106	169.626	137.666	316.650	−5.012
3400	58.022	404.240	352.643	175.428	137.347	322.079	−4.948
3500	58.032	405.922	354.141	181.231	137.010	327.517	−4.888
3600	58.041	407.557	355.602	187.035	136.657	332.965	−4.831
3700	58.050	409.147	357.028	192.839	136.289	338.423	−4.778
3800	58 058	410.695	358.420	198.644	135.908	343.892	−4.727
3900	58.065	412.203	359.780	204.451	135.517	349.370	−4.679
4000	58.072	413.673	361 109	210.257	135.116	354.858	−4.634
4100	58.078	415.107	362.409	216.065	134.707	360.357	−4.591
4200	58.084	416.507	363.680	221.873	134.291	365.866	−4.550
4300	58.089	417.874	364.925	227.682	133.870	371.385	−4.511
4400	58.094	419.209	366.143	233 491	133.444	376.913	−4.475
4500	58.099	420.515	367.337	239.300	133.014	382.451	−4.439
4600	58.103	421.792	368.507	245.111	132.581	387.998	−4.406
4700	58.107	423.042	369.654	250.921	132.145	393.556	−4.374
4800	58.111	424.265	370.779	256.732	131.707	399.122	−4.343
4900	58.115	425.463	371.883	262.543	131.266	404.698	−4.314
5000	58.118	426.637	372.966	268.355	130.823	410.283	−4.286
5100	58.121	427.788	374.030	274.167	130.377	415.877	−4.259
5200	58.125	428.917	375.075	279.979	129.928	421.479	−4.234
5300	58.127	430.024	376.101	285.792	129.475	427.091	−4.209
5400	58.130	431.111	377.110	291.605	129.018	432.710	−4.186
5500	58.133	432.177	378.101	297.418	128.557	438.338	−4.163
5600	58.135	433.225	379.076	303.231	128.089	443.975	−4.141
5700	58.137	434.254	380.035	309.045	127.615	449.620	−4.120
5800	58.140	435.265	380.979	314 859	127.134	455.273	−4.100
5900	58.142	436.259	381.907	320.673	126.644	460.934	−4.081
6000	58 144	437.236	382.821	326.487	126.143	466.605	−4.062

PREVIOUS: CURRENT: March 1996 (1 bar)

$S°(298.15\ K) = [288.8 \pm 3]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [116.1 \pm 40]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [108.0 \pm 40]\ kJ·mol^{-1}$

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

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
1487 (1)
[250] (1)
[160] (1)

Point Group: C_s $\sigma = 1$
Bond Distances: Br–O = [2.0] Å; O–O = [1.25] Å
Bond Angle: Br–O–O = [115]°
Product of the Moments of Inertia: $I_A I_B I_C = [588.4497 \times 10^{-117}]\ g^3·cm^6$

Enthalpy of Formation

Ip and Burns[1] determined the recombination rate constants of bromine atoms in the presence of six different third bodies (helium, neon, argon, krypton, oxygen and nitrogen) over the temperature range of 300 and 1273° K The authors refer to two earlier studies Rabinowitch and Wood[2] and Strong *et al.*[3] Based on these data, Blake *et al* [4] calculated interaction potentials between atomic bromine, oxygen and an inert third body (such as a rare gas). A value is given for $Br–O_2$. BrOO was thought to be unstable with a bond energy (Br–OO) of approximately 1 $kcal·mol^{-1}$ (at 298.15 K) which translated to an enthalpy of formation of 108.0 kJ mol^{-1}.

Heat Capacity and Entropy

Butkovskaya *et al.*[5] estimated the structure of this molecule to be bent with a Br–O–O angle of [115]° and bond lengths, r(Br–O) = [2.0] Å and r(O–O) = [1.25] Å. Butkovskaya *et al.* assumed this structure in an attempt to explain the formation of BrO_2 from the reaction of O + Br_2 in a flow discharge system. Under the experimental conditions studied, OBrO was actually formed The principal moments of inertia (in $g·cm^2$) are: $I_A = [1.2011 \times 10^{-39}]$, $I_B = [21.5417 \times 10^{-39}]$, and $I_C = [22.7428 \times 10^{-39}]$.

The recommended vibrational frequency for ν_1 is that suggested by Jacox [6] In addition, we adopt ν_2=[250] and ν_3=[160] cm^{-1} based on an assumed trend of the FOO(g) and ClOO(g) vibrational frequencies.[7] ν_1 is based on the infrared spectra of the argon matrix isolated radical as studied by Tevault and Smardzewski.[8] Michael and Payne[9] calculated (BEBO method) a stretching frequency of 872 cm^{-1} for ν_1 which is in conflict with the observed frequency by Tevault and Smardzewski[8] and the corresponding value for ClOO. FOO(g) and ClOO(g) have ν_1(O–O stretch) values of 11487 and 1443 cm^{-1}, respectively.[7] Thus, ν_1=1487 cm^{-1} for BrOO appears reasonable. The authors suggested that the bending frequency of 100 cm^{-1} was consistent with their kinetic data. The recent study by Maier and Bothur[10] suggested a ν_1 value in agreement with the adopted value.

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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	.000	.000	INFINITE	−12.851	116.087	116.087	INFINITE
50	35.382	212.021	435.344	−11.166	115.907	113.639	−118.718
100	41.818	238.630	330.908	−9.228	115.409	111.569	−58.278
150	45.376	256.347	303.261	−7.037	114.981	109.743	−38.216
200	47.128	269.668	293.267	−4.720	114.555	108.061	−28.223
250	48.143	280.301	289.646	−2.336	114.073	106.491	−22.250
298.15	48 875	288.845	288.845	.000	108.000	105.736	−18.524
300	48.901	289.148	288.846	.090	107.966	105.722	−18.408
400	50.265	303.404	290.781	5.049	92.714	108.119	−14.119
500	51.562	314.761	294.479	10.141	92.901	111.949	−11.695
600	52.707	324.266	298.672	15.356	93.097	115.741	−10.076
700	53.657	332.465	302.928	20.676	93.293	119.499	−8.917
800	54.421	339.682	307.080	26.082	93.485	123.230	−8.046
900	55.031	346.128	311.067	31.555	93.671	126.936	−7.367
1000	55.517	351.952	314.869	37.084	93.851	130.623	−6.823
1100	55.907	357.263	318.485	42.656	94.022	134.292	−6.377
1200	56.222	362.141	321.922	48.263	94.184	137.946	−6.005
1300	56.480	366.652	325.192	53.898	94.336	141.586	−5.689
1400	56.692	370.845	328.305	59.557	94.477	145.215	−5.418
1500	56.869	374.763	331.273	65.235	94.605	148.835	−5.183
1600	57.017	378.438	334.107	70.930	94.717	152.446	−4.977
1700	57 142	381.899	336.817	76.638	94.813	156.051	−4.795
1800	57.249	385.168	339.414	82.358	94.890	159.651	−4.633
1900	57.341	388.266	341.904	88.087	94.946	163.247	−4.488
2000	57.421	391.209	344.296	93.825	94.979	166.841	−4.357
2100	57.490	394.012	346.597	99.571	94.987	170.434	−4.239
2200	57.550	396.688	348.814	105.323	94.969	174.028	−4.132
2300	57.603	399.247	350.951	111.081	94.923	177.622	−4.034
2400	57.650	401.700	353.015	116.843	94.849	181.219	−3.944
2500	57.692	404.054	355.010	122.611	94.746	184.820	−3.862
2600	57.729	406.318	356.940	128.382	94.614	188.425	−3.786
2700	57.763	408.497	358.810	134.156	94.454	192.036	−3.715
2800	57.792	410.598	360.622	139.934	94.266	195.654	−3.650
2900	57.819	412.627	362.380	145.715	94.050	199.278	−3.589
3000	57.844	414.587	364.088	151.498	93.809	202.911	−3.533
3100	57.866	416.484	365.748	157.283	93.543	206.553	−3 480
3200	57.886	418.322	367.362	163.071	93.254	210.202	−3.431
3300	57.905	420.104	368.934	168.861	92.944	213.861	−3.385
3400	57.922	421.832	370.464	174.652	92.614	217.531	−3.342
3500	57.937	423.512	371.956	180.445	92.267	221.209	−3.301
3600	57.951	425.144	373.411	186.239	91.905	224.899	−3.263
3700	57.965	426.732	374.831	192.035	91.528	228.598	−3.227
3800	57.977	428.278	376.217	197.832	91.139	232.308	−3.193
3900	57.988	429.784	377.571	203.630	90.740	236.028	−3.161
4000	57.998	431.252	378.895	209.430	90.331	239.759	−3.131
4100	58.008	432.685	380.189	215.230	89.915	243.499	−3.102
4200	58.017	434.083	381.456	221.031	89.493	247.250	−3.075
4300	58.025	435.448	382.696	226.833	89.065	251.012	−3.049
4400	58.033	436.782	383.910	232.636	88.633	254.783	−3.025
4500	58 040	438.086	385.099	238.440	88.197	258.563	−3.001
4600	58.047	439.362	386.265	244.244	87.759	262.354	−2.979
4700	58.054	440.610	387.408	250.049	87.317	266.154	−2.958
4800	58.060	441.833	388.529	255.855	86.874	269.964	−2.938
4900	58.065	443.030	389.630	261.661	86.428	273.784	−2.919
5000	58 071	444.203	390.709	267.468	85.979	277.612	−2.900
5100	58.076	445.353	391.769	273.276	85.529	281.449	−2.883
5200	58.081	446.481	392.811	279.083	85.075	285.294	−2.866
5300	58.085	447.587	393.834	284.892	84 618	289.150	−2.850
5400	58.089	448.673	394.839	290.700	84.157	293.013	−2.834
5500	58.093	449 739	395.828	296.510	83.692	296.884	−2.820
5600	58.097	450.786	396.800	302.319	83.220	300.766	−2.805
5700	58.101	451.814	397.756	308.129	82.743	304.654	−2.792
5800	58.104	452.824	398.697	313.939	82.258	308.552	−2.779
5900	58.107	453.818	399.623	319.750	81 764	312.457	−2.766
6000	58.111	454.794	400.534	325.561	81.260	316.372	−2.754

PREVIOUS: CURRENT March 1996 (1 bar)

$\Delta_a H°(298.15\ K) = [625 \pm 50]\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = [284.5 \pm 2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [233 \pm 50]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [221 \pm 50]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
state	ϵ_i, cm^{-1}	g_i
$[^2A_1]$	0.0	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[442](1)
[800](1)
[350](2)
[828](2)

Point Group: C_{3v} $\sigma = 3$
Bond Distance: Br–O = [1.68]Å
Bond Angle: O–Br–O = [89]°
Product of the Moments of Inertia: $I_A I_B I_C = 2198.7927 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

We adopt an enthalpy of formation value which is based on an assumed relationship of $\Delta_a H°(BrO_3,g)/3 \approx 0.9 D°_0(BrO)$.

An enthalpy of formation value (at 298.15 K) has been reported by Farkas and Klein.[1] This value, 23 $kcal \cdot mol^{-1}$ (96 $kJ \cdot mol^{-1}$), was derived from absorption spectra measurements of bromate ions in solutions. There is considerable uncertainty in this value, both in terms of the experimental measurements and the fact that the authors have interchanged BrO_3 and BrO_3^-. This corresponds to an average bond energy of 254 $kJ \cdot mol^{-1}$. In comparison $D°_0(BrO) = 231\ kJ \cdot mol^{-1}$.

Heat Capacity and Entropy

The structure of this molecule is estimated to be pyramidal with a O–Br–O angle of [89]° and a bond length of [1.68] Å, in analogy with the corresponding chlorine and iodine oxide molecules. Venkateswarlu and Sundaram,[2] Venkateswarlu and Rajalakshmi,[3] Rao and Santhamma,[4] Rao,[5] and Thirugnanasambandam and Mohan[6] assumed the same structure and bond angle for ClO_3, BrO_3, and IO_3. Using Badgers' rule, the authors examined the relationship between the vibrational frequencies and force constants for the three pyramidal molecules – ClO_3, BrO_3, and IO_3. Although these authors refer to early measurements of the vibrational frequencies, the values appear to be in part, those of the ion BrO_3^-. The vibrational frequencies are derived from the force constants which describe the other halogen oxide molecules. The principal moments of inertia (in g cm^2) are: $I_A = 12.2156 \times 10^{-39}$, $I_B = 12.2156 \times 10^{-39}$, and $I_C = 14.7352 \times 10^{-39}$.

Byberg,[7] in an EPR study, suggested the molecule had C_{3v} symmetry with a bond angle of 112° and bond length of 1.57 Å. In contrast, Begum *et al.*,[8] in a radiolysis study, suggested a bond length of 114° with C_{3v} symmetry. In calculating atomic phase shifts, Lee and Beni[9] calculated a bond length of 1 66 Å in solution. In these cases, there is no definitive evidence as to the geometry Values were suggested which would be consistent with experimental observations.

References

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[2] K. Venkateswarlu and S. Sundaram, Proc. Phys. Soc. (London) A69, 180 (1956).
[3] K. Venkateswarlu and K. V. Rajalakshmi, Indian J. Pure Appl. Phys. 1, 380 (1963).
[4] C. G. R. Rao and C. Santhamma, Current Sci. 33(22), 677 (1964).
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[6] P. Thirugnanasambandam and S. Mohan, Indian J. Phys. 52B(3), 173 (1978).
[7] J. R. Byberg, J. Chem. Phys 83(3), 919 (1985).
[8] A. Begum, S. Subramanuan, and M. C. R. Symons, J. Chem. Soc. 6, 918 (1970).

Enthalpy Reference Temperature = T_r = 298.15 K					Standard State Pressure = $p°$ = 0.1 MPa		
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
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	−13.101	233.000	233.000	INFINITE
50	33.333	209.520	438.271	−11.438	232.073	233.759	−244.206
100	36.646	233.329	330.438	−9.711	230.636	235.992	−123.269
150	43.085	249.376	300.850	−7.721	229.279	238.971	−83.217
200	49.535	262.667	289.684	−5.403	228.126	242.381	−63.303
250	55.297	274.354	285.471	−2.779	227.156	246.060	−51.411
298.15	59.999	284.509	284.509	.000	220.821	250.432	−43.875
300	60.162	284.880	284.510	.111	220.781	250.616	−43.636
400	67.300	303.241	286.965	6.511	205.483	263.728	−34.439
500	71.849	318.785	291.815	13.485	206.024	278.233	−29.067
600	74.791	332.164	297.452	20.827	206.767	292.607	−25.474
700	76.759	343.850	303.263	28.411	207.599	306.849	−22.897
800	78.125	354.194	308.995	36.159	208.466	320.969	−20.957
900	79.105	363.456	314.541	44.023	209.340	334.979	−19.442
1000	79.829	371.830	319.858	51.972	210.208	348.892	−18.224
1100	80.377	379.465	324.935	59.983	211.065	362 719	−17.224
1200	80.801	386.478	329.775	68.043	211.905	376.469	−16.387
1300	81.136	392.959	334.389	76.140	212.728	390.149	−15.676
1400	81.404	398.982	338.791	84.268	213.530	403.767	−15.065
1500	81.623	404.606	342.993	92.420	214.311	417.327	−14.533
1600	81.803	409.880	347.010	100.591	215.067	430.837	−14.065
1700	81.953	414 844	350.856	108.779	215.797	444.300	−13.652
1800	82.080	419.532	354.542	116.981	216.498	457.721	−13.283
1900	82.187	423.972	358.080	125.195	217.168	471.104	−12.952
2000	82.279	428.190	361.481	133.418	217.805	484.452	−12.653
2100	82.358	432.207	364.754	141.650	218.406	497.770	−12.381
2200	82.428	436.040	367.908	149.889	218.971	511.060	−12.134
2300	82.488	439.705	370.951	158.135	219.499	524.324	−11.908
2400	82.541	443.217	373.889	166.387	219.987	537.566	−11.700
2500	82.588	446.587	376.730	174.643	220.436	550.790	−11.508
2600	82.630	449.827	379.480	182.904	220.846	563.996	−11.331
2700	82.667	452.947	382.143	191.169	221.217	577.187	−11.166
2800	82.700	455.954	384.726	199.437	221.551	590.365	−11.013
2900	82.730	458.856	387.232	207.709	221.847	603.531	−10 871
3000	82.757	461.661	389.667	215.983	222.108	616.688	−10.737
3100	82.781	464.375	392.033	224.260	222.336	629.838	−10.613
3200	82.804	467.004	394.335	232.539	222.532	642.979	−10.496
3300	82.824	469.552	396.576	240.821	222.698	656.115	−10.385
3400	82.843	472.025	398.759	249.104	222.837	669.247	−10.282
3500	82.859	474.427	400.887	257.389	222.950	682.374	−10.184
3600	82.875	476.761	402.962	265.676	223.040	695.500	−10.091
3700	82.889	479.032	404.988	273.964	223.109	708.622	−10.004
3800	82.903	481.243	406.965	282.254	223.158	721.745	−9.921
3900	82.915	483.396	408.898	290.545	223.190	734.865	−9.842
4000	82.926	485.496	410.786	298.837	223.207	747.984	−9.768
4100	82.937	487.543	412.634	307.130	223.209	761.104	−9.697
4200	82.946	489.542	414.441	315.424	223.199	774.223	−9.629
4300	82.956	491.494	416.210	323.719	223.178	787.343	−9.564
4400	82.964	493.401	417.943	332.015	223.145	800.463	−9.503
4500	82.972	495.266	419.641	340.312	223.104	813.584	−9.444
4600	82.979	497.089	421.305	348.609	223.053	826.706	−9.388
4700	82.986	498.874	422.936	356.908	222.994	839.830	−9.334
4800	82.993	500.621	424.537	365.207	222.926	852.955	−9.282
4900	82.999	502.333	426.107	373.506	222.849	866.082	−9.233
5000	83.005	504.009	427.648	381.807	222.764	879.210	−9.185
5100	83.010	505.653	429.162	390.107	222.670	892.340	−9.139
5200	83.015	507.265	430.648	398.409	222.565	905.471	−9.096
5300	83.020	508.846	432.109	406.710	222.451	918.606	−9.053
5400	83.025	510.398	433.544	415.013	222.324	931.741	−9.013
5500	83.029	511.922	434.955	423.315	222.185	944.879	−8.974
5600	83.033	513.418	436.343	431.618	222.032	958.022	−8.936
5700	83.037	514.888	437.708	439.922	221.863	971.165	−8.900
5800	83.041	516.332	439.052	448.226	221.678	984.313	−8.865
5900	83.044	517.751	440.373	456.530	221.474	997.462	−8.831
6000	83.048	519.147	441.675	464.835	221.250	1010.617	−8.798

PREVIOUS: CURRENT. March 1996 (1 bar)

$S°(298.15\ K)$ = [249.2] J·K^{-1}·mol^{-1}

$\Delta_f H°(0\ K)$ = [170.7] kJ·mol^{-1}
$\Delta_f H°(298.15\ K)$ = [162.6] kJ·mol^{-1}

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

ω_e = [400] cm^{-1} $\omega_e x_e$ = [1.5] cm^{-1} σ = 1
B_e = [0.1519] cm^{-1} α_e = [0.0008] cm^{-1} r_e = [2.23] Å

Enthalpy of Formation

$\Delta_f H°(0\ K)$ was estimated as 40.8 kcal·mol^{-1} by Gordon[1] with white (α) phosphorus as the reference state.

Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1]

Reference

[1] J. S. Gordon, Astrosystems International, Livingston, New Jersey, personal communication, (August 25, 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	−9.508	170.707	170.707	INFINITE
100	30.017	213.468	279.294	−6.583	171.349	154.463	−80.683
200	33.551	235.417	252.392	−3.395	169.823	137.906	−36.017
250	34.666	243.032	249.783	−1.688	169.030	130.016	−27.165
298.15	35.394	249.204	249.204	0.	162.601	123.238	−21.591
300	35.417	249.423	249.205	0.065	162.552	122.994	−21.415
350	35.935	254.924	249.638	1.850	146.076	117.345	−17.513
400	36.304	259.748	250.606	3.657	145.651	113.270	−14.791
450	36.578	264.040	251.865	5.479	145.237	109.247	−12.681
500	36.786	267.905	253.279	7.313	144.830	105.270	−10.997
600	37.083	274.640	256.294	11.008	144.032	97.433	−8.482
700	37.285	280.373	259.335	14.727	143.249	89.729	−6.696
800	37.434	285.362	262.283	18.463	142.476	82.136	−5.363
900	37.552	289.778	265.097	22.212	141.711	74.639	−4.332
1000	37.649	293.739	267.767	25.973	140.952	67.228	−3.512
1100	37.734	297.332	270.294	29.742	140.197	59.892	−2.844
1200	37.810	300.618	272.686	33.519	75.873	53.703	−2.338
1300	37.879	303.648	274.953	37.304	75.900	51.854	−2.084
1400	37.943	306.457	277.104	41.095	75.924	50.004	−1.866
1500	38.004	309.077	279.149	44.892	75.945	48.152	−1.677
1600	38.062	311.532	281.097	48.695	75.963	46.298	−1.511
1700	38.118	313.841	282.956	52.504	75.978	44.444	−1.366
1800	38.173	316.021	284.733	56.319	75.989	42.588	−1.236
1900	38.226	318.086	286.434	60.139	75.996	40.732	−1.120
2000	38.278	320.048	288.066	63.964	75.997	38.876	−1.015
2100	38.329	321.917	289.634	67.794	75.992	37.021	−0.921
2200	38.380	323.701	291.142	71.630	75.980	35.165	−0.835
2300	38.430	325.409	292.595	75.470	75.961	33.310	−0.756
2400	38.479	327.045	293.997	79.316	75.933	31.456	−0.685
2500	38.529	328.617	295.351	83.166	75.898	29.604	−0.619
2600	38.577	330.129	296.659	87.021	75.854	27.753	−0.558
2700	38.626	331.586	297.926	90.882	75.802	25.904	−0.501
2800	38.674	332.992	299.153	94.747	75.743	24.057	−0.449
2900	38.722	334.350	300.344	98.616	75.677	22.212	−0.400
3000	38.770	335.663	301.499	102.491	75.605	20.370	−0.355
3100	38.817	336.935	302.622	106.370	75.528	18.530	−0.312
3200	38.865	338.168	303.714	110.254	75.448	16.692	−0.272
3300	38.912	339.365	304.776	114.143	75.366	14.857	−0.235
3400	38.959	340.527	305.810	118.037	75.282	13.025	−0.200
3500	39.007	341.657	306.819	121.935	75.198	11.195	−0.167
3600	39.054	342.757	307.802	125.838	75.116	9.368	−0.136
3700	39.100	343.827	308.761	129.746	75.038	7.543	−0.106
3800	39.147	344.871	309.698	133.658	74.963	5.719	−0.079
3900	39.194	345.888	310.613	137.575	74.894	3.898	−0.052
4000	39.241	346.881	311.507	141.497	74.831	2.078	−0.027
4100	39.288	347.851	312.382	145.424	74.776	0.260	−0.003
4200	39.334	348.798	313.237	149.355	74.731	−1.557	0.019
4300	39.381	349.724	314.075	153.290	74.694	−3.373	0.041
4400	39.427	350.630	314.896	157.231	74.668	−5.188	0.062
4500	39.474	351.517	315.700	161.176	74.654	−7.002	0.081
4600	39.520	352.385	316.488	165.126	74.651	−8.817	0.100
4700	39.567	353.235	317.261	169.080	74.661	−10.632	0.118
4800	39.613	354.069	318.019	173.039	74.684	−12.447	0.135
4900	39.660	354.886	318.763	177.003	74.720	−14.262	0.152
5000	39.706	355.688	319.493	180.971	74.770	−16.078	0.168
5100	39.753	356.474	320.211	184.944	74.834	−17.896	0.183
5200	39.799	357.247	320.916	188.922	74.912	−19.715	0.198
5300	39.845	358.005	321.608	192.904	75.004	−21.536	0.212
5400	39.892	358.750	322.289	196.891	75.110	−23.358	0.226
5500	39.938	359.483	322.959	200.882	75.231	−25.183	0.239
5600	39.984	360.203	323.618	204.878	75.367	−27.010	0.252
5700	40.030	360.911	324.266	208.879	75.516	−28.839	0.264
5800	40.077	361.608	324.903	212.884	75.680	−30.671	0.276
5900	40.123	362.293	325.531	216.894	75.858	−32.507	0.288
6000	40.169	362.968	326.150	220.909	76.051	−34.345	0.299

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

$S°(298.15\ K) = 272.47 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 79.91 \pm 42\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 70.92 \pm 42\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X\ ^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	[8300]	2
$A[^2\Sigma]$	20884.3	[2]
$B[^2\Sigma]$	34523.7	[2]

$\omega_e = 206.56\ cm^{-1}$ $\omega_e x_e = 0.495\ cm^{-1}$ $\sigma = 1$

$B_e = 0.0451\ cm^{-1}$ $\alpha_e = [0.00014]\ cm^{-1}$ $r_e = 2.546\ Å$

Enthalpy of Formation

$\Delta_f H°(0\ K) = 19.10 \pm 10\ kcal \cdot mol^{-1}$ ($79.914 \pm 42\ kJ \cdot mol^{-1}$) is calculated and rounded from the $D_0° = 2.43$ eV ($56.04\ kcal \cdot mol^{-1}$) determined by Singh from emission spectra,[1] $\Delta_f H°(Pb, g, 0\ K) = 46.91 \pm 0.13\ kcal \cdot mol^{-1}$,[2] and $\Delta_f H°(Br, g, 0\ K) = 28.188\ kcal \cdot mol^{-1}$.[2] Rosen[3] and Gaydon[4] recommended $57 \pm 9\ kcal \cdot mol^{-1}$ and $58 \pm 9\ kcal \cdot mol^{-1}$, respectively, for $D_0°$. A linear Birge–Sponer extrapolation of the ground state vibrational constants, as derived from absorption spectra (v, 0–11) observed by Morgan,[5] gives a dissociation energy of 2.66 eV. Correction for the ionic character of PbBr as proposed by Hildenbrand[6] gives $D_0° = 2.44$ eV which is in good agreement with the value determined by Singh.[1] $\Delta_f H°(298.15\ K) = 16.95 \pm 10\ kcal \cdot mol^{-1}$ is calculated from the adopted $\Delta_f H°(0\ K) = 19.10 \pm 10\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The vibrational constants are from the compilation of Rosen,[3] corrected for the natural isotopic abundance of ^{79}Br and ^{81}Br. Analogous to PbF[2] and PbCl,[2] a $^2\Pi_{3/2}$ state at 8300 cm^{-1} is added to the electronic states and levels listed by Rosen.[3] The assignment of the first excited state remains uncertain; the choice appears to be between $^2\Sigma$ state, tentatively assigned to PbF[2] and PbCl,[2] and $^2\Delta$, tentatively assigned to PbI.[2] The $^2\Sigma$ state is adopted. The entropy is increased by $0.009\ cal \cdot K^{-1} \cdot mol^{-1}$ at 4000 K and $0.012\ cal \cdot K^{-1} \cdot mol^{-1}$ at 6000 K if the $^2\Delta$ state is used. The adopted value of B_e was determined by Lal and Khanna[7] and is adjusted for the natural abundance of the bromine isotopes. The value of r_e is calculated from the adopted B_e. The value of α_e is calculated assuming a Morse potential function.

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
	$J \cdot K^{-1} \cdot mol^{-1}$		$kJ \cdot mol^{-1}$			
0	0.	0. INFINITE	−10.146	79.910	79.910	INFINITE
100	33.337	233.663 304.665	−7.100	79.793	62.802	−32.804
200	36.150	257.867 275.829	−3.592	78.326	46.349	−12.105
250	36.638	265.991 273.077	−1.771	77.433	38.455	−8.035
298.15	36.922	272.471 272.471	0.	70.923	31.692	−5.552
300	36.930	272.699 272.471	0.068	70.872	31.448	−5.476
350	37.123	278.407 272.922	1.920	55.044	25.756	−3.844
400	37.260	283.374 273.925	3.780	54.614	21.602	−2.821
450	37.363	287.769 275.223	5.645	54.162	17.502	−2.032
500	37.446	291.710 276.678	7.516	53.691	13.454	−1.405
600	37.572	298.549 279.770	11.267	52.693	5.499	−0.479
700	37.671	304.348 282.878	15.029	46.764	−1.485	0.111
800	37.754	309.384 285.883	18.801	45.642	−8.301	0.542
900	37.830	313.835 288.746	22.580	44.554	−14.978	0.869
1000	37.904	317.825 291.458	26.367	43.499	−21.536	1.125
1100	37.980	321.441 294.022	30.161	42.477	−27.990	1.329
1200	38.062	324.749 296.447	33.963	41.489	−34.352	1.495
1300	38.155	327.799 298.743	37.773	40.529	−40.633	1.633
1400	38.262	330.631 300.920	41.594	39.582	−46.841	1.748
1500	38.385	333.274 302.990	45.426	38.641	−52.981	1.845
1600	38.524	335.756 304.961	49.272	37.699	−59.058	1.928
1700	38.680	338.096 306.842	53.132	36.753	−65.077	2.000
1800	38.852	340.312 308.641	57.008	35.801	−71.039	2.062
1900	39.038	342.417 310.363	60.903	34.841	−76.949	2.115
2000	39.237	344.425 312.017	64.816	33.872	−82.807	2.163
2100	39.446	346.344 313.606	68.750	−144.328	−81.502	2.027
2200	39.663	348.184 315.136	72.706	−144.927	−78.497	1.864
2300	39.886	349.952 316.612	76.683	−145.603	−75.462	1.714
2400	40.112	351.655 318.037	80.683	−146.359	−72.397	1.576
2500	40.339	353.297 319.414	84.706	−147.195	−69.298	1.448
2600	40.566	354.883 320.748	88.751	−148.109	−66.165	1.329
2700	40.791	356.418 322.041	92.819	−149.101	−62.994	1.219
2800	41.012	357.906 323.295	96.909	−150.165	−59.786	1.115
2900	41.230	359.349 324.514	101.021	−151.297	−56.538	1.018
3000	41.441	360.750 325.699	105.155	−152.492	−53.251	0.927
3100	41.648	362.112 326.851	109.309	−153.743	−49.922	0.841
3200	41.848	363.438 327.974	113.484	−155.042	−46.553	0.760
3300	42.041	364.728 329.068	117.678	−156.382	−43.142	0.683
3400	42.228	365.986 330.136	121.892	−157.756	−39.689	0.610
3500	42.407	367.213 331.178	126.124	−159.155	−36.197	0.540
3600	42.581	368.410 332.195	130.373	−160.574	−32.663	0.474
3700	42.747	369.579 333.190	134.640	−162.003	−29.091	0.411
3800	42.907	370.721 334.163	138.922	−163.438	−25.479	0.350
3900	43.061	371.838 335.114	143.221	−164.870	−21.830	0.292
4000	43.210	372.930 336.046	147.534	−166.295	−18.144	0.237
4100	43.352	373.999 336.959	151.863	−167.707	−14.423	0.184
4200	43.489	375.045 337.853	156.205	−169.101	−10.668	0.133
4300	43.621	376.070 338.730	160.560	−170.473	−6.879	0.084
4400	43.749	377.074 339.590	164.929	−171.820	−3.059	0.036
4500	43.872	378.059 340.434	169.310	−173.137	0.791	−0.009
4600	43.991	379.024 341.263	173.703	−174.422	4.671	−0.053
4700	44.106	379.971 342.076	178.108	−175.674	8.578	−0.095
4800	44.217	380.901 342.875	182.524	−176.889	12.511	−0.136
4900	44.325	381.814 343.661	186.951	−178.067	16.469	−0.176
5000	44.430	382.711 344.433	191.389	−179.207	20.451	−0.214
5100	44.531	383.591 345.192	195.837	−180.308	24.455	−0.250
5200	44.631	384.457 345.939	200.295	−181.369	28.480	−0.286
5300	44.727	385.308 346.674	204.763	−182.390	32.526	−0.321
5400	44.821	386.145 347.397	209.240	−183.372	36.590	−0.354
5500	44.914	386.968 348.109	213.727	−184.315	40.672	−0.386
5600	45.004	387.778 348.810	218.223	−185.219	44.771	−0.418
5700	45.092	388.576 349.501	222.728	−186.085	48.886	−0.448
5800	45.178	389.361 350.181	227.241	−186.914	53.015	−0.477
5900	45.263	390.134 350.852	231.763	−187.706	57.159	−0.506
6000	45.346	390.895 351.513	236.294	−188.463	61.315	−0.534

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

$S°(298.15\ K) = 247.42 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 240.8 \pm 46.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 235.3 \pm 46.0\ kJ·mol^{-1}$

Electronic States and Molecular Constants

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	Source
$X\ ^2\Pi_{1/2}$	0	2	423.2	1.5	0.1669	0.0019	2.210	(5)
$^2\Pi_{3/2}$	419.2	2	423.2	1.5	0.1669	0.0019	2.210	(5)
$A\ ^2\Sigma$	20937.6	2	249.6	0.5	[0.1669]	[0.0019]	[2.210]	(6)
$B'\ ^2\Delta$	23920	4	394	4	[0.1669]	[0.0019]	[2.210]	(1)
$B\ ^2\Sigma$	33572.7	2	573.6	4.0	0.1793	[0.0019]	2.132	(5)
$C\ ^2\Pi$	41057	4	529.2	2.0	[0.1669]	[0.0019]	[2.210]	(10)

Enthalpy of Formation

Kuznetsova and Kuzyakov[1] suggested a value of $D_0° = 85.8 \pm 11.4\ kcal·mol^{-1}$ based on linear Birge–Sponer extrapolations of the ground state and B' $^2\Delta$ state vibrational data. We correct this value for the ionic character of the bond according to Hildenbrand[2] and obtain $D_0° = 77.3 \pm 10.3\ kcal\ mol^{-1}$. With auxiliary JANAF data[3] this yields the adopted $\Delta_f H°(0\ K) = 57.543\ kcal·mol^{-1}$ (240.760 kJ mol^{-1}). Tandon and Tandon[4] obtained $D_0° = 85.3\ kcal·mol^{-1}$ from a theoretical treatment based on Sutherland's potential function in good agreement with the adopted value. The value of $D_0°$ may be compared to the average (per bond) enthalpy of atomization of 80.58 and 77.89 $kcal·mol^{-1}$ for $SiBr_2(g)$ and $SiBr_4(g)$, respectively.[3]

Heat Capacity and Entropy

Molecular constant data for the ground state are from Mishra and Khanna.[5] The vibrational data is in good agreement with data from Rao and Haranath,[6] Kuznetsova *et al.*,[7] and Jevons and Bashford.[8] Data for the A $^2\Sigma$ and B' $^2\Delta$ states are from Rao and Haranath[6] and Kuznetsova and Kuzyakov,[1] respectively. The B $^2\Sigma$ state data are from Mishra and Khanna[5] and the vibrational data agree well with Jevons and Bashford.[8] Slightly different values for the rotational constants for both this state and the ground state have been obtained by Kuznetsova and Kuzyakov.[9] Data for the C $^2\Pi$ state is from Oldershaw and Robinson[10] who also reported data for several higher states, these are not included due to uncertainties in their assignments and degeneracies. Splittings of 18 and 12 cm^{-1} for the B' $^2\Delta$ and C $^2\Pi$ states,[1,10] respectively, have not been included in our calculations. The $^4\Sigma$ state observed for SiF and SiI has not been observed for SiBr. It is expected to lie near 24000 cm^{-1} by analogy with SiF and SiI[3] which is very near the B' $^2\Delta$ state. This raises the possibility that this state may have been missed, or the $^2\Delta$ state misassigned, due to the large number of lines in this region[1]. A high resolution re-examination of this region of the spectrum is desirable to clarify the situation. We have assigned an uncertainty of $\pm 0.05\ cal·K^{-1}·mol^{-1}$ to $S°(298.15\ K)$ in view of these uncertainties. All molecular constant data has been corrected to the natural abundances of Si and Br assuming the observed data was for $^{28}Si\ ^{79}Br$. The ground state is treated as two distinct levels due to the splitting of this state as expressed by the spin coupling constant ($A = 419.2\ cm^{-1}$). This approximation gives slightly biased results at low temperature: the stated uncertainty in $S°(298.15\ K)$ should account for this.

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
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−10.040	240.758	240.758	INFINITE
100	30.564	209.105	280.168	−7.106	242.029	224.194	−117.107
200	36.635	232.296	250.917	−3.724	241.782	206.398	−53.906
298.15	38.731	247.418	247.418	0.	235.325	189.859	−33.262
300	38.746	247.658	247.419	0.072	235.290	189.577	−33.008
400	39.025	258.862	248.945	3.967	219.824	177.510	−23.180
500	38.903	267.559	251.831	7.864	219.597	166.955	−17.442
600	38.742	274.638	255.060	11.746	219.244	156.458	−13.621
700	38.615	280.600	258.294	15.614	218.794	146.028	−10.897
800	38.529	285.750	261.412	19.471	218.266	135.668	−8.858
900	38.477	290.285	264.373	23.321	217.672	125.379	−7.277
1000	38.449	294.337	267.170	27.167	217.020	115.158	−6.015
1100	38.440	298.001	269.809	31.011	216.317	105.006	−4.986
1200	38.446	301.346	272.300	34.855	215.566	94.919	−4.132
1300	38.462	304.424	274.654	38.701	214.771	84.897	−3.411
1400	38.486	307.275	276.884	42.548	213.931	74.938	−2.796
1500	38.517	309.931	278.999	46.398	213.048	65.041	−2.265
1600	38.552	312.418	281.011	50.252	212.120	55.204	−1.802
1700	38.591	314.757	282.928	54.109	160.972	45.873	−1.409
1800	38.634	316.964	284.758	57.970	160.187	39.125	−1.135
1900	38.679	319.054	286.509	61.836	159.398	32.421	−0.891
2000	38.726	321.039	288.186	65.706	158.606	25.758	−0.673
2100	38.775	322 930	289.796	69.581	157.810	19 135	−0.476
2200	38.826	324.735	291.343	73.461	157.008	12.550	−0.298
2300	38.879	326 462	292.833	77.346	156.201	6.002	−0.136
2400	38.933	328.117	294.269	81.237	155.388	−0.511	0.011
2500	38.989	329.708	295.655	85.133	154.570	−6.990	0.146
2600	39.047	331.238	296.994	89.035	153.745	−13.436	0.270
2700	39.107	332.713	298.290	92.942	152.916	−19.850	0.384
2800	39.170	334.136	299.545	96.856	152.082	−26.234	0.489
2900	39.235	335.512	300.761	100.777	151.244	−32.587	0.587
3000	39.304	336.843	301.942	104.704	150.403	−38.912	0.678
3100	39.376	338.133	303.089	108.638	149.562	−45.209	0.762
3200	39.451	339.385	304.204	112.579	148.721	−51.478	0.840
3300	39.530	340.600	305.288	116.528	147.882	−57.721	0.914
3400	39.614	341.781	306.344	120.485	147.046	−63.939	0.982
3500	39.702	342.931	307.373	124.451	146.216	−70.133	1.047
3600	39.796	344.050	308.377	128.426	−238.758	−65.841	0.955
3700	39 894	345.142	309.356	132.410	−239.158	−61.033	0.862
3800	39.998	346.207	310.311	136.405	−239.548	−56.213	0.773
3900	40.107	347.248	311.245	140.410	−239.927	−51.384	0.688
4000	40.223	348.265	312.158	144.426	−240.292	−46.545	0.608
4100	40.344	349.259	313.051	148.455	−240.642	−41.697	0.531
4200	40 471	350.233	313.925	152.495	−240.975	−36.840	0.458
4300	40.604	351.187	314.780	156.549	−241.289	−31.976	0.388
4400	40 743	352.122	315.618	160.616	−241.582	−27.105	0.322
4500	40.888	353.039	316 440	164.698	−241.853	−22.227	0.258
4600	41.040	353.939	317.245	168.794	−242.100	−17.344	0.197
4700	41.197	354.824	318.035	172.906	−242.323	−12 456	0.138
4800	41.360	355.693	318.811	177.034	−242.520	−7.563	0.082
4900	41.529	356.547	319.572	181.178	−242.690	−2.666	0.028
5000	41.703	357.388	320.320	185.340	−242.832	2.234	−0.023
5100	41 883	358.216	321.055	189.519	−242.945	7.137	−0.073
5200	42.069	359.031	321.778	193.717	−243.029	12.041	−0.121
5300	42.259	359.834	322.488	197.933	−243.084	16.947	−0.167
5400	42.454	360.626	323.187	202.169	−243.108	21.853	−0.211
5500	42.654	361 406	323.875	206.424	−243.101	26.760	−0.254
5600	42.859	362.177	324.552	210 700	−243.064	31.666	−0.295
5700	43.067	362.937	325.219	214.996	−242.995	36.572	−0.335
5800	43.280	363.688	325.875	219.313	−242.896	41 475	−0.374
5900	43.496	364.430	326.523	223.652	−242.766	46.377	−0.411
6000	43.716	365.163	327.161	228.013	−242.603	51.276	−0.446

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

$S°(298.15\ K) = 263.8 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -80.4 \pm 42\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -89.1 \pm 42\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$X\ ^2\Sigma^+$	0	2	$E\ ^2\Sigma$	32052.5	2
$A_1\ ^2\Pi_{1/2}$	14699.4	2	$F_1\ ^2\Pi_{1/2}$	33131.7	2
$A_2\ ^2\Pi_{3/2}$	15000.7	2	$F_2\ ^2\Pi_{3/2}$	33215.0	2
$B\ ^2\Sigma$	15352.0	2	$G_1\ ^2\Delta_{3/2}$	34257.0	2
$C_1\ ^2\Pi_{1/2}$	24343.7	2	$G_2\ ^2\Delta_{3/2}$	34282.8	2
$C_2\ ^2\Pi_{3/2}$	24665.8	2	$H\ ^2\Sigma$	34357.7	2
$D\ ^2\Sigma$	28958.2	2			

$\omega_e = 216.5\ cm^{-1}$ $\omega_e x_e = 0.51\ cm^{-1}$ $\sigma = 1$

$B_e = [0.054924]\ cm^{-1}$ $\alpha_e = [0.000171]\ cm^{-1}$ $r_e = [2.71]$ Å

Enthalpy of Formation

The selected value, $\Delta_f H°(298.15\ K) = -21.3\ kcal \cdot mol^{-1}$ ($-89.119\ kJ \cdot mol^{-1}$), is obtained from an analysis of spectroscopic data. Herzberg[1] suggested $D_0^\circ = 2.8$ eV for SrBr(g) which was derived from a linear Birge–Sponer extrapolation of the ground state vibrational levels. Later, Gaydon[2] claimed that this value is unreliable and suggested that the true value may be much higher. The adopted ground state vibrational constants give $D_0^\circ = 2.84$ eV by a similar extrapolation. We note that JANAF analyses[3] of the spectroscopic and thermochemical data for SrF(g) and SrCl(g) show that the ionicity corrections of Hildenbrand[4] bring the Birge–Sponer extrapolations into reasonable agreement with adopted D_0° values. Based on this correction for SrBr(g), we obtain $D_0^\circ = 3.76$ eV (86.7 $kcal \cdot mol^{-1}$) which is adopted. The adopted value of D_0° corresponds to $\Delta_f H°(298\ 15\ K) = 21.3\ kcal\ mol^{-1}$. We also find $D_0^\circ(SrBr)/\Delta_a H°(SrBr_2) = 0\ 46$ which is quite consistent with values of this ratio for other alkaline earth halide systems.[5]

Ionic model calculations[6,7] have led to D_0° values of 5.07 eV[6] and 3.53 eV.[7] The latter result is believed to represent a minimum value for D_0°. Two other experimental values for D_0° which bracket the selected value, have been reported. Flame studies[8] gave $D_0^\circ = 3.4$ eV, and chemiluminescence[9] from reaction of Sr atoms with Br_2 gave a lower limit to D_0° of 4 1 eV. We assign an uncertainty of ±10 kcal mol^{-1} to $\Delta_f H°(298.15\ K)$ to include the possibility that these studies are correct.

Heat Capacity and Entropy

The value of r_e is obtained from that for gaseous $SrBr_2$[3] with $r_e(SrBr)/r_e(SrBr_2) = 0.96$. This value for the ratio is calculated from bond lengths[5] for several other alkaline earth halide systems. Our adopted value for r_e agrees with that (2.74 Å) estimated by Krasnov and Karaseva,[7] while two other estimated values[6,10] lie somewhat higher (~0.2 Å). The rotational constant is calculated from the estimated value for r_e. The value of α_e is obtained from a Morse potential function. The vibrational constants and first seven electronic states and levels are taken from the compilation of Rosen.[11] The E state energy has been measured by Reddy and Rao,[12] while the F, G, and H state energies are due to Reddy *et al.*[13] The five uppermost states were associated with transitions between the excited states of SrBr, and their assignments[13] were made by analogy with the observed spectrum for SrCl(g).

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
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−10.105	−80.401	−80.401	INFINITE
100	33.079	225.114	295.842	−7.073	−80.265	−97.279	50.813
200	36.028	249.184	267.101	−3.584	−81.715	−113.767	29.713
250	36.551	257.285	264.356	−1.768	−82.609	−121.685	25.425
298.15	36.856	263.751	263.751	0.	−89.119	−128.461	22.506
300	36.866	263.979	263.751	0.068	−89.171	−128.705	22.410
350	37.073	269.678	264.201	1.917	−105.000	−134 416	20.060
400	37.219	274.639	265.202	3.774	−105.433	−138.589	18.098
450	37.329	279.029	266.500	5.638	−105.892	−142.706	16.565
500	37.416	282.967	267.953	7.507	−106.375	−146.771	15.333
600	37.548	289.801	271.042	11.255	−107.416	−154.754	13.473
700	37.649	295.597	274.146	15.015	−108.559	−162.554	12.130
800	37.733	300.630	277.149	18.785	−109.805	−170.184	11.112
900	37.808	305.078	280.010	22.562	−111.784	−177.579	10.306
1000	37.877	309.065	282.719	26.346	−112.921	−184.829	9.655
1100	37.941	312.678	285.281	30.137	−121.958	−191.600	9.098
1200	38.003	315.982	287.704	33.934	−124.003	−197.841	8.612
1300	38.063	319.027	289.998	37.738	−126.046	−203.911	8.193
1400	38.122	321.849	292.173	41.547	−128.088	−209.824	7.829
1500	38.181	324.482	294.240	45.362	−130.128	−215.591	7.508
1600	38.241	326.948	296.208	49.183	−132.168	−221.222	7.222
1700	38.303	329.268	298.085	53.010	−271.122	−225.546	6.930
1800	38.368	331.459	299.879	56.844	−271.301	−222.860	6.467
1900	38.438	333.535	301.596	60.684	−271.487	−220.163	6.053
2000	38.515	335.509	303.243	64.531	−271.682	−217.457	5.679
2100	38.601	337.390	304.825	68.387	−271.890	−214.741	5.341
2200	38.696	339.188	306.346	72.252	−272.115	−212.014	5 034
2300	38.803	340.910	307.812	76.127	−272.363	−209.277	4.753
2400	38.924	342.564	309.226	80.013	−272.640	−206.528	4.495
2500	39.059	344 156	310.591	83.912	−272.951	−203.767	4 257
2600	39.209	345.691	311.912	87.825	−273.305	−200.993	4.038
2700	39.376	347.173	313.190	91.754	−273.706	−198.205	3.834
2800	39.559	348.609	314.430	95.701	−274.164	−195.400	3.645
2900	39 760	350.000	315.633	99.667	−274.686	−192.578	3.469
3000	39.977	351.352	316.801	103.653	−275.279	−189.737	3.304
3100	40.212	352.667	317.937	107.663	−275.951	−186.875	3.149
3200	40 463	353.947	319.042	111.696	−276.709	−183.989	3.003
3300	40.730	355.196	320.119	115.756	−277.559	−181.079	2.866
3400	41.012	356.416	321.168	119.843	−278.508	−178.141	2.737
3500	41.309	357.609	322.193	123.959	−279.562	−175.174	2.614
3600	41.619	358.777	323.193	128.105	−280.725	−172.175	2.498
3700	41.942	359.922	324.170	132.283	−282.000	−169.143	2.388
3800	42.277	361.045	325.126	136.494	−283.392	−166.074	2.283
3900	42.622	362.148	326.061	140.739	−284.901	−162.968	2.183
4000	42.977	363.231	326.977	145.018	−286.528	−159.821	2.087
4100	43.341	364.297	327.874	149.334	−288.274	−156.632	1.996
4200	43.712	365.346	328.754	153.687	−290.132	−153.399	1.908
4300	44 089	366.379	329.617	158.077	−292.108	−150.120	1.824
4400	44.472	367.397	330.464	162.505	−294.194	−146.794	1.743
4500	44.859	368.400	331.296	166.971	−296.386	−143.420	1.665
4600	45.250	369.391	332.113	171.477	−298.614	−140.001	1.590
4700	45 643	370.368	332.917	176.021	−300.984	−136.527	1.517
4800	46.037	371.333	333.707	180.605	−303.437	−133.002	1.447
4900	46.433	372.286	334.485	185.229	−305.969	−129.426	1.380
5000	46 828	373.228	335.250	189.892	−308.564	−125.797	1.314
5100	47.222	374.160	336.004	194.594	−311.201	−122.117	1.251
5200	47.614	375.080	336.747	199.336	−313.909	−118.384	1.189
5300	48 004	375.991	337.478	204 117	−316.661	−114.597	1.129
5400	48.391	376.892	338.200	208.937	−319.447	−110.758	1.071
5500	48 774	377 783	338.912	213.795	−322.260	−106.868	1.015
5600	49 153	378.666	339.614	218.692	−325.092	−102.926	0.960
5700	49.527	379.539	340.306	223.626	−327.934	−98.934	0.907
5800	49.895	380.404	340.990	228.597	−330.780	−94 892	0.855
5900	50.257	381.260	341.666	233.605	−333.411	−90.824	0.804
6000	50.613	382.107	342.333	238 648	−336.211	−86.689	0.755

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K)$ = [260.25 ± 8.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [219.7 ± 42] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [212.5 ± 42] $kJ·mol^{-1}$

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

ω_e = [295] cm^{-1} $\omega_e x_e$ = [2.21] cm^{-1} σ = 1
B_e = [0.0904] cm^{-1} α_e = [0.00067] cm^{-1} r_e = [2.5] Å

Enthalpy of Formation

$\Delta_f H°$(TiBr, g, 298.15 K) is calculated from the dissociation energy which is estimated as 104 $kcal·mol^{-1}$. This estimate is obtained from the relation $\Delta_{at}H°(TiBr_4) < D°_0(TiBr) < \Delta_{at}H°(TiBr_3)$, 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]

Heat Capacity and Entropy

The vibrational frequency, ω_e, and the anharmonic vibrational term, $\omega_e x_e$, are estimated from those of TiCl(g) and comparisons of the mercury and alkali monohalides. The interatomic distance is estimated from Guggenheimer's relation.[2] B_e is calculated from r_e. The ground state term and electronic levels are estimated from the ground state multiplet of Ti^+.[3] α_e is estimated from the Morse potential function.

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	−9.938	219.694	219.694	INFINITE
100	31.427	222.442	292.172	−6.973	220.702	201.976	−105.501
200	35.424	245.604	263.646	−3.608	219.699	183.565	−47.942
250	36.809	253.660	260.868	−1.802	218.934	174.618	−36.484
298.15	38.020	260.249	260.249	0.	212.547	166.815	−29.225
300	38.065	260.484	260.249	0.070	212.501	166.531	−28.996
350	39.192	266.438	260.717	2.002	196.821	159.737	−23.839
400	40.173	271.737	261.769	3.987	196.564	154.457	−20.170
450	41.000	276.518	263.147	6.017	196.316	149.209	−17.320
500	41.678	280.874	264.705	8.085	196.076	143.988	−15.042
600	42.651	288.566	268.058	12.305	195.611	133.614	−11.632
700	43.232	295.189	271.472	16.602	195.150	123.317	−9.202
800	43.559	300.985	274.806	20.943	194.690	113.087	−7.384
900	43.734	306.127	278.006	25.309	194.183	102.916	−5.973
1000	43.829	310.740	281.053	29.687	193.553	92.807	−4.848
1100	43.887	314.920	283.945	34.073	192.733	82.771	−3.930
1200	43.933	318.741	286.687	38.464	187.733	72.938	−3.175
1300	43.980	322.259	289.290	42.860	187.248	63.391	−2.547
1400	44.034	325.520	291.763	47.260	186.685	53.884	−2.010
1500	44.097	328.561	294.116	51.667	186.032	44.420	−1.547
1600	44.169	331.409	296.359	56.080	185.276	35.003	−1.143
1700	44.249	334.089	298.500	60.501	184.404	25.637	−0.788
1800	44.336	336.621	300.548	64.930	183.402	16.326	−0.474
1900	44.426	339.020	302.510	69.368	182.258	7.075	−0.195
2000	44.519	341.301	304.393	73.816	166.270	−1.659	0.043
2100	44.612	343.475	306.203	78.272	164.051	−10.001	0.249
2200	44.704	345.553	307.945	82.738	161.831	−18.237	0.433
2300	44.794	347.542	309.624	87.213	159.610	−26.372	0.599
2400	44.881	349.450	311.244	91.697	157.386	−34.410	0.749
2500	44.965	351.284	312.809	96.189	155.159	−42.356	0.885
2600	45.044	353.049	314.323	100.689	152.929	−50.213	1.009
2700	45.119	354.751	315.789	105.198	150.696	−57.984	1.122
2800	45.190	356.393	317.210	109.713	148.460	−65.672	1.225
2900	45.256	357.980	318.588	114.235	146.220	−73.280	1.320
3000	45.318	359.515	319.927	118.764	143.977	−80.810	1.407
3100	45.376	361.002	321.228	123.299	141.732	−88.266	1.487
3200	45.430	362.444	322.494	127.839	139.486	−95.650	1.561
3300	45.481	363.842	323.726	132.385	137.239	−102.963	1.630
3400	45.528	365.201	324.926	136.935	134.993	−110.208	1.693
3500	45.572	366.521	326.095	141.490	132.748	−117.387	1.752
3600	45.614	367.806	327.236	146.050	130.506	−124.502	1.806
3700	45.653	369.056	328.350	150.613	−280.831	−123.767	1.747
3800	45.690	370.274	329.437	155.180	−281.831	−119.508	1.643
3900	45.726	371.461	330.499	159.751	−282.880	−115.223	1.543
4000	45.760	372.619	331.538	164.325	−283.977	−110.910	1.448
4100	45.793	373.750	332.554	168.903	−285.119	−106.570	1.358
4200	45.825	374.854	333.548	173.484	−286.303	−102.201	1.271
4300	45.856	375.932	334.521	178.068	−287.527	−97.803	1.188
4400	45.887	376.987	335.474	182.655	−288.788	−93.376	1.109
4500	45.918	378.018	336.408	187.245	−290.084	−88.920	1.032
4600	45.949	379.028	337.324	191.839	−291.412	−84.435	0.959
4700	45.980	380.016	338.222	196.435	−292.769	−79.921	0.888
4800	46.011	380.985	339.103	201.035	−294.154	−75.378	0.820
4900	46.042	381.934	339.967	205.637	−295.564	−70.806	0.755
5000	46.074	382.864	340.816	210.243	−296.996	−66.204	0.692
5100	46.106	383.777	341.649	214.852	−298.447	−61.574	0.631
5200	46.140	384.673	342.468	219.464	−299.917	−56.915	0.572
5300	46.173	385.552	343.273	224.080	−301.402	−52.228	0.515
5400	46.208	386.415	344.064	228.699	−302.901	−47.513	0.460
5500	46.244	387.263	344.841	233.322	−304.411	−42.769	0.406
5600	46.280	388.097	345.606	237.948	−305.930	−37.998	0.354
5700	46.318	388.916	346.359	242.578	−307.458	−33.200	0.304
5800	46.356	389.722	347.100	247.212	−308.991	−28.376	0.256
5900	46.395	390.515	347.829	251.849	−310.528	−23.524	0.208
6000	46.436	391.295	348.547	256.491	−312.068	−18.647	0.162

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

$S°(298.15\ K) = [272.6]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [593.7 \pm 84]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [586.2 \pm 84]\ kJ·mol^{-1}$

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

$\omega_e = [321.4]\ cm^{-1}$ $\omega_e x_e = [0.80]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.05254]\ cm^{-1}$ $\alpha_e = [0.00015]\ cm^{-1}$ $r_e = [2.40]$ Å

Enthalpy of Formation

$\Delta_f H°$(WBr, g, 298.15 K) = 140.1 kcal·mol^{-1} (586.178 kJ·mol^{-1}) is calculated from the bond dissociation energy, $\Delta_{at} H°$(W–Br, 298.15 K) = 90 ± 20 kcal·mol^{-1}. This value is estimated to be slightly higher than the average bond dissociation energy of WBr_6(g), by analogy with the WCl_x system.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in WBr_6(g). The distance is then used with Guggenheimer's relation[1] for polar molecules to calculate the fundamental vibrational freqency, ω_e. The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e / (D° + 0.5\ \omega_e) = 0.0025$. The rotational constant B_e is calculated from the estimated bond istance. 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

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	−9 726	593.680	593.680	INFINITE
100	30.915	235.768	303.535	−6 777	594.581	574.657	−300.170
200	34.595	258.493	275.876	−3.477	593.422	555.121	−144.983
250	35.487	266.317	273.208	−1.723	592.612	545.636	−114.004
298.15	36.032	272.617	272.617	0	586.178	537.325	−94.137
300	36.049	272.840	272.618	0.067	586.130	537.022	−93.504
350	36.421	278.427	273.058	1.879	570.393	529.709	−79.055
400	36.681	283.308	274.041	3.707	570.067	523.919	−68.417
450	36.870	287.640	275.316	5.546	569.733	518.171	−60.148
500	37.013	291.533	276.746	7.393	569.393	512.460	−53.536
600	37.218	298.300	279.791	11.105	568.688	501.139	−43.628
700	37.366	304.049	282.856	14.835	567.947	489 939	−36.560
800	37.494	309.047	285.824	18.578	567.169	478.847	−31.266
900	37.622	313.471	288.655	22.334	566.354	467.856	−27.154
1000	37.761	317.441	291.339	26.103	565.502	456.957	−23.869
1100	37.914	321.048	293.878	29.886	564.615	446.145	−21.186
1200	38.082	324.354	296.282	33.686	563.695	435.415	−18.953
1300	38.260	327.409	298.560	37.503	562.741	424.764	−17.067
1400	38.445	330.251	300.723	41.338	561.756	414.187	−15.453
1500	38.635	332.910	302.782	45.192	560.738	403.681	−14.057
1600	38.824	335.409	304.743	49.065	559.686	393.245	−12.838
1700	39.013	337.769	306.617	52.957	558.600	382.876	−11.764
1800	39.200	340.004	308.411	56 868	557.480	372.571	−10.812
1900	39.386	342.128	310.130	60.797	556.322	362.330	−9.961
2000	39.572	344.153	311.781	64 745	555.126	352.150	−9.197
2100	39 760	346.088	313.369	68 712	553.891	342.032	−8.508
2200	39.952	347.943	314.898	72.697	552.616	331.973	−7.882
2300	40.151	349.723	316.374	76.702	551.299	321.973	−7.312
2400	40.358	351.436	317.799	80.728	549.942	312.031	−6.791
2500	40.576	353.088	319.178	84 774	548.546	302.147	−6.313
2600	40.806	354.684	320.513	88.843	547.113	292.319	−5.873
2700	41.050	356.228	321.808	92.936	545.618	282.548	−5.466
2800	41.307	357.726	323.064	97.054	544.029	272.833	−5.090
2900	41.578	359.180	324.284	101.198	542.308	263.177	−4.740
3000	41.863	360.594	325.471	105.370	540.431	253.584	−4.415
3100	42.162	361.972	326.626	109.571	538.356	244.056	−4.112
3200	42.473	363.315	327.752	113.803	536.055	234.598	−3.829
3300	42.795	364.627	328.850	118.066	533.504	225.216	−3.565
3400	43.126	365.910	329.921	122.362	530.671	215.916	−3.317
3500	43.465	367.165	330.967	126.691	527.494	206.704	−3.085
3600	43.810	368.394	331.990	131.055	523.879	197.589	−2.867
3700	44.159	369.599	332.990	135.453	484.961	188.771	−2.665
3800	44.510	370.781	333.969	139.887	483.760	180.782	−2.485
3900	44.861	371.942	334.928	144.355	482.597	172.824	−2.315
4000	45.210	373.082	335.867	148.859	481.472	164.896	−2.153
4100	45.556	374.203	336.789	153.397	480.386	156.995	−2.000
4200	45.896	375.305	337.693	157.970	479.340	149.120	−1.855
4300	46.230	376.389	338.580	162.576	478.334	141.270	−1.716
4400	46.555	377.455	339.452	167.216	477.368	133.442	−1.584
4500	46.870	378.505	340.308	171.887	476.441	125.636	−1.458
4600	47.174	379.538	341.149	176.589	475.554	117.851	−1.338
4700	47.466	380.556	341.977	181.321	474.706	110.084	−1.223
4800	47.746	381.558	342.791	186 082	473.896	102.334	−1.114
4900	48.012	382.546	343.592	190.870	473.123	94.602	−1.008
5000	48.264	383.518	344.381	195.684	472.386	86.884	−0.908
5100	48.501	384.476	345.158	200.522	471.685	79.181	−0.811
5200	48.723	385.420	345.923	205.384	471.017	71.491	−0.718
5300	48.931	386.350	346.677	210.267	470.381	63.815	−0.629
5400	49.123	387.267	347.421	215.169	469.776	56.149	−0.543
5500	49.301	388.170	348.153	220.091	469.200	48.495	−0.461
5600	49.463	389.060	348.876	225.029	468.653	40.851	−0.381
5700	49.611	389.936	349.588	229.983	468.132	33.216	−0.304
5800	49.744	390.800	350.292	234.951	467.635	25.590	−0.230
5900	49.863	391.652	350.985	239.931	467.162	17.973	−0.159
6000	49.969	392.491	351.670	244.923	466.711	10.363	−0.090

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

$S°(298.15\ K) = [265.6 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [309.3 \pm 42]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [301.2 \pm 2]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
[$^4\Sigma$]	0	[4]
	[3000]	[4]
	[6000]	[4]
	[12000]	[4]
	[18000]	[4]
	[24000]	[4]
	[30000]	[4]

$\omega_e = [317]\ cm^{-1}$ $\omega_e x_e = [0.69]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.065]\ cm^{-1}$ $\alpha_e = [0.00018]\ cm^{-1}$ $r_e = [2.47]$ Å

Enthalpy of Formation

$\Delta_f H°$(ZrBr, g, 298.15 K) = 72 kcal·mol^{-1} (301.248 kJ·mol^{-1}) is derived from the estimated bond dissociation energy, $\Delta_a H°$ (Zr–Br, 298.15 K) = 103.5 ± 10 kcal·mol^{-1}. This value of is calculated from the relation $\Delta_a H°$(Zr–Br, 298.15 K)/$\Delta_a H°$(Ti–Br, 298.15 K) = $\Delta_a H°$(ZrBr4, 298.15 K)/$\Delta_a H°$(TiBr4, 298.15 K) where the average bond dissociation energies, $\Delta_a H°(ZrBr_4, 298.15\ K = 102.2$ kcal·mol^{-1}, $\Delta_a H°(TiBr_4, 298.15\ K) = 87.9$ kcal·mol^{-1} and $\Delta_a H°$(TiBr, 298.15 K) = 89.0 kcal·mol^{-1}, all calculated from JANAF $\Delta_f H°$(298.15 K) for $ZrBr_4$(g), $TiBr_4$(g), TiBr(g), Zr(g), Ti(g) and Br(g).

Heat Capacity and Entropy

The bond distance is assumed to be the same as that in $ZrBr_4$(g), which was estiamted as 2.47 Å by Godnev *et al.*[1] The estimated bond distance is then used with Guggenheimer's[2] relation for polar molecules to calculate the fundamental frequency ω_e. The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4\ (\Delta_a H° + 0.5\ \omega_e) = 0.0021$ 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 is taken from the ground state multiplet of Zr^+ reported by Moore.[3] The electronic levels and quantum weights are estimated to be the same as those of ZrF(g).

References

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[2] K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 416 (1946).
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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	−9.739	309.261	309.261	INFINITE
100	30.981	228.641	296.521	−6.788	309.929	291.163	−152.088
200	34.653	251.415	268.819	−3.481	308.592	272.862	−71.264
250	35.530	259.250	266.148	−1.725	307.725	264.027	−55.165
298.15	36.065	265.557	265.557	0.	301.248	256.351	−44.912
300	36.082	265.780	265.557	0.067	301.198	256.073	−44.586
350	36.451	271.371	265.998	1.881	285.416	249.427	−37.225
400	36.719	276.257	266.982	3.710	285.042	244.311	−31.904
450	36.936	280.595	268.258	5.552	284.658	239.243	−27.771
500	37.133	284.496	269.690	7.403	284.265	234.218	−24.469
600	37.542	291.302	272.741	11.137	283.447	224.284	−19.526
700	38.018	297.124	275.818	14.914	282.589	214.491	−16.006
800	38.558	302.235	278.807	18.743	281.691	204.824	−13.374
900	39.134	306.810	281.669	22.627	280.746	195.272	−11.333
1000	39.714	310.963	284.394	26.569	279.746	185.828	−9.707
1100	40.274	314.775	286.985	30.569	278.682	176.487	−8.381
1200	40.798	318.302	289.449	34.623	273.839	167.468	−7.290
1300	41.277	321.587	291.796	38.727	273.174	158.630	−6.374
1400	41.705	324.662	294.035	42.877	272.508	149.844	−5.591
1500	42.082	327.552	296.174	47.067	271.825	141.106	−4.914
1600	42.410	330.279	298.222	51.292	271.108	132.415	−4.323
1700	42.691	332.858	300.184	55.547	270.342	123.769	−3.803
1800	42.929	335.306	302.068	59.828	269.511	115.171	−3.342
1900	43.129	337.632	303.879	64.131	268.599	106.621	−2.931
2000	43.295	339.849	305.622	68.453	267.591	98.122	−2.563
2100	43.432	341.964	307.303	72.789	266.472	89.675	−2.231
2200	43.543	343.988	308.925	77.138	243.906	82.031	−1.948
2300	43.633	345.925	310.492	81.497	242.108	74.713	−1.697
2400	43.705	347.784	312.007	85.864	240.308	67.473	−1.469
2500	43.763	349.569	313.474	90.238	238.502	60.309	−1.260
2600	43.808	351.286	314.895	94.616	236.690	53.217	−1.069
2700	43.844	352.940	316.274	98.999	234.871	46.195	−0.894
2800	43.872	354.535	317.612	103.385	233.044	39.240	−0.732
2900	43.894	356.075	318.912	107.773	231.210	32.351	−0.583
3000	43.911	357.564	320.176	112.164	229.369	25.525	−0.444
3100	43.926	359.004	321.405	116.555	227.521	18.761	−0.316
3200	43.938	360.399	322.602	120.949	225.667	12.056	−0.197
3300	43.948	361.751	323.768	125.343	223.809	5.410	−0.086
3400	43.958	363.063	324.905	129.738	221.947	−1.181	0.018
3500	43.968	364.337	326.013	134.134	220.083	−7.716	0.115
3600	43.977	365.576	327.095	138.532	218.219	−14.198	0.206
3700	43.988	366.781	328.151	142.930	216.355	−20.628	0.291
3800	43.999	367.954	329.183	147.329	214.492	−27.009	0.371
3900	44.011	369.097	330.192	151.730	212.633	−33.340	0.447
4000	44.024	370.212	331.179	156.131	210.779	−39.623	0.517
4100	44.038	371.299	332.144	160.535	208.930	−45.860	0.584
4200	44.053	372.360	333.089	164.939	207.088	−52.052	0.647
4300	44.070	373.397	334.015	169.345	205.254	−58.201	0.707
4400	44.088	374.411	334.921	173.753	203.429	−64.306	0.763
4500	44.107	375.402	335.810	178.163	201.613	−70.371	0.817
4600	44.127	376.371	336.681	182.574	199.808	−76.395	0.867
4700	44.148	377.320	337.536	186.988	198.014	−82.380	0.916
4800	44.171	378.250	338.374	191.404	−364.705	−76.710	0.835
4900	44.194	379.161	339.197	195.822	−366.127	−70.695	0.754
5000	44.219	380.054	340.006	200.243	−367.553	−64.651	0.675
5100	44.244	380.930	340.799	204.666	−368.982	−58.579	0.600
5200	44.270	381.789	341.580	209.092	−370.412	−52.479	0.527
5300	44.296	382.633	342.346	213.520	−371.842	−46.351	0.457
5400	44.323	383.461	343.100	217.951	−373.269	−40.196	0.389
5500	44.351	384.275	343.841	222.385	−374.694	−34.015	0.323
5600	44.379	385.074	344.570	226.821	−376.113	−27.808	0.259
5700	44.408	385.860	345.288	231.261	−377.527	−21.576	0.198
5800	44.437	386.633	345.994	235.703	−378.933	−15.319	0.138
5900	44.466	387.392	346.689	240.148	−380.331	−9.038	0.080
6000	44 495	388.140	347.374	244.596	−381.720	−2.733	0.024

PREVIOUS: June 1970 (1 atm) CURRENT June 1970 (1 bar)

REFERENCE STATE

0	to	265.90 K	crystal
265.90	to	332.62 K	liquid
above		332.62 K	ideal diatomic gas

Refer to the individual tables for details.

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	−24.509	0.	0.	0.
100	43.587	53.847	271.009	−21.716	0.	0.	0.
200	53.761	87.421	171.496	−16.815	0.	0.	0.
265.900	61.630	103.687	152.725	−13.039	CRYSTAL <--> LIQUID TRANSITION		
265.900	77.724	143.445	152.725	−2.468			
298.15	75.674	152.206	152.206	0.	0.	0.	0.
300	75.624	152.674	152.208	0.140	0.	0.	0.
332.503	75.302	160.429	152.639	2.590	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
332.503	36.332	249.341	152.639	32.153			
400	36.723	256.093	169.543	34.620	0.	0.	0.
500	37.077	264.329	187.706	38.312	0.	0.	0.
600	37.301	271.110	201.058	42.031	0.	0.	0.
700	37.460	276.873	211.488	45.770	0.	0.	0.
800	37.586	281.883	219.981	49.522	0.	0.	0.
900	37.692	286.316	227.110	53.286	0.	0.	0.
1000	37.787	290.293	233.233	57.060	0.	0.	0.
1100	37.876	293.898	238.586	60.843	0.	0.	0.
1200	37.962	297.198	243.335	64.635	0.	0.	0.
1300	38.049	300.240	247.597	68.436	0.	0.	0.
1400	38.140	303.063	251.459	72.245	0.	0.	0.
1500	38.239	305.697	254.988	76.064	0.	0.	0.
1600	38.348	308.169	258.236	79.893	0.	0.	0.
1700	38.471	310.497	261.242	83.734	0.	0.	0.
1800	38.611	312.700	264.040	87.588	0.	0.	0.
1900	38.769	314.792	266.657	91.457	0.	0.	0.
2000	38.945	316.785	269.114	95.342	0.	0.	0.
2100	39.137	318.690	271.429	99.246	0.	0.	0.
2200	39.345	320.515	273.619	103.170	0.	0.	0.
2300	39.563	322.269	275.697	107.116	0.	0.	0.
2400	39.789	323.957	277.673	111.083	0.	0.	0.
2500	40.018	325.586	279.557	115.074	0.	0.	0.
2600	40.244	327.160	281.358	119.087	0.	0.	0.
2700	40.463	328.683	283.082	123.122	0.	0.	0.
2800	40.672	330.158	284.737	127.179	0.	0.	0.
2900	40.864	331.589	286.328	131.256	0.	0.	0.
3000	41.038	332.977	287.860	135.351	0.	0.	0.
3100	41.190	334.326	289.338	139.463	0.	0.	0.
3200	41.318	335.635	290.764	143.589	0.	0.	0.
3300	41.420	336.908	292.143	147.726	0.	0.	0.
3400	41.496	338.146	293.478	151.872	0.	0.	0.
3500	41.545	339.350	294.772	156.024	0.	0.	0.
3600	41.567	340.521	296.026	160.180	0.	0.	0.
3700	41.563	341.659	297.244	164.337	0.	0.	0.
3800	41.533	342.767	298.428	168.492	0.	0.	0.
3900	41.480	343.846	299.578	172.642	0.	0.	0.
4000	41.404	344.895	300.698	176.787	0.	0.	0.
4100	41.306	345.916	301.789	180.922	0.	0.	0.
4200	41.190	346.910	302.851	185.047	0.	0.	0.
4300	41.056	347.878	303.887	189.160	0.	0.	0.
4400	40.907	348.820	304.898	193.258	0.	0.	0.
4500	40.744	349.738	305.884	197.341	0.	0.	0.
4600	40.569	350.631	306.847	201.407	0.	0.	0.
4700	40.383	351.502	307.788	205.454	0.	0.	0.
4800	40.189	352.350	308.708	209.483	0.	0.	0.
4900	39.987	353.176	309.607	213.492	0.	0.	0.
5000	39.780	353.982	310.486	217.480	0.	0.	0.
5100	39.568	354.768	311.347	221.448	0.	0.	0.
5200	39.353	355.534	312.189	225.394	0.	0.	0.
5300	39.136	356.282	313.014	229.318	0.	0.	0.
5400	38.917	357.011	313.822	233.221	0.	0.	0.
5500	38.698	357.723	314.614	237.102	0.	0.	0.
5600	38.480	358.419	315.390	240.961	0.	0.	0.
5700	38.263	359.098	316.151	244.798	0.	0.	0.
5800	38.047	359.761	316.897	248.613	0.	0.	0.
5900	37.834	360.410	317.629	252.407	0.	0.	0.
6000	37.624	361.044	318.347	256.180	0.	0.	0.

PREVIOUS. September 1961 (1 atm) CURRENT June 1982 (1 bar)

$S°(298.15\ K) = 152.21 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 265.90 \pm 0.05\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 10.571 \pm 0.008\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity for crystalline and liquid bromine was measured by Hildenbrand *et al.*,[1] 179 data points in the range 15–310 K. The reported values are corrected for the current relative molecular weight and converted to joules. The liquid phase heat capacity is extrapolated to a constant value of 18.0 cal $K^{-1} \cdot mol^{-1}$ for temperatures above 320 K. The value recommended by CODATA[2] for $S°(Br_2, l, 298.15\ K)$ is the same as adopted here and is based on the same study. References to earlier work are given by Hildenbrand *et al.*[1] They are not used in this analysis.

Fusion Data

The adopted values for the fusion point and the enthalpy of fusion are from the study of Hildenbrand *et al.*[1]

Vaporization Data

The enthalpy of vaporization of bromine at 25°C was measured by Hildenbrand *et al.*[1] Six vaporization determinations were made using 14 to 18 gram samples of bromine. Correcting their reported values for the current relative atomic mass and converting to Joules yields $\Delta_{vap}H$ (Br_2, l, 298.15 K) = 30.91 ± 0.11 $kJ \cdot mol^{-1}$. CODATA[2] has recommended the same value based on the same study.

Vapor pressure studies include: Fischer and Bingle (298–389 K),[3] Frey and Gregory (177–195 K),[4] Henglein, *et al.* (177–241 K),[5] Ramsay and Young (256–329 K)[6] and Scheffer and Voogd (253–362 K).[7] For the liquid region, the data of Fischer and Bingle[3] and Scheffer and Voogd[7] show a decided decrease of $\Delta_{vap}H°$ with increasing temperature. The data of Ramsey and Young[6] show only a small temperature trend and are in good agreement with the adopted calorimetric study. For the crystal region, the data are too scattered to be conclusive.

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	−24.509	0.	0.	0.
100	43.587	53.847	271.009	−21.716	0.	0.	0.
200	53.761	87.421	171.496	−16.815	0.	0.	0.
250	59.225	99.965	155.962	−13.999	0.	0.	0.
265.900	61.630	103.687	152.725	−13.039	CRYSTAL <--> LIQUID		
265.900	77.724	143.445	152.725	−2.468	TRANSITION		
298.15	75.674	152.206	152.206	0.	0.	0.	0.
300	75.624	152.674	152.208	0.140	0.	0.	0.
332.503	75.302	160.429	152.639	2.590	FUGACITY = 1 bar		
350	75.302	164.291	153.126	3.908	−28.882	1.538	−0.230
400	75.302	174.347	155.164	7.673	−26.947	5.752	−0.751
450	75.302	183.216	157.798	11.438	−25.023	9.723	−1.129
500	75.302	191.150	160.743	15.203	−23.108	13.481	−1.408

PREVIOUS *September 1961* CURRENT: June 1982

D_0° = 191 154 ± 0.001 kJ·mol^{-1} (natural abundance)
S°(298.15 K) = 245.394 ± 0.050 J·K^{-1}·mol^{-1}

$\Delta_f H^\circ$(0 K) = 45.70 ± 0.121 kJ·mol^{-1}
$\Delta_f H^\circ$(298.15 K) = 30.911 ± 0.11 kJ·mol^{-1}

Spectroscopic Data for $^{79}Br_2$ in cm^{-1}

State	T_e	D°	ω_e	$\omega_e x_e$	B_e	$10^3 \cdot \alpha_e$	$10^7 \cdot D_e$	r_e, Å	Reference
$^1\Sigma_g^+$	0	15894.6	325.3213	1.07742[a]	0.082107	0.31873	0.2092	2.28107	1
$^3\Pi_{2u}$	13400	15894.6	160	2.4	0.057	0.5	0.29	2.74	2
$^3\Pi_{1u}$	13904	15894.6	153.8	2.78	0.0588	0.72	0.34	2.695	3
$^1\Pi_u^-$	15850	15894.6	70	6.2	0.06	2.8	1.76	2.67	2
$^3\Pi_{0_u^+}$	15902.47	19579.76	166.546	1.61517[b]	0.059589	0.489095[c]	0.3013	2.6776	4d

(a) $-2\,29798 \times 10^{-3}(v + 1/2)^3$
(b) $-7.53588 \times 10^{-3}(v + 1/2)^3 - 2.44989 \times 10^{-4}(v + 1/2)^4 + 0.991688 \times 10^{-5}(v + 1/2)^5 - 6.97853 \times 10^{-6}(v + 1/2)^6$
(c) $-6.6369 \times 10^{-6}(v + 1/2)^2$
(d) $^3\Pi_{0_u^+}$ constants for natural abundance Br_2, actual coefficients for $^{79}Br_2$ will differ slightly from these according to the scaling method of Herzberg.[5]
(e) The dissociation energy of each state is relative to the lowest level of the ground state.

Enthalpy of Formation

We adopt the enthalpy of formation values of CODATA[6] as follows: $\Delta_f H^\circ$(298.15 K) = 30.91 ± 0.11 kJ·mol^{-1} and $\Delta_f H^\circ$(0 K) = 45 71 ± 0.12 kJ·mol^{-1}. These values were based on the heat capacity and enthalpy of vaporization measurements of Hildenbrand *et al* [7] Note that the latter value of $\Delta_f H^\circ$ is deduced from the former using the CODATA values of H°(298 15 K)–H°(0 K) for Br_2(g) and Br_2(l). Our calculated value of H°(298.15 K)–H°(0 K) for Br_2(g) is only 1.3 J mol^{-1} smaller than the recommended value of CODATA. Our adopted dissociation energy for the natural abundance mixture is derived from the isotopic values reported by Barrow *et al.*[1] as given by Huber and Herzberg.[1] The CODATA value for $D_0^\circ(Br_2, g)$, as deduced from the $\Delta_f H^\circ$(0 K) data for Br_2(g) and Br(g), is 190.14 kJ·mol^{-1}. The 0.01 kJ·mol^{-1} discrepancy is due to CODATA's adoption of D_0° for $^{79}Br^{81}Br$ based on earlier work of Horsley and Barrow [8] Refer to the monatomic bromine gas table for additional 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 four lowest lying excited states Spectroscopic constants for the ground state are taken from Barrow, *et al* [1] for $^{79}Br_2$ while the excited state constants are from Gurvich *et al.*[2-4] Note that Barrow, *et al.*[1] presented constants for the $^3\Pi_{0_u^+}$ state of $^{79}Br_2$ for v ≤10 only. Therefore for this state we adopted the constants of Gurvich, *et al.*[2] which are fit to the experimental data up to the dissociation limit. For the ground state and the $^3\Pi_{1u}$ and $^3\Pi_{0_u^+}$ excited states, the calculation is performed including the quasi-bound rotational levels above the dissociation limit (see Cl_2(g) table) using J_{lim} and v_{max} given by Gurvich *et al.*[2] Splitting of the rotational levels due to the rotational–electronic interaction in the $^3\Pi_{2u}$ and $^3\Pi_{1u}$ states is taken into account only insofar as the statistical weight of the rotational levels is doubled. The rotational levels are extrapolated to high J values according to the method of Khachkuruzov[9] who proposed a simpler form of Wooley's method.[10] The spectroscopic constants for the hypothetical natural abundance species are determined from the $^{79}Br_2$ constants using a standard reduced mass scaling scheme. The calculated value of S°(298.15 K) is 0.07 J·mol^{-1}·K^{-1} smaller than that adopted by CODATA[6] and also by Gurvich *et al.*[2] For this comparison, the entropy value reported by CODATA and Gurvich is increased by 0.1094 J·K^{-1} mol^{-1} to account for a change in the standard state pressure from 1 atm to 1 bar.

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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})	$-[G^\circ-H^\circ(T_r)]/T$ (J·K^{-1}mol^{-1})	$H^\circ-H^\circ(T_r)$ (kJ·mol^{-1})	$\Delta_f H^\circ$ (kJ·mol^{-1})	$\Delta_f G^\circ$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.722	45.697	45.697	INFINITE
100	30.884	208.563	276.306	−6.774	45.852	30.380	−15.869
200	34.582	231.269	248.653	−3.477	44.248	15.479	−4.043
250	35 489	239.092	245.984	−1.723	43 186	8 404	−1.756
298.15	36.048	245.394	245.394	0.	30.910	3.126	−0.548
300	36.066	245 617	245.394	0.067	30.837	2.954	−0.514
332.503	36.332	249.341	245.601	1.243	----- FUGACITY = 1 bar -----		
350	36.451	251.207	245.835	1.880	0.	0.	0.
400	36.723	256.093	246.818	3 710	0.	0.	0.
450	36.923	260.431	248.094	5.551	0.	0.	0.
500	37.077	264.329	249.526	7.402	0.	0.	0.
600	37.301	271.110	252.575	11.121	0.	0.	0.
700	37.460	276.873	255.645	14.860	0.	0.	0.
800	37.586	281.883	258.618	18.612	0.	0.	0.
900	37.692	286.316	261.454	22.376	0.	0.	0.
1000	37 787	290.293	264.143	26.150	0.	0.	0.
1100	37.876	293.898	266.686	29.933	0.	0.	0.
1200	37.962	297.198	269.093	33 725	0.	0.	0.
1300	38.049	300.240	271.374	37.526	0.	0.	0.
1400	38 140	303.063	273.538	41.335	0.	0.	0.
1500	38.239	305.697	275.595	45.154	0.	0.	0.
1600	38.348	308.169	277.554	48.983	0.	0.	0.
1700	38.471	310.497	279.424	52.824	0	0.	0.
1800	38.611	312.700	281.212	56.678	0.	0.	0.
1900	38.769	314.792	282.925	60.547	0.	0.	0.
2000	38 945	316.785	284.569	64.432	0.	0.	0.
2100	39 137	318.690	286.148	68.336	0.	0	0
2200	39.345	320.515	287.669	72.260	0.	0.	0.
2300	39.563	322.269	289.136	76.206	0.	0.	0.
2400	39 789	323.957	290.552	80.173	0.	0.	0.
2500	40 018	325.586	291.921	84.164	0.	0.	0.
2600	40.244	327.160	293.246	88 177	0	0	0.
2700	40.463	328.683	294.530	92.212	0.	0	0.
2800	40.672	330 158	295.777	96.269	0.	0.	0.
2900	40 864	331.589	296.987	100.346	0.	0.	0.
3000	41 038	332.977	298.164	104.441	0.	0.	0.
3100	41.190	334.326	299.308	108.553	0.	0.	0.
3200	41.318	335.635	300.423	112.679	0.	0	0.
3300	41.420	336.908	301.510	116.816	0.	0.	0.
3400	41.496	338 146	302.569	120.962	0.	0.	0.
3500	41.545	339.350	303.603	125.114	0.	0.	0.
3600	41.567	340.521	304.612	129.270	0.	0.	0.
3700	41.563	341.659	305.598	133.427	0	0	0
3800	41.533	342.767	306.562	137.582	0	0	0
3900	41.480	343.846	307.504	141.732	0.	0.	0.
4000	41.404	344.895	308.426	145.877	0.	0.	0.
4100	41.306	345.916	309.328	150.012	0.	0.	0.
4200	41.190	346.910	310.211	154.137	0.	0.	0.
4300	41.056	347.878	311 076	158.250	0.	0.	0.
4400	40.907	348.820	311.923	162.348	0	0	0.
4500	40 744	349.738	312.753	166.431	0.	0	0.
4600	40.569	350.631	313.567	170.497	0.	0.	0.
4700	40.383	351.502	314.365	174.544	0.	0.	0.
4800	40 189	352.350	315.147	178.573	0.	0.	0.
4900	39 987	353.176	315.915	182.582	0.	0.	0.
5000	39.780	353.982	316.668	186.570	0.	0.	0.
5100	39.568	354.768	317.408	190.538	0.	0.	0.
5200	39.353	355.534	318.133	194.484	0.	0.	0
5300	39.136	356.282	318.846	198 408	0	0.	0.
5400	38.917	357 011	319.546	202.311	0.	0.	0.
5500	38.698	357.723	320.234	206.192	0.	0.	0.
5600	38.480	358.419	320.910	210.051	0.	0.	0.
5700	38.263	359.098	321.574	213.888	0.	0.	0.
5800	38.047	359.761	322.226	217.703	0.	0.	0.
5900	37 834	360.410	322 868	221.497	0.	0.	0.
6000	37.624	361.044	323 499	225.270	0	0	0.

PREVIOUS December 1961 (1 atm) CURRENT June 1982 (1 bar)

$S°(298.15\ K) = [129.7 \pm 4.2]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1015\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -683.2 \pm 4.2\ kJ·mol^{-1}$
$\Delta_{fus} H° = 29.079 \pm 0.63\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation is the mean of three values derived from two independent paths. One path involves the enthalpy of solution of Ca(cr) and $CaBr_2$(cr) in HBr·555 H_2O which were measured by Ehrlich *et al.*[1] Recalculation of their results using recent thermal data[2,3] for aqueous HBr yields $\Delta_f H°(CaBr_2, cr, 298.15\ K) = -164.0\ kcal·mol^{-1}$. The uncertainty in this value could approach $\pm 1.0\ kcal·mol^{-1}$ due primarily to the rather impure metal (99.3% free Ca) used in these measurements.

An alternate path used to obtain values for $\Delta_f H°$ involves the results of measurements on the enthalpy of solution of $CaBr_2$(cr) in aqueous solution. The work[4-6] reported in this area has been reviewed by Bichowsky and Rossini.[7] Recalculation of these results using $\Delta_f H°(Ca^{+2}, \infty\ aq, 298.15\ K) = -129.74\ kcal·mol^{-1}$[18] and $\Delta_f H°(Br^-, \infty\ aq, 298.15\ K) = -29.039 \pm 0.036\ kcal·mol^{-1}$[12] yields values for $\Delta_f H°$ of $CaBr_2$(cr) in $kcal·mol^{-1}$ of -162.3,[4] -160.2,[5] and -163.6.[6] The disagreement in these values is disturbing but can be mostly accounted for when one considers the difficulties involved in the preparation[6] of "pure" anhydrous $CaBr_2$.

A mean value ($-163.3\ kcal·mol^{-1}$, $683.247\ kJ·mol^{-1}$) for $\Delta_f H°(CaBr_2, cr, 298.15\ K)$ of three results[1,4,6] is preferred because of the difficulties reported in obtaining and keeping samples free of impurities. NBS[8] has selected essentially the same value ($-163.2\ kcal·mol^{-1}$) from their analysis of the available data.

Heat Capacity and Entropy

No low temperature $C_p°$ data have been reported for $CaBr_2$, thus, the value of $S°(298.15\ K)$ must be estimated. Application of the Berthelot principle[9] to the process $SrBr_2(cr) + Ca(cr) = CaBr_2(cr) + Sr(cr)$ gives $S°(298.15\ K) = 31.7 \pm 1.5\ cal·K^{-1}mol^{-1}$ for $CaBr_2$. Auxiliary entropies are taken from the JANAF Tables.[10] Also, JANAF entropies[10] for the other three calcium dihalides suggest a value near $30.5\ cal·K^{-1}·mol^{-1}$ for $CaBr_2$. We adopt $S°(298.15\ K) = 31 \pm 1\ cal·K^{-1}·mol^{-1}$ which is the value selected by NBS.[8] Other reported estimates for $S°(298.15\ K)$ in $cal·K^{-1}·mol^{-1}$ are 32.0 ± 2.8,[11] 32.2 ± 0.7,[12] and 33.[13]

$C_p°$ at 298.15 K has not been measured. However, Janz *et al.*[14] measured relative enthalpies (434–1013 K) for $CaBr_2$ and reported the results in equation form. Their equation gives $C_p° = 16.3\ cal·K^{-1}·mol^{-1}$ at 298.15 K which appears to be too low by about 2 units when compared with JANAF $C_p°$ data for several other alkaline earth dihalides. The only other enthalpy study that has been reported is that of Dworkin and Bredig[15] who measured $H°(1015\ K) - H°(298.15\ K) = 14.00\ kcal·mol^{-1}$ in a copper block drop-calorimeter. We adopt this result. JANAF data[10] are used to obtain $C_p°$ at 298.15 K from the process $CaCl_2(cr) + 2\ KBr(cr) = CaBr_2(cr) + 2\ KCl(cr)$ by assuming $\Delta C_p° = 0$. Data in the temperature range 300–1013 K are estimated by comparison with those for CaF_2 and $CaCl_2$.[10] More weight is given to the results for $CaCl_2$, since it has the same crystal structure[15] as $CaBr_2$ and nearly the same melting temperature (1045 K)[10] and enthalpy $H°(1045\ K) - H°(298.15\ K) = 14.2\ kcal·mol^{-1}$[10] at T_{fus} as does $CaBr_2$. The $C_p°$ estimates are also made so as to reproduce as closely as possible the adopted enthalpy at 1015 K. Our estimated $C_p°$ data give a value of $H°(1015\ K) - H°(298.15\ K) = 13.994\ kcal·mol^{-1}$ which agrees with the measured value[15] to within 6 $cal·mol^{-1}$. $C_p°$ data above 1015 K are obtained by graphical extrapolation. The enthalpies obtained from the equation of Janz *et al.*[14] are systematically lower than our adopted values. The deviation is -0.4% at 1015 K; it increases at lower temperatures and reaches a maximum value of -2.7% at 600 K.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is calculated as the difference in the adopted enthalpies of formation for the ideal gas and crystal at 298.15 K.

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			
100							
200							
298.15	75.040	129.704	129.704	0.	−683.247	−664.139	116.354
300	75.124	130.168	129.705	0.139	−683.296	−664.020	115.616
400	77.990	152.206	132.691	7.806	−712.744	−651.460	85.072
500	79.454	169.774	138.410	15.682	−711.325	−636.304	66.474
600	80.500	184.352	144.887	23.679	−709.990	−621.427	54.100
700	81.630	196.836	151.437	31.780	−708.767	−606.765	45.277
800	83.471	207.851	157.813	40.030	−708.463	−592.168	38.665
900	85.856	217.816	163.935	48.493	−707.289	−577.703	33.529
1000	88.617	227.004	169.788	57.216	−706.160	−563.365	29.427
1015.000	89.036	228.327	170.643	58.549	--- CRYSTAL <--> LIQUID ---		
1100	91.922	235.601	175.384	66.238	−705.045	−549.139	26.076
1200	95.563	243.753	180.745	75.611	−711.624	−534.394	23.262
1300	99.412	251.554	185.893	85.358	−709.177	−519.722	20.883
1400	103.387	259.067	190.853	95 499	−706.346	−505.252	18.851
1500	107.320	266.334	195.644	106.034	−703.129	−490.998	17.098

PREVIOUS: CURRENT June 1974

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$S°(298.15\ K) = [147.861]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1015\ K$

$\Delta_f H°(298.15\ K) = [-662.989]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 29.079 \pm 0.63\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding of $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1015\ K)–H°(298.15\ K)$, between the crystal and liquid. Toguri *et al.*[1] have reported a K_p value for the anion exchange equilibrium $0.5\ CaBr_2(l) + HCl(g) = 0.5\ CaCl_2(l) + HBr(g)$ at 1073 K. A 3rd law analysis of this single value gives $\Delta_f H°(298.15\ K) = -0.22\ kcal·mol^{-1}$ with JANAF functions. The 3rd law enthalpy leads to $\Delta_f H°(l, 298.15\ K) = -157.9\ kcal·mol^{-1}$ which supports our adopted value by an independent path.

Heat Capacity and Entropy

$C_p°$ of the liquid above 700 K is the value ($27.0\ cal·K^{-1}·mol^{-1}$) determined by Dworkin and Bredig[2] from enthalpy measurements in the vicinity of the melting point. A similar enthalpy study (1013–1132 K) by Janz *et al.*[3] suggests only a slightly higher value ($27.38\ cal·K^{-1}·mol^{-1}$) for $C_p°$ of $CaBr_2(l)$. A glass transition is assumed at 700 K below which $C_p°$ is that of the crystal.

The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The adopted value of T_{fus} is that measured calorimetrically by Dworkin and Bredig.[2] Similar measurements by Janz *et al.*[3] gave essentially the same value (1013 K). Other reported values for T_{fus} are 1018 K,[4] 1003 K,[5–7] and 1016 K.[8]

$\Delta_{fus}H°$ is that measured by Dworkin and Bredig[2] in a copper block drop-calorimeter. Another calorimetrically etermined value[3] ($\Delta_{fus}H° = 6.86 \pm 0.09\ kcal·mol^{-1}$) and one based on cryoscopic measurements[4] ($\Delta_{fus}H° = 7.03 \pm 0.35\ kcal·mol^{-1}$) bracket the selected value.

Vaporization Data

T_{vap} (f = 1 bar) is the temperature at which $\Delta_r G°$ for the process $CaBr_2(l) = CaBr_2(g)$ approaches zero. $\Delta_{vap}H°$ is the difference in the enthalpies of formation of the gas and liquid at T_{vap}. Peterson and Hutchison[9] obtained T_{vap} = 2088 K (at 1 atm) from vapor pressure measurements on the liquid (1149–1321 K). This value is nearly identical to our result.

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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							
100							
200							
298.15	75.040	147.861	147.861	0.	−662.989	−649.294	113.754
300	75.124	148.325	147.862	0.139	−663.038	−649.209	113.037
400	77.990	170.363	150.847	7.806	−692.486	−638.465	83.375
500	79.454	187.931	156.567	15.682	−691.067	−625.125	65.306
600	80.500	202.508	163.043	23.679	−689.732	−612.063	53.285
700	81.631	215.001	169.594	31.785	−688.503	−599.217	44.714
700.000	81.631	215.001	169.594	31.785	GLASS <--> LIQUID TRANSITION		
700.000	112.968	215.001	169.594	31.785			
800	112.968	230.086	176.234	43.082	−685.153	−586.647	38.304
900	112.968	243.392	182.971	54.378	−681.146	−574.578	33.348
1000	112.968	255.294	189.619	65.675	−677.444	−562.938	29.405
1100	112.968	266.061	196.087	76.972	−674.053	−551.654	26.196
1200	112.968	275.891	202.333	88.269	−678.708	−540.043	23.507
1300	112.968	284.933	208.344	99.566	−674.712	−528.650	21.241
1400	112.968	293.305	214.117	110.862	−670.724	−517.564	19.311
1500	112.968	301.099	219.659	122.159	−666.746	−506.763	17.647
1600	112.968	308.389	224.979	133.456	−662.779	−496.226	16.200
1700	112.968	315.238	230.089	144.753	−658.823	−485.938	14.931
1800	112.968	321.695	235.001	156.050	−803.554	−473.671	13.746
1900	112.968	327.803	239.726	167.346	−798.212	−455.490	12.522
2000	112.968	333.598	244.276	178.643	−792.893	−437.590	11.429
2100	112.968	339.109	248.662	189.940	−787.600	−419.955	10.446
2200	112.968	344.365	252.893	201.237	−782.338	−402.572	9.558
2300	112.968	349.386	256.980	212.534	−777.112	−385.427	8.753
2400	112.968	354.194	260.931	223.830	−771.927	−368.508	8.020
2500	112.968	358.806	264.755	235.127	−766.790	−351.805	7.351

PREVIOUS: CURRENT: June 1974

209.15	to	1015 K	crystal
above		1015 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⁻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	75.040	129.704	129.704	0.	−683.247	−664.139	116.354
300	75.124	130.168	129.705	0.139	−683.296	−664.020	115.616
400	77.990	152.206	132.691	7.806	−712.744	−651.460	85.072
500	79.454	169.774	138.410	15.682	−711.325	−636.304	66.474
600	80.500	184.352	144.887	23.679	−709.990	−621.427	54.100
700	81.630	196.836	151.437	31.780	−708.767	−606.765	45.277
800	83.471	207.851	157.813	40.030	−708.463	−592.168	38.665
900	85.856	217.816	163.935	48.493	−707.289	−577.703	33.529
1000	88.617	227.004	169.788	57.216	−706.160	−563.365	29.427
1015.000	89.036	228.327	170.643	58.549	CRYSTAL <--> LIQUID TRANSITION		
1015.000	112.968	256.976	170.643	87.628			
1100	112.968	266.061	177.670	97.230	−674.053	−551.654	26.196
1200	112.968	275.891	185.452	108.527	−678.708	−540.043	23.507
1300	112.968	284.933	192.761	119.824	−674.712	−528.650	21.241
1400	112.968	293.305	199.647	131.120	−670.724	−517.564	19.311
1500	112.968	301.099	206.154	142.417	−666.746	−506.763	17.647
1600	112.968	308.389	212.318	153.714	−662.779	−496.226	16.200
1700	112.968	315.238	218.173	165.011	−658.823	−485.938	14.931
1800	112.968	321.695	223.747	176.308	−803.554	−473.671	13.746
1900	112.968	327.803	229.064	187.604	−798.212	−455.490	12.522
2000	112.968	333.598	234.147	198.901	−792.893	−437.590	11.429
2100	112.968	339.109	239.015	210.198	−787.600	−419.955	10.446
2200	112.968	344.365	243.685	221.495	−782.338	−402.572	9.558
2300	112.968	349.386	248.172	232.792	−777.112	−385.427	8.753
2400	112.968	354.194	252.491	244.088	−771.927	−368.508	8.020
2500	112.968	358.806	256.652	255.385	−766.790	−351.805	7.351

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K)$ = [314.8 ± 8.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -370.5 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -384.9 \pm 8.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[148](1)
[47](2)
330 (1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance. Ca–Br = 2.67 ± 0.03 Å;
Bond Angle: Br–Ca–Br = 180°
Rotational Constant: B_o = 0.014797 cm^{-1}

Enthalpy of Formation

The selection of $\Delta_f H°(298.15\ K) = -92.0 \pm 2.0\ kcal·mol^{-1}$ ($-384.928 \pm 8.4\ kJ·mol^{-1}$) for $CaBr_2$(g) is based on results derived from two independent means. Peterson and Hutchison[1,2] have reported results of an extensive study of the vapor pressures (1149–1321 K) for liquid $CaBr_2$. Measurements were made by the Knudsen effusion method on a sample which had been prepared by direct union of high purity elements. X–ray diffraction patterns on the final product showed no metal or oxide lines. Schofield and Sugden[3] investigated the equilibrium Ca(g) + 2 HBr(g) = $CaBr_2$(g) + 2 H(g) in H_2–O_2–N_2 flames and reported K_p data for temperatures in the range 2137–2532 K. Results of our 2nd and 3rd law analysis of these data are tabulated below. We assume that the dibromide monomer is the only vapor species produced in the volatilization of $CaBr_2$(l). Support for this assumption is provided by mass spectra for some of the other alkaline earth dihalides.[4] These studies indicate that the saturated vapors consist predominately of the metal dihalide monomer and agree with predictions which were made by Brewer *et al.*[5] for these dihalide molecules. Included in the table for comparison are results of our analysis of older vapor pressure data[6,7] which have been reviewed by Brewer *et al.*[5]

Source	Method	Reaction	Data Points	T/K	$\Delta_r H°$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Peterson and Hutchison[1,2]	Knudsen Effusion	A	18(a)	1149–1321	65.7	67.70 ± 0.60	1.6 ± 1.3	−90.8 ± 1.6
Brewer[5,6]		B	1	990		68.9		−94.4
Brewer[5,7]	Boiling Point	A	2	1180;1480	62.5	64.76 ± 0.7	1.7	−93.7 ± 1.7
Schofield and Sugden[3]	Flame K_p	C	8(a)	2137–2532	−9.4	−14.38 ± 1.7	−2.1 ± 3.2	−93.2 ± 2.0

Reactions: (A) $CaBr_2$(l) = $CaBr_2$(g) (B) $CaBr_2$(cr) = $CaBr_2$(g) (C) Ca(g) + 2 HBr(g) = $CaBr_2$(g) + 2 H(g)
(a)One point rejected due to failure of a statistical test.

In the selection of $\Delta_f H°$, no weight is given to those measurements made prior to 1965. Also, we note that Schofield and Sugden[3] reported in the same paper similar results for $SrCl_2$ and $BaCl_2$ which lead to $\Delta_f H°$ values that are quite consistent with JANAF enthalpies of formation.[4] We, therefore, choose to select an average value of the results of Peterson and Hutchison[1,2] and Schofield and Sugden.[3] An earlier analysis[14] of the vapor pressure data[1,2] with older functions[5] gave $\Delta_f H°$ of −95.2 kcal·mol^{-1}.

Heat Capacity and Entropy

The bond length is from the high–temperature electron diffraction work of Akishin and Spiridonov.[8] Electron diffraction patterns[8] were satisfactorily explained on the basis of a linear model (180° ± 10°). Later studies by Wharton *et al.*,[9] using electric deflection of molecular beams to detect dipole moments, showed no polarity in the $CaBr_2$ molecule. The absence of dipolar character is most reasonably explained by a linear and centrosymmetric configuration.

The antisymmetric stretching frequency (υ_3) was observed in the high–temperature infrared spectra of $CaBr_2$ vapor by Baikov.[10] The symmetric stretching (υ_1) and bending (υ_2) frequencies are calculated from force constants by the valence force method.[11] The observed value of υ_3 gives k = 1.028 × 10^5 dynes/cm which leads to υ_1 = 148 cm^{-1}. Other estimates that have been reported for υ_1 (in cm^{-1}) are 148,[10] 164,[5] and 172.[13] A comparison of values for the ratio of the stretch to bend force constants for the linear molecules $CaCl_2$[4][(ratio = 81)] and $SrBr_2$[4][(ratio = [100])] suggests a value near 100 for $CaBr_2$ This value for the ratio gives $k\delta/l^2$ = 1.028 × 10^3 dynes/cm, or υ_2 = 47 cm^{-1} However, similar data for $BeBr_2$[12] indicate that the value of the ratio could be as low as 41. This leads to a υ_2 = 73 cm^{-1} which agrees with the value (85 cm^{-1}) recommended by Krasnov and Svettsov [13] Brewer *et al.*[5] choose υ_2 = 52 cm^{-1} We prefer the lowest value of υ_2(47 cm^{-1}) at this time but include in the uncertainty (±2.0 cal·K^{-1}mol^{-1}) assigned to the value of $S°(298.15\ K)$ the possibility that the highest value (85 cm^{-1}) is correct. The singlet ground state is assigned by analogy with that for $BaCl_2$.[4]

Continued on page 548

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	−15.799	−370.482	−370.482	INFINITE
100	52.538	252.373	366.898	−11.452	−369.908	−388.164	202.756
200	58.448	290.991	320.226	−5.847	−371.473	−405.889	106.007
250	59.666	304.176	315.742	−2.892	−372.583	−414.370	86.578
298.15	60.387	314.752	314.752	0.	−384.928	−420.991	73.756
300	60.409	315.125	314.753	0.112	−385.004	−421.215	73.340
350	60.889	324.476	315.490	3.145	−415.927	−425.550	63.510
400	61.214	332.629	317.134	6.198	−416.033	−426.918	55.750
450	61.443	339.853	319.264	9.265	−416.170	−428.271	49.712
500	61.611	346.336	321.653	12.341	−416.346	−429.606	44.881
600	61.833	357.590	326.732	18.515	−416.835	−432.216	37.628
700	61.970	367.133	331.840	24.705	−417.522	−434.728	32.440
800	62.059	375.414	336.780	30.907	−419.266	−437.023	28.535
900	62.121	382.727	341.487	37.116	−420.347	−439.181	25.489
1000	62.166	389.275	345.944	43.331	−421.727	−441.202	23.046
1100	62.199	395.201	350.157	49.549	−423.415	−443.070	21.040
1200	62.224	400.615	354.139	55.770	−433.145	−444.149	19.333
1300	62.244	405.596	357.909	61.994	−434.222	−445.022	17.881
1400	62.260	410.209	361.482	68.219	−435.307	−445.813	16.633
1500	62.272	414.505	364 875	74.445	−436.399	−446.525	15.549
1600	62.283	418.525	368.104	80.673	−437.500	−447 164	14.598
1700	62.291	422.301	371.182	86.902	−438.613	−447.734	13.757
1800	62.298	425.861	374.122	93.131	−588.411	−446.027	12.943
1900	62.304	429.230	376.934	99.362	−588 136	−438.125	12.045
2000	62.310	432.426	379.630	105.592	−587.883	−430.236	11.237
2100	62.314	435.466	382.217	111.823	−587.655	−422.359	10.506
2200	62.318	438.365	384.704	118.055	−587.458	−414.493	9.841
2300	62.321	441.135	387.097	124.287	−587.297	−406.635	9.235
2400	62.324	443 788	389.405	130.519	−587.177	−398.782	8.679
2500	62.327	446.332	391.631	136 752	−587.104	−390.934	8.168
2600	62.329	448.776	393.782	142.985	−587.084	−383.088	7.696
2700	62.331	451.129	395.863	149.218	−587.124	−375.241	7.259
2800	62.333	453.396	397.877	155.451	−587.228	−367.392	6.854
2900	62.335	455.583	399.830	161.684	−587.405	−359.538	6.476
3000	62.337	457 696	401.724	167.918	−587.659	−351.677	6.123
3100	62.338	459.740	403.562	174.152	−587.997	−343.805	5.793
3200	62.339	461.720	405.349	180.386	−588.425	−335.921	5.483
3300	62.340	463.638	407.086	186.620	−588.949	−328.023	5.192
3400	62.341	465.499	408.777	192.854	−589.574	−320.107	4 918
3500	62.342	467.306	410.424	199.088	−590.305	−312.171	4.659
3600	62.343	469.062	412.028	205.322	−591.147	−304.212	4.414
3700	62.344	470.770	413.593	211.556	−592.105	−296.229	4.182
3800	62.345	472.433	415.120	217.791	−593.181	−288.219	3.962
3900	62.345	474.052	416.610	224.025	−594.380	−280.178	3.753
4000	62.346	475.631	418.066	230.260	−595.703	−272.105	3.553
4100	62.347	477.170	419.489	236.495	−597.152	−263.997	3.363
4200	62.347	478.673	420.880	242.729	−598.728	−255.853	3.182
4300	62.348	480.140	422.241	248.964	−600.433	−247.669	3.009
4400	62.348	481.573	423.573	255.199	−602.262	−239.445	2.843
4500	62.348	482.974	424.878	261 434	−604.203	−231 178	2.683
4600	62.349	484.345	426.156	267.669	−606.274	−222.866	2.531
4700	62.349	485.686	427.408	273.903	−608.469	−214.508	2.384
4800	62.350	486.998	428.636	280.138	−610.780	−206.102	2.243
4900	62.350	488.284	429.840	286.373	−613.205	−197.646	2.107
5000	62.350	489.544	431.022	292.608	−615.738	−189.140	1.976
5100	62.351	490.778	432.181	298.843	−618.374	−180.581	1.850
5200	62.351	491.989	433.320	305 078	−621.105	−171.971	1.727
5300	62.351	493.177	434.438	311.314	−623.930	−163.307	1.609
5400	62.351	494.342	435.537	317.549	−626.842	−154.589	1.495
5500	62.352	495.486	436.616	323.784	−629.834	−145.816	1.385
5600	62.352	496.610	437.678	330.019	−632.890	−136.989	1.278
5700	62.352	497.713	438.721	336.254	−636.021	−128.106	1.174
5800	62.352	498.798	439.748	342.489	−639.212	−119.168	1.073
5900	62.352	499.864	440.758	348.725	−642.458	−110.174	0.975
6000	62.353	500.912	441.752	354.960	−645.751	−101.124	0.880

PREVIOUS June 1974 (1 atm) CURRENT June 1974 (1 bar)

$S°(298.15\ K) = 140.67 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 650\ K$
$T_{fus} = 964\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -248.9 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.4184\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [50.208 \pm 13]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpies of solution of Fe(cr), Br_2(l) and $FeBr_2$(cr) in Br_2–KBr aqueous solution were measured by use of an ice calorimeter by Hieber and Woerner.[1] From the results obtained, the enthalpy of formation for $FeBr_2$(cr) was reported to be −59.87 kcal mol^{-1}. The enthalpies of solution of $FeBr_2$(cr) in water were determined by Li and Gregory[2] and by Paoletti[3] to be -20.1 ± 0.4 and -20.06 ± 0.06 kcal mol^{-1}, respectively. Using $\Delta_f H°(298.15\ K) = -29.05$ and -21.3 kcal·mol^{-1} for Br^-(aq, ∞) and Fe^{++}(aq, ∞), the corresponding $\Delta_f H°(298.15\ K)$ for $FeBr_2$(cr) were calculated as −59.3 and −59.34 kcal·mol^{-1}. The value of $\Delta_f H°(Br^-, aq, ∞, 298.15\ K)$ was taken from.[4] The value of $\Delta_f H°(Fe^{++}, aq, ∞, 298.15\ K)$ was derived from enthalpies of solution and formation for $FeCl_2$(cr) using $\Delta_f H°(Cl^-, aq, ∞, 298.15\ K) = -39.952$ kcal·mol^{-1} from.[4]

The value of $\Delta_f H°(FeBr_2, cr, 298.15\ K)$ adopted is -59.5 ± 0.5 kcal·mol^{-1} (-248.948 ± 2.1 kJ·mol^{-1}).

Heat Capacity and Entropy

The heat capacities, 323–633 K, were measured by Gregory and O'Neal.[5] Those for temperatures below 232 K and above 633 K were estimated by linear extrapolation. Low temperature $C_p°$, 12–110 K, were reported by Miljutin and Nachimowitsch.[6] However, these data are inadequate for obtaining an accurate entropy at 298.15 K. The adopted $S°(298.15\ K)$ value was reported by Gregory and MacLaren[7] and was obtained from Westrum.[8] A magnetic transition at 11 K was reported by Bizette *et al.*[9]

Transition Data

T_{trs} and $\Delta_{trs} H°$ were taken from Gregory and O'Neal.[5]

Fusion Data

T_{fus} adopted was reported by MacLaren and Gregory.[10] The value was calculated from the vapor pressure equations and is slightly above 684°C (957 K) reported by Ferrari *et al.*[11] However, it agrees well with 962 ± 2 K obtained by the differential thermocouple cooling curve analysis.[10] The $\Delta_{fus} H°$ value was estimated from the vapor pressure data in order to obtain good agreement between the 2nd and 3rd law heats of vaporization. See the $FeBr_2$(g) table for details.

Sublimation Data

$\Delta_{sub} H°$(monomer → 298.15 K) is calculated as the difference between $\Delta_f H°(298.15\ K)$ for $FeBr_2$(g) and $FeBr_2$(cr). $\Delta_{sub} H°$(dimer → 298.15 K) is calculated as the difference between those for Fe_2Br_4(g) and 2 $FeBr_2$(cr).

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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							
100							
200							
298.15	80.232	140.666	140.666	0.	−248.948	−237.362	41.585
300	80.274	141.163	140.668	0.148	−248.986	−237.290	41.316
400	82.500	164.560	143.843	8.287	−277.955	−227.334	29.687
500	84.726	183.209	149.912	16.648	−276.138	−214.890	22.449
600	86.952	198.853	156.799	25.232	−274.360	−202.807	17.656
650.000	88.061	205.857	160.306	29.608	I <--> II		
650.000	88.069	206.500	160.306	30.026	TRANSITION		
700	89.178	213.067	163.843	34.457	−272.199	−191.053	14.257
800	91.404	225.121	170.763	43.486	−270.537	−179.575	11.725
900	93.630	236.015	177.417	52.738	−269.078	−168.295	9.768
964.000	95.054	242.495	181.525	58.776	----- II <--> LIQUID -----		
1000	95.855	245.995	183.783	62.212	−268.125	−157.156	8.209
1100	98.081	255.236	189.864	71.909	−267.854	−146.056	6.936
1200	100.307	263.865	195.675	81.828	−266.817	−135.047	5.878
1300	102.533	271.982	201.235	91.970	−263.919	−124.183	4.990
1400	104.759	279.662	206.565	102.335	−260.891	−113.547	4.236
1500	106.985	286.965	211.684	112.922	−257.733	−103.132	3.591

PREVIOUS: CURRENT: September 1966

Iron Bromide ($FeBr_2$) LIQUID $M_r = 215.655$

$S°(298.15\ K) = [169.376]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 964\ K$

$\Delta_f H°(298\ 15\ K) = [-211.005]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [50.208 \pm 13]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(964\ K)-H°(298.15\ K)$, between $FeBr_2$(cr) and $FeBr_2$(l).

Heat Capacity and Entropy

The heat capacity is assumed to be constant in the temperature range from 298.15 to 2000 K and is estimated on the basis of 8.5 $cal·K^{-1}·mol^{-1}$ per atom. $S°(298.15\ K)$ is calculated in a manner similar 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 total pressure of $FeBr_2$(g) and Fe_2Br_4(g) over $FeBr_2$(l) equals one bar. Based on the vapor composition and the values of $\Delta_{vap}H°$ for both the monomer and dimer at T_{vap} for both the monomer and dimer at T_{vap}, the enthalpy of vaporization is derived.

Iron Bromide ($FeBr_2$) Br_2Fe_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	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	106.692	169.376	169.376	0.	−211.005	−207.978	36.437
300	106.692	170.036	169.378	0.197	−210.994	−207.960	36.209
400	106.692	200.729	173.563	10.867	−237.433	−201.279	26.284
500	106.692	224.537	181.465	21.536	−233.308	−192.723	20.134
600	106.692	243.989	190.314	32.205	−229.444	−184.974	16.103
700	106.692	260.436	199.187	42.874	−225.839	−177.850	13.271
800	106.692	274.683	207.753	53.543	−222.537	−171.224	11.180
900	106.692	287.249	215.902	64.213	−219.661	−164.988	9.576
1000	106.692	298.490	223.608	74.882	−217.513	−159.039	8.307
1100	106.692	308.659	230.885	85.551	−216.269	−153.237	7.277
1200	106.692	317.942	237.759	96.220	−214.482	−147.605	6.425
1300	106.692	326.482	244.260	106.889	−211.057	−142.172	5.713
1400	106.692	334.389	250.419	117.559	−207.724	−136.998	5.111
1500	106.692	341.750	256.265	128.228	−204.485	−132.060	4.599
1600	106.692	348.636	261.825	138.897	−201.339	−127.335	4.157
1700	106.692	355.104	267.124	149.566	−199.239	−122.785	3.773
1800	106.692	361.202	272.183	160.235	−196.620	−118.364	3.435
1900	106.692	366.971	277.021	170.905	−208.198	−113.383	3.117
2000	106.692	372.443	281.657	181.574	−206.017	−108.449	2.832

PREVIOUS: CURRENT. September 1966

Iron Bromide ($FeBr_2$) Br_2Fe_1(l)

298.15	to	650 K	crystal, I
650	to	964 K	crystal, II
above		964 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°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0							
100							
200							
298.15	80.232	140.666	140.666	0.	−248.948	−237.362	41.585
300	80.274	141.163	140.668	0.148	−248.986	−237.290	41.316
400	82.500	164.560	143.843	8.287	−277.955	−227.334	29.687
500	84.726	183.209	149.912	16.648	−276.138	−214.890	22.449
600	86.952	198.853	156.799	25.232	−274.360	−202.807	17.656
650.000	88.061	205.857	160.306	29.608	I <--> II		
650.000	88.069	206.500	160.306	30.026	TRANSITION		
700	89.178	213.067	163.843	34.457	−272.199	−191.053	14.257
800	91.404	225.121	170.763	43.486	−270.537	−179.575	11.725
900	93.630	236.015	177.417	52.738	−269.078	−168.295	9.768
964.000	95.054	242.495	181.525	58.776	II <--> LIQUID		
964.000	106.692	294.578	181.525	108.984	TRANSITION		
1000	106.692	298.490	185.666	112.825	−217.513	−159.039	8.307
1100	106.692	308.659	196.392	123.494	−216.269	−153.237	7.277
1200	106.692	317.942	206.140	134.163	−214.482	−147.605	6.425
1300	106.692	326.482	215.073	144.832	−211.057	−142.172	5.713
1400	106.692	334.389	223.317	155.501	−207.724	−136.998	5.111
1500	106.692	341.750	230.970	166.171	−204.485	−132.060	4.599
1600	106.692	348.636	238.111	176.840	−201.339	−127.335	4.157
1700	106.692	355.104	244.805	187.509	−199.239	−122.785	3.773
1800	106.692	361.202	251.103	198.178	−196.620	−118.364	3.435
1900	106.692	366.971	257.051	208.847	−208.198	−113.383	3.117
2000	106.692	372.443	262.685	219.517	−206.017	−108.449	2.832

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K) = [337.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-28.43 \pm 2.1]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-41\ 42 \pm 2.1]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[10]
[4450]	[10]
[6900]	[5]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[150](1)
[35](2)
[300](1)

Point Group [$D_{\infty h}$] $\sigma = [2]$
Bond Distance: Fe–Br = [2.24] Å
Bond Angle: Br–Fe–Br = [180]°
Rotational Constant: $B_e = [0.021023]\ cm^{-1}$

Enthalpy of Formation

The vapor pressures of $FeBr_2$(cr) and $FeBr_2$(l) have been measured in the temperature range from 623.15 to 962.15 K.[1,2] Using the reported data the corresponding enthalpy changes for the reactions (A) $FeBr_2(cr) = FeBr_2(g)$ and (B) $FeBr_2(l) = FeBr_2(g)$ were evaluated by both the 2nd and 3rd law methods. The results obtained are presented in the following table. The values of $\Delta_f H°(298.15\ K)$ for $FeBr_2(g)$ are calculated based on the 3rd law values for $\Delta_f H°(298.15\ K)$. The value of $\Delta_f H°(298.15\ K)$ for $FeBr_2(g)$ adopted is -9.9 ± 0.5 kcal mol^{-1} (-41.422 $kJ·mol^{-1}$).

Source	Method	Reaction	T/K	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
[1]	Transpiration	(A)	673.15– 962.15	50.04	49.56	− 0.75	−9.94
[1]	Effusion	(A)	623.15– 718.15	49.21	50.14	+ 1.37	−9.36
[1]	Diaphragm	(A)	873.15– 962.15	59.20	49.95	− 10.09	−9.55
[2]	Torsion–Effusion	(A)	670.0 – 740.0	49.11	49.59	+ 0.71	−9.91
[1]	Diaphragm	(B)	962.15–1182.15	39.77	40.84	+ 0.93	−9.59

Heat Capacity and Entropy

The molecular structure was assumed to be linear. The electronic levels and quantum weights were estimated by comparison with those for $FeCl_2$(g) reported by DeKock and Gruen.[3] The bond distance was estimated by Brewer *et al.*[4] The vibrtional frequencies were estimated in order to obtain good agreement between the 2nd and 3rd law enthalpies of sublimation and vaporization.

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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	−16.019	−28.425	−28.425	INFINITE
100	53.226	274.411	389.883	−11.547	−27 169	−48.619	25.396
200	58.914	313.454	342.863	−5.882	−28.174	−69.790	18.227
250	60.014	326.729	338.354	−2.906	−29.151	−80.088	16.733
298.15	60.653	337.359	337.359	0.	−41.422	−88.479	15.501
300	60.672	337.734	337.360	0.112	−41.496	−88.771	15.456
350	61.093	347.120	338.100	3.157	−72.387	−94.953	14.171
400	61.376	355.298	339.750	6.219	−72.497	−98.170	12.820
450	61.575	362.539	341.887	9.293	−72.661	−101.370	11.767
500	61.722	369.035	344.283	12.376	−72.884	−104.548	10.922
600	61.932	380.307	349.375	18.559	−73.506	−110.827	9.648
700	62.102	389.867	354.494	24.761	−74.369	−116.982	8.729
800	62.284	398.171	359.446	30.980	−75.517	−122.995	8.031
900	62.506	405.520	364.165	37.219	−77.071	−128.842	7.478
1000	62 777	412.119	368.636	43.483	−79.328	−134.483	7.025
1100	63.094	418.117	372.866	49.776	−82.461	−139.832	6.640
1200	63.445	423.622	376.869	56.103	−85.016	−144.954	6.310
1300	63.819	428.715	380.664	62.466	−85.897	−149.913	6.024
1400	64.202	433.458	384.267	68.867	−86.832	−154.803	5.776
1500	64.582	437.901	387.696	75.306	−87.823	−159.624	5.559
1600	64.949	442.080	390.966	81.783	−88.870	−164.377	5.366
1700	65.295	446.028	394.090	88.295	−90.926	−169.043	5.194
1800	65.614	449.770	397.080	94.841	−92.431	−173.596	5.038
1900	65.902	453.325	399.948	101.417	−108.102	−177.360	4.876
2000	66.158	456.712	402.702	108.020	−109 987	−180.956	4.726
2100	66.380	459.945	405.351	114.648	−111.866	−184.459	4.588
2200	66.570	463.038	407.904	121.295	−113.744	−187.871	4.461
2300	66.728	466 001	410.366	127.960	−115.627	−191.199	4.342
2400	66.855	468.843	412.743	134.640	−117.518	−194.444	4.232
2500	66.955	471.575	415.042	141.331	−119.420	−197.610	4.129
2600	67.029	474.202	417.268	148.030	−121.336	−200.700	4.032
2700	67.080	476.733	419.423	154.736	−123.268	−203.716	3.941
2800	67.110	479.173	421.514	161.445	−125.218	−206.660	3.855
2900	67.121	481.528	423.543	168.157	−127.185	−209.534	3.774
3000	67.116	483.804	425.514	174.869	−129.171	−212.340	3.697
3100	67.096	486 004	427.430	181.580	−131.174	−215.079	3.624
3200	67.065	488.134	429.294	188.288	−481.494	−210.330	3.433
3300	67.023	490.197	431.108	194.992	−481.628	−201.854	3.195
3400	66.971	492.197	432.876	201.692	−481.809	−193.373	2.971
3500	66.913	494.138	434.599	208.386	−482.035	−184.887	2.759
3600	66.848	496.022	436.279	215.074	−482.305	−176.393	2.559
3700	66.778	497.852	437.918	221.756	−482.617	−167.891	2.370
3800	66.704	499.632	439.519	228.430	−482.970	−159.380	2.191
3900	66.626	501.364	441.083	235.096	−483.364	−150.860	2.021
4000	66.546	503.050	442.611	241.755	−483.796	−142.328	1.859
4100	66.465	504.692	444.105	248.405	−484.265	−133.786	1.704
4200	66.382	506.293	445.567	255.048	−484.772	−125.232	1.557
4300	66.299	507.854	446.997	261.682	−485.315	−116.665	1.417
4400	66.215	509.377	448.398	268.308	−485.894	−108.085	1.283
4500	66.132	510.864	449.769	274.925	−486.507	−99.492	1.155
4600	66 049	512.317	451.113	281.534	−487.156	−90.884	1.032
4700	65.966	513.736	452.431	288.135	−487.840	−82.262	0.914
4800	65.885	515.124	453.723	294.727	−488.558	−73.625	0.801
4900	65.805	516.482	454.990	301.312	−489.312	−64.973	0.693
5000	65.726	517.810	456.233	307.888	−490.102	−56.305	0.588
5100	65.648	519.111	457.453	314.457	−490.928	−47.621	0.488
5200	65.572	520.385	458.651	321.018	−491.791	−38.921	0.391
5300	65.497	521.633	459.828	327.571	−492.692	−30.203	0.298
5400	65.424	522.857	460.983	334.117	−493.634	−21.468	0.208
5500	65.352	524.057	462.119	340.656	−494.616	−12.715	0.121
5600	65.283	525.234	463.236	347.188	−495.641	−3.944	0.037
5700	65.215	526.389	464.334	353.713	−496.711	4.846	−0.044
5800	65.148	527.522	465.414	360.231	−497.828	13.654	−0.123
5900	65.083	528.635	466.476	366.742	−498.994	22.483	−0.199
6000	65.020	529.729	467.521	373.248	−500.213	31.332	−0.273

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

$S°(298.15\ K) = [310.05 \pm 1.3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-168.4 \pm 17]\ kJ\ mol^{-1}$
$\Delta_f H°(298.15\ K) = [-190.4 \pm 17]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2206(1)	2232(1)
942(1)	556(1)
407(1)	843(1)
122(1)	471(1)
688(1)	

Ground State Quantum Weight: [1] σ = [2]
Point Group [C_{2v}]
Bond Distances Si–H = [1.49] Å; Si–Br = [2.19] Å
Bond Angles: H–Si–H = [111]°; Br–Si–Br = [110]°
Product of the Moments of Inertia: $I_A I_B I_C = [6.36266 \times 10^{-111}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°$(298.15 K) is estimated by linear interpolation between the values[1] of $SiBr_4$(g) and SiH_4(g). The only experimental $\Delta_f H°$ for $SiHBr_3$(g) appears to be too uncertain to justify a nonlinear interpolation such as that adopted for SiH_3Cl.[1] Normally we would seek a comparison with $\Delta_f H°$ values of CH_nBr_{4-n}. These were recently reviewed by Kudchadker and Kudchadker.[2] They adopted a cubic variation of $\Delta_f H°$ with n, based on $\Delta_f H°$ values of $CHBr_3$ and CBr_4 selected by Wagman *et al.*[3] We presume that Wagman's values are calculated rather than experimental. Uncertainty in these values[4–6] precludes their use as a comparison for SiH_nBr_{4-n}. We conclude, as did Hunt and Sirtl,[7] that the available data justify only linear interpolation of $\Delta_f H°$.

Heat Capacity and Entropy

The molecular structure is estimated by comparison with SiH_3Br, $SiHBr_3$ and the chlorosilanes.[1] Bond distances are assumed to be intermediate between those of SiH_3Br and $SiHBr_3$.[1] The principal moments of inertia are $I_A = 7.9748 \times 10^{-39}$, $I_B = 85.9075 \times 10^{-39}$, and $I_C = 92.8728 \times 10^{-39}\ g \cdot cm^2$.

Vibrational frequencies are those selected by Shimanouchi[8] based on gas-phase infrared spectra[9] and liquid-phase Raman spectra.[10] Gas-phase frequencies are adopted except for $\nu_4 = 122\ cm^{-1}$ and infrared inactive $\nu_5 = 688\ cm^{-1}$.

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_3Br and SiH_2Cl_2.[1]

References

[1]JANAF Thermochemical Tables: Br_4Si(g), Br_3HSi(g), BrH_3Si(g), ClH_3Si(g), Cl_2H_2Si(g), Cl3HSi(g)12–31–76; H_4Si(g) 6–30–76.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
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	−14.272	−168.449	−168.449	INFINITE
100	41.215	253.984	360 165	−10.618	−170.854	−180.412	94.237
200	53 911	286.243	315.696	−5.891	−174.900	−188.449	49.218
250	60.273	298 971	311.102	−3.033	−177.104	−191.584	40.029
298.15	65.545	310.051	310.051	0.	−190.372	−192.860	33 788
300	65.730	310.457	310.053	0.121	−190.481	−192.875	33.583
350	70.258	320.941	310.870	3.525	−222.212	−191.509	28.581
400	74.012	330.575	312.739	7 134	−222.976	−187.069	24.429
450	77.170	339.480	315.222	10.916	−223.620	−182.541	21 189
500	79.882	347.754	318 066	14.844	−224.158	−177.947	18.590
600	84.357	362.730	324.289	23.065	−224.962	−168.624	14.680
700	87.937	376.013	330.747	31.686	−225.465	−159 190	11.879
800	90.864	387.952	337 164	40.631	−225.734	−149 702	9.775
900	93.276	398.798	343.419	49.841	−225.824	−140.191	8.136
1000	95.273	408 733	349.461	59.272	−225.782	−130.677	6.826
1100	96.931	417.893	355.271	68.885	−225.647	−121 172	5.754
1200	98.315	426.389	360.848	78.649	−225.452	−111.683	4.861
1300	99.476	434.305	366.197	88.540	−225.222	−102.211	4.107
1400	100.455	441.714	371.329	98.538	−224 981	−92 758	3 461
1500	101.285	448.674	376.256	108.626	−224.743	−83 322	2.902
1600	101.994	455.234	380.989	118 791	−224.525	−73.901	2.413
1700	102.603	461 436	385.541	129.022	−274.514	−64 046	1 968
1800	103.128	467.316	389.922	139.309	−274 134	−51.677	1.500
1900	103.584	472.904	394.143	149.645	−273.759	−39.328	1.081
2000	103.982	478.228	398.216	160.024	−273.396	−26.999	0.705
2100	104.331	483.309	402.148	170.440	−273.049	−14 688	0.365
2200	104 638	488.170	405.948	180.889	−272.722	−2.393	0.057
2300	104 910	492.828	409.625	191.366	−272.420	9.888	−0.225
2400	105.152	497.298	413 185	201.870	−272.145	22.156	−0 482
2500	105.368	501.595	416.636	212.396	−271.899	34.414	−0 719
2600	105.561	505 731	419.984	222.943	−271.683	46.662	−0 937
2700	105.735	509.718	423.234	233.508	−271 497	58 902	−1 140
2800	105.892	513.567	426.392	244.089	−271.342	71 136	−1.327
2900	106.034	517.285	429.462	254.686	−271.216	83.366	−1.502
3000	106.162	520 882	432.450	265.295	−271 118	95.591	−1 664
3100	106.280	524.365	435.359	275.918	−271.047	107.813	−1 817
3200	106.387	527 741	438.194	286.551	−271.001	120.033	−1.959
3300	106.484	531 016	440.957	297 195	−270.977	132.253	−2.093
3400	106.574	534.196	443.653	307.848	−270.974	144 472	−2.220
3500	106.656	537.287	446.284	318.509	−270.989	156.691	−2.338
3600	106.732	540.293	448.854	329.179	−655 172	179.372	−2.603
3700	106.803	543.218	451.365	339.855	−654.802	202.548	−2.859
3800	106.867	546.067	453.820	350.539	−654.445	225.715	−3.103
3900	106.928	548.844	456.221	361.229	−654 098	248.873	−3.333
4000	106.983	551.552	458.571	371.924	−653.759	272.021	−3.552
4100	107 035	554.194	460.871	382.625	−653.425	295.162	−3.760
4200	107.084	556.774	463.124	393.331	−653.095	318.294	−3.959
4300	107 129	559.294	465.331	404.042	−652.765	341.418	−4.147
4400	107.171	561.757	467.494	414.757	−652.435	364.535	−4.328
4500	107.210	564.166	469.616	425.476	−652.103	387.644	−4.500
4600	107.247	566.523	471.697	436.199	−651.767	410.746	−4.664
4700	107.282	568.830	473.739	446.926	−651.426	433.840	−4.822
4800	107.315	571.089	475.744	457.655	−651.078	456.928	−4.972
4900	107.345	573.302	477.713	468.388	−650.724	480.007	−5.117
5000	107.374	575.471	479.646	479.124	−650.361	503.080	−5.256
5100	107.402	577.598	481.546	489.863	−649.989	526.145	−5.389
5200	107.427	579.683	483.413	500.605	−649.607	549.203	−5.517
5300	107.452	581.730	485.249	511.349	−649.215	572.254	−5.640
5400	107.475	583.739	487.054	522.095	−648.811	595.296	−5.758
5500	107.496	585.711	488.830	532.844	−648.395	618.331	−5.872
5600	107.517	587.648	490.578	543.594	−647.968	641.359	−5 982
5700	107.537	589.551	492.297	554.347	−647.528	664.379	−6.088
5800	107.555	591.422	493.990	565.102	−647.075	687.391	−6.191
5900	107.573	593.260	495.657	575.858	−646.609	710.394	−6.289
6000	107.590	595.068	497.299	586.616	−646.128	733.390	−6.385

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

$S°(298.15\ K) = [170.314 \pm 6.3]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 514\ K$

$\Delta_f H°(0\ K) =$ Unknown
$\Delta_f H°(298.15\ K) = -169.45 \pm 2.1\ kJ·mol^{-1}$
$\Delta_{fus} H° = 17.908 \pm 0.33\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is taken from.[1]

Heat Capacity and Entropy

$C_p°$ is assumed to be a linear function of temperature and is fitted to the data of Guinchant[2] and Janz and Goodkin.[3] The entropy is estimated by adjusting its value until the melting, sublimation, and vaporization data are in agreement.

Fusion Data

T_{fus} is from NBS;[1] $\Delta_{fus} H°$ is from Janz and Goodkin.[3]

References

[1]U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
[2]M. Guinchant, Comp. Rend. 145, 320 (1907).
[3]G.J. Janz and J. Goodkin, J. Phys. Chem. 63, 1975 (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	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	75.312	170.314	170.314	0.	−169.452	−152.183	26.662
300	75.366	170.780	170.315	0.139	−169.504	−152.076	26.479
400	78.321	192.861	173.306	7.822	−199.068	−140.110	18.297
500	81.206	210.688	179.055	15.816	−197.492	−125.547	13.116
600	84.157	225.738	185.612	24.076	−195.666	−111.325	9.692
700	87.086	238.931	192.305	32.638	−252.316	−90.860	6.780
800	90.015	250.751	198.885	41.493	−249.292	−67.998	4.440
900	92.943	261.522	205.255	50.641	−245.987	−45.531	2.643
1000	95.872	271.466	211.385	60.082	−242.399	−23.448	1.225
1100	98.801	280.741	217.273	69.815	−238.527	−1.738	0.083
1200	101.730	289.464	222.929	79.842	−234.371	19.607	−0.853
1300	104.659	297.722	228.367	90.161	−229.931	40.593	−1.631
1400	107.587	305.585	233.604	100.774	−225.206	61.227	−2.284
1500	110.516	313.108	238.655	111.679	−220.199	81.514	−2.839

PREVIOUS. CURRENT: March 1962

$S°(298.15\ K) = [192.172]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 514\ K$

$\Delta_f H°(298.15\ K) = [-156.626]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 17.908 \pm 0.33\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(514\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is obtained from the data of Janz and Goodkin[1] in the range 507–544 K; it is assumed constant above and below this range. $S°(298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Fusion and Vaporization Data

T_{fus} and T_{vap} (1 atm) are from.[2] $\Delta_{fus} H°$ is the value given by Janz and Goodkin,[1] and $\Delta_{vap} H$ (1 atm) is obtained from the data of Prideaux[3] and Johnson.[4]

References

[1]G. J. Janz and J. Goodkin, J. Phys. Chem. 63, 1975 (1959).
[2]U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
[3]E. B. R. Prideaux, J. Chem. Soc. (London) 97, 2032 (1910).
[4]F. M. G. Johnson, J. Am. Chem. Soc. 33, 777 (1911).

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	102.090	192.172	192.172	0.	−156.626	−145.874	25.557
300	102.090	192.804	192.174	0.189	−156.629	−145.807	25.387
400	102.090	222.173	196.179	10.398	−183.665	−136.433	17.816
500	102.090	244.954	203.740	20.607	−179.875	−125.064	13.065
600	102.090	263.567	212.207	30.816	−176.100	−114.456	9.964
700	102.090	279.304	220.697	41.025	−231.103	−97.908	7.306
800	102.090	292.936	228.894	51.234	−226.726	−79.179	5.170
900	102.090	304.961	236.691	61.443	−222.359	−60.998	3.540
1000	102.090	315.717	244.065	71.652	−218.003	−43.303	2.262
1100	102.090	325.447	251.028	81.861	−213.656	−26.043	1.237
1200	102.090	334.330	257.605	92.070	−209.317	−9.179	0.400
1300	102.090	342.502	263.826	102.278	−204.987	7.323	−0.294
1400	102.090	350.067	269.719	112.487	−200.666	23.493	−0.877
1500	102.090	357.111	275.313	122.696	−196.355	39.354	−1.370

PREVIOUS: CURRENT: March 1962

298.15 to 514 K crystal
above 514 K liquid

Refer to the individual tables for details.

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

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
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							
100							
200							
298.15	75.312	170.314	170.314	0.	−169.452	−152.183	26.662
300	75.366	170.780	170.315	0.139	−169.504	−152.076	26.479
400	78.321	192.861	173.306	7.822	−199.068	−140.110	18.297
500	81.206	210.688	179.055	15.816	−197.492	−125.547	13.116
514.000	81.437	212.933	179.948	16.955	CRYSTAL <--> LIQUID		
514.000	102.090	247.773	179.948	34.862	TRANSITION		
600	102.090	263.567	190.830	43.642	−176.100	−114.456	9.964
700	102.090	279.304	202.374	53.851	−231.103	−97.908	7.306
800	102.090	292.936	212.861	64.060	−226.726	−79.179	5.170
900	102.090	304.961	222.440	74.269	−222.359	−60.998	3.540
1000	102.090	315.717	231.239	84.478	−218.003	−43.303	2.262
1100	102.090	325.447	239.368	94.687	−213.656	−26.043	1.237
1200	102.090	334.330	246.917	104.896	−209.317	−9.179	0.400
1300	102.090	342.502	253.960	115.105	−204.987	7.323	−0.294
1400	102.090	350.067	260.557	125.314	−200.666	23.493	−0.877
1500	102.090	357.111	266.762	135.523	−196.355	39.354	−1.370

PREVIOUS: CURRENT. March 1962

$S°(298.15\ K) = 320.223\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -67.26 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -85.45 \pm 8.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
225(1)
41(2)
293(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Hg–Br = 2.4 Å
Bond Angle: Br–Hg–Br = 180°
Rotational Constant. $B_o = 0.018162\ cm^{-1}$

Enthalpy of Formation

$\Delta_f H°$(cr, 298.15 K)[1] is combined with the 3rd law $\Delta_{sub} H°$(298 15 K) derived from the data of Niwa and Shibata[2] and Johnson.[3]

Heat Capacity and Entropy

The vibrational constants are those given by Klemperer and Lindeman.[4] The bond length is an average of the values given by Braune and Knoke,[5] Gregg *et al.*,[6] and Akishin *et al.*[7]

References

[1]U. S Nat. Bur. Stand. Circ 500, 1268 pp. (1952).
[2]K. Niwa and Z. Shibata, J. Fac Sci. Hokkaido, Imp. Univ. Ser. III 2, 183 (1938).
[3]F. M. G. Johnson, J. Am. Chem Soc. 33, 777 (1911).
[4]W. Klemperer and L. Lindeman, J. Chem. Phys. 25, 397 (1956).
[5]H. Braune and S. Knoke, Z. Phys. Chem. B23, 163 (1933).
[6]A. H. Gregg, G. C. Hampson, G I. Jenkins, P. L. F Jones, and L. E. Sutton, Trans. Faraday Soc. 33, 852 (1937).
[7]P. A. Akishin, V. P Spiridinov, and A. N. Khodchenkov, Zh. Fiz. Khim. 33, 20 (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	−15.658	−67.260	−67.260	INFINITE
100	51.210	258.441	372.093	−11.365	−67.466	−84.203	43.983
200	58.139	296.540	325.684	−5.829	−69.415	−100.235	26.179
250	59.492	309.672	321.212	−2.885	−72.984	−107.644	22.491
298.15	60.276	320.223	320.223	0.	−85.454	−112.881	19.776
300	60.300	320.596	320.225	0.112	−85.534	−113.051	19 684
350	60.814	329.933	320.961	3.140	−116.545	−115.929	17.302
400	61.160	338.078	322.602	6.190	−116.701	−115.831	15.126
450	61.403	345.296	324.730	9.255	−116.845	−115.713	13.432
500	61.579	351.775	327.116	12.329	−116.981	−115.580	12.075
600	61.812	363.025	332.191	18.500	−117.244	−115.275	10.036
700	61.955	372.565	337.295	24.689	−176.267	−108.354	8.086
800	62.048	380.844	342.232	30.889	−175.898	−98.678	6.443
900	62.113	388.156	346.937	37.097	−175.532	−89.047	5.168
1000	62.159	394.703	351.392	43.311	−175.171	−79.457	4.150
1100	62.193	400.629	355.603	49.529	−174.815	−69.903	3.319
1200	62.219	406.042	359.584	55.750	−174.465	−60.381	2.628
1300	62.240	411.023	363.351	61.973	−174 121	−50.888	2.045
1400	62.256	415.636	366.923	68 197	−173.785	−41.421	1.545
1500	62.269	419.932	370.316	74.424	−173.456	−31.978	1.114
1600	62.280	423.951	373.544	80.651	−173.136	−22.557	0.736
1700	62.289	427 727	376.621	86.880	−172.827	−13.155	0.404
1800	62.296	431.287	379.560	93.109	−172.531	−3.772	0 109
1900	62.303	434.656	382.372	99.339	−172.248	5.596	−0.154
2000	62.308	437.851	385.067	105.569	−171.982	14.950	−0.390
2100	62.313	440.891	387.653	111.800	−171.733	24.290	−0.604
2200	62.317	443.790	390.139	118.032	−171.504	33.619	−0.798
2300	62.320	446.561	392.533	124.264	−171.296	42.938	−0.975
2400	62.323	449.213	394.840	130.496	−171.110	52.248	−1.137
2500	62.326	451.757	397.066	136.728	−170.947	61.552	−1.286
2600	62.328	454.202	399.217	142.961	−170.806	70.849	−1.423
2700	62.331	456.554	401.297	149.194	−170.687	80.141	−1.550
2800	62.333	458.821	403.311	155.427	−170.589	89.429	−1.668
2900	62.334	461.008	405.263	161.661	−170.511	98.714	−1.778
3000	62.336	463.121	407.157	167.894	−170.452	107.996	−1.880
3100	62.337	465.165	408.995	174.128	−170.408	117.277	−1.976
3200	62.338	467.145	410.782	180.362	−170.379	126.557	−2.066
3300	62.340	469.063	412.519	186.595	−170.361	135.836	−2.150
3400	62.341	470 924	414.209	192.829	−170.351	145 114	−2.229
3500	62.342	472.731	415.856	199.064	−170.348	154.392	−2.304
3600	62.343	474 487	417.460	205.298	−170.349	163.671	−2.375
3700	62.343	476 195	419.025	211.532	−170.350	172.949	−2.442
3800	62.344	477.858	420.551	217.766	−170.349	182.227	−2.505
3900	62.345	479.477	422.041	224.001	−170.345	191.506	−2.565
4000	62.346	481.056	423.497	230.235	−170.334	200.784	−2.622
4100	62.346	482.595	424.920	236.470	−170.314	210.062	−2.676
4200	62.347	484.098	426.311	242.705	−170.284	219.339	−2.728
4300	62.347	485.565	427.672	248.939	−170.242	228.615	−2.777
4400	62.348	486.998	429.004	255.174	−170.186	237.890	−2.824
4500	62.348	488.399	430.308	261.409	−170.115	247.164	−2.869
4600	62.349	489.770	431.586	267.644	−170.028	256.436	−2.912
4700	62.349	491.111	432.838	273.879	−169.923	265.706	−2.953
4800	62.349	492.423	434.066	280.114	−169.800	274.973	−2.992
4900	62.350	493.709	435.270	286.349	−169.658	284.238	−3.030
5000	62.350	494.968	436.452	292.584	−169.498	293.499	−3 066
5100	62.350	496.203	437.611	298.819	−169.318	302.758	−3.101
5200	62.351	497.414	438.750	305.054	−169.118	312.012	−3.134
5300	62.351	498.602	439.868	311.289	−168.898	321.263	−3.166
5400	62.351	499.767	440.966	317.524	−168.660	330.509	−3.197
5500	62.351	500 911	442.046	323.759	−168.402	339.750	−3.227
5600	62.352	502.035	443.107	329.994	−168.125	348.987	−3.255
5700	62.352	503.138	444 151	336.229	−167.829	358.218	−3.283
5800	62.352	504.223	445.177	342.464	−167.516	367.444	−3.309
5900	62.352	505.288	446.187	348.700	−167.186	376.665	−3.335
6000	62.352	506.336	447.181	354 935	−166.839	385.880	−3.359

PREVIOUS. March 1962 (1 atm) CURRENT March 1962 (1 bar)

$S°(298.15\ K) = 218.75 \pm 3.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -204.18 \pm 0.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The average of the values obtained from the cell measurements of Dakin and Ewing[1] and Ishikawa and Ueda[2] is adopted.

Heat Capacity and Entropy

The heat capacity is estimated by analogy with Hg_2Cl_2(cr). The entropy was obtained from the Gibbs energy and enthalpy of formation.[1,2]

Sublimation Data

According to Jung and Ziegler,[3] the vapor pressure over Hg_2Br_2(cr) reaches one atmosphere at 666 K where the vapor is dissociated into Hg(g) and $HgBr_2$(g).

References

[1]T. W. Dakin and D. T. Ewing, J. Am. Chem. Soc. **62**, 2280 (1940).
[2]F. Ishikawa and Y. Ueda, J. Chem. Soc. Japan **51**, 59 (1930).
[3]G. Jung and W. Ziegler, Z. Phys. Chem. **A150**, 139 (1930).

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
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	104.600	218.752	218.752	0.	−204.179	−178.684	31.305
300	104.703	219.399	218.754	0.194	−204.229	−178.526	31.084
400	109.621	250.226	222.924	10.921	−233.513	−163.837	21.395
500	113.052	275.074	230.948	22.063	−231.518	−146.642	15.320
600	115.604	295.921	240.086	33.501	−229.227	−129.878	11.307
700	117.529	313.890	249.376	45.160	−344.254	−100.372	7.490
800	119.118	329.691	258.447	56.995	−340.329	−65.797	4.296
900	120.416	343.797	267.161	68.973	−336.272	−31.723	1.841
1000	121.545	356.544	275.472	81.072	−332.104	1.893	−0.099
1100	122.539	368.176	283.379	93.277	−327.840	35.087	−1.666
1200	123.470	378.878	290.897	105.578	−323.488	67.889	−2.955
1300	124.209	388.789	298.050	117.960	−319.064	100.325	−4.031
1400	125.143	398.027	304.865	130.426	−314.564	132.417	−4.941
1500	126.273	406.698	311.368	142.995	−309.971	164.185	−5.717

PREVIOUS: CURRENT: March 1962

$S°(298.15\ K)$ = [376.2] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -522.9 \pm 17\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -540.6 \pm 17\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[135](1)	[80](1)
[80](1)	[125](1)
[130](1)	[150](1)

Ground State Quantum Weight: 1 σ = [4]
Point Group: [D_{2h}]
Bond Distances: K–Br = [3.07] Å; K–K = [1.94] Å: Br–Br = [2.39] Å
Bond Angles: Br–K–Br = [102]°; K–Br–K = [78]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.46082 × 10^{-111}] $g^3·cm^6$

Enthalpy of Formation

Vapor densities and vapor pressures of KBr were measured, using a liquid gold isoteniscope, by Hagemark *et al.*,[1] and Hagemark.[2] Based on the equilibrium constants for the reaction 2KBr(g) = K_2Br_2(g) in the temperature range 1267–1434 K, the enthalpy change $\Delta_r H°(298.15\ K)$ of this reaction is evaluated by the 2nd and 3rd law methods to be −42.80 ± 4.26 and −43.12 $kcal·mol^{-1}$, respectively. The enthalpy of formation for K_2Br_2(g) is calculated to be −129.2 ± 4 $kcal·mol^{-1}$, using the 3rd law $\Delta_r H°(298.15\ K)$ value and $\Delta_f H°$(KBr, g, 298.15 K) = −43.04 $kcal·mol^{-1}$. The drift in the 3rd law $\Delta_r H°(298.15\ K)$ values is 0.01 ± 3.2 $cal·K^{-1}·mol^{-1}$.

Heat Capacity and Entropy

The molecular structure and bond distances were estimated by Berkowitz,[3] and are tentatively adopted. Berkowitz[4] has calculated vibrational frequencies on the basis of the potential function for an ionic model. These values are adjusted so that the 3rd law $\Delta_r H°(298.15\ K)$ value for the reaction 2KBr(g) = K_2Br_2(g) agrees with the 2nd law value. The prinicpal moments of inertia are: I_A = 48.4690 × 10^{-39}, I_B = 151.0555 × 10^{-39}, and I_C = 199.5245 × 10^{-39} $g·cm^2$.

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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	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.014	−522.913	−522.913	INFINITE
100	72.670	290.395	447.575	−15.718	−523.875	−540.409	282.281
200	80.188	343.855	383.672	−7.964	−526.211	−556.100	145.238
250	81.223	361.872	377.574	−3.926	−527.737	−563.402	117.717
298.15	81.782	376.230	376.230	0.	−540.573	−568.802	99.652
300	81.799	376.736	376.231	0.151	−540.671	−568.977	99.068
350	82.151	389.374	377.229	4.251	−577.004	−571.752	85.329
400	82.381	400.359	379.448	8.364	−577.894	−570.940	74.557
450	82.540	410.072	382.322	12.488	−578.740	−570.020	66.166
500	82.654	418.775	385.540	16.618	−579.548	−569.007	59.444
600	82.803	433.859	392.374	24.891	−581.073	−566.754	49.340
700	82.893	446.630	399.236	33.176	−582.518	−564.253	42.105
800	82.952	457.703	405.867	41.469	−583.932	−561.547	36.665
900	82.992	467.476	412.180	49.766	−585.364	−558.663	32.424
1000	83.021	476.222	418.155	58.067	−586.863	−555.617	29.022
1100	83.042	484.135	423.799	66.370	−746.380	−543.196	25.794
1200	83.058	491.362	429.132	74.675	−746.024	−524.740	22.841
1300	83.071	498.010	434.178	82.982	−745.676	−506.314	20.344
1400	83.081	504.167	438.960	91.289	−745.336	−487.914	18.204
1500	83.089	509.899	443.501	99.598	−745.006	−469.539	16.351
1600	83.096	515.262	447.820	107.907	−744.687	−451.185	14.730
1700	83.101	520.300	451.937	116.217	−744.383	−432.850	13.300
1800	83.106	525.050	455.868	124.527	−744.097	−414.533	12.029
1900	83.110	529.543	459.629	132.838	−743.833	−396.231	10.893
2000	83.113	533.806	463.232	141.149	−743.596	−377.942	9.871
2100	83.116	537.862	466.690	149.461	−743.391	−359.665	8.946
2200	83.119	541.728	470.013	157.772	−743.224	−341.396	8.106
2300	83.121	545.423	473.212	166.084	−743.101	−323.135	7.339
2400	83.123	548.961	476.295	174.397	−743.027	−304.877	6.635
2500	83.124	552.354	479.270	182.709	−743.008	−286.621	5.989
2600	83.126	555.614	482.144	191.021	−743.050	−268.365	5.392
2700	83.127	558.751	484.924	199.334	−743.157	−250.106	4.839
2800	83.128	561.775	487.615	207.647	−743.336	−231.842	4.325
2900	83.129	564.692	490.223	215.960	−743.590	−213.570	3.847
3000	83.130	567.510	492.752	224.273	−743.926	−195.288	3.400
3100	83.131	570.236	495.208	232.586	−744.348	−176.994	2.982
3200	83.132	572.875	497.594	240.899	−744.862	−158.684	2.590
3300	83.133	575.433	499.914	249.212	−745.453	−140.358	2.222
3400	83.133	577.915	502.172	257.526	−746.157	−122.011	1.874
3500	83.134	580.325	504.371	265.839	−746.961	−103.643	1.547
3600	83.135	582.667	506.513	274.152	−747.880	−85.250	1.237
3700	83.135	584.945	508.602	282.466	−748.916	−66.829	0.943
3800	83.136	587.162	510.641	290.779	−750.076	−48.380	0.665
3900	83.136	589.321	512.631	299.093	−751.366	−29.898	0.400
4000	83.136	591.426	514.574	307.407	−752.781	−11.381	0.149
4100	83.137	593.479	516.474	315.720	−754.341	7.172	−0.091
4200	83.137	595.482	518.331	324.034	−756.061	25.766	−0.320
4300	83.137	597.438	520.148	332.348	−757.939	44.403	−0.539
4400	83.138	599.350	521.927	340.661	−759.431	63.031	−0.748
4500	83.138	601.218	523.668	348.975	−761.514	81.746	−0.949
4600	83.138	603.045	525.374	357.289	−763.755	100.510	−1.141
4700	83.139	604.833	527.046	365.603	−766.117	119.319	−1.326
4800	83.139	606.584	528.684	373.917	−768.425	138.157	−1.503
4900	83.139	608.298	530.292	382.231	−771.105	157.072	−1.674
5000	83.139	609.978	531.869	390.544	−773.949	176.043	−1.839
5100	83.139	611.624	533.416	398.858	−776.961	195.073	−1.998
5200	83.140	613.238	534.936	407.172	−780.140	214.162	−2.151
5300	83.140	614.822	536.428	415.486	−783.488	233.316	−2.299
5400	83.140	616.376	537.895	423.800	−787.005	252.533	−2.443
5500	83.140	617.902	539.335	432.114	−790.688	271.818	−2.582
5600	83.140	619.400	540.752	440.428	−794.536	291.170	−2.716
5700	83.140	620.871	542.145	448.742	−797.858	310.498	−2.845
5800	83.140	622.317	543.514	457.056	−801.941	329.978	−2.972
5900	83.141	623.738	544.862	465.370	−806.172	349.530	−3.095
6000	83.141	625.136	546.188	473.684	−810.546	369.155	−3.214

PREVIOUS: March 1967 (1 atm) CURRENT. March 1967 (1 bar)

$S°(298.15\ K) = [314.53]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°K) = -483.8 \pm 21\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -500.8 \pm 21\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[202](1)	[327](1)
[203](1)	413 (1)
[353](1)	295 (1)

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: D_{2h}
Bond Distances: Li–Br = 2.35 Å; Li–Li = 2.70 Å
Bond Angle: Br–Li–Br = 110°
Product of the Moments of Inertia: $I_A I_B I_C = 4.22259 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

This was obtained from the enthalpy of formation of the liquid and the selected enthalpy of vaporization to the dimer, which derivation has been given in the LiBr(g) table.

Heat Capacity and Entropy

Berkowitz[1] has calculated the molecular structure and vibrational frequencies based on an ionic model. The planar rhombic structure for dimeric lithium bromide, proposed by Berkowitz, has been confirmed by the lack of polarity in electric deflection by Buchler *et al.*[2] The selected bond distances and angle were obtained from the electron diffraction studies of monomer–dimer vapor by Akischin and Rambidi.[3] The bond distances (r_{Br-Br} = 4.20 Å and r_{Li-Li} = 2.60 Å) calculated by Berkowitz are in reasonable agreement with those selected. The principal moments of inertia are: $I_A = 4.1882 \times 10^{-39}$, $I_B = 98.3375 \times 10^{-39}$, and $I_C = 102.5257 \times 10^{-39}\ g·cm^2$.

Bauer *et al.*[4] have estimated six vibrational frequencies (576, 576, 202, 230, 329 and 365 cm^{-1}) for $Li_2Br_2(g)$ in the electron diffraction studies of $Li_2Cl_2(g)$. Klemperer and Norris[5] have observed two fundamental vibrational frequencies (413 and 295 cm^{-1}) in the infrared spectrum and tentatively assigned them as B_{2u} and B_{3u} modes; and these have been adopted in the tabulation. The remaining four vibrational frequencies were obtained from Berkowitz[1] because his model and derivation are self-consistent.

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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	−16.696	−483.767	−483.767	INFINITE
100	47.860	245.752	375.407	−12.966	−483.820	−501.542	261.979
200	67.533	285.942	321.206	−7.053	−486.491	−518.265	135.357
250	72.201	301.555	315.755	−3.550	−488.060	−526.031	109.908
298.15	75.049	314.534	314.534	0.	−500.825	−531.879	93.183
300	75.136	314.998	314.535	0.139	−500.917	−532.072	92.642
350	77.065	326.735	315.458	3.947	−532.285	−535.530	79.923
400	78.388	337 117	317.529	7.835	−532.902	−535.953	69.988
450	79.329	346 407	320.231	11.780	−533.645	−536.291	62.251
500	80.020	354.803	323.275	15.764	−540.530	−535.925	55.988
600	80.943	369.481	329.787	23.816	−542.164	−534.847	46.563
700	81.513	382.005	336.374	31.941	−543.628	−533.510	39.811
800	81.888	392.915	342.775	40.112	−545.002	−531.970	34.734
900	82 148	402.576	348.893	48.315	−546.345	−530.260	30.775
1000	82.335	411.242	354 702	56.540	−547.667	−528.402	27.601
1100	82 474	419.096	360.205	64.780	−548.972	−526.412	24.997
1200	82.580	426.277	365.416	73.033	−550.263	−524.304	22.822
1300	82.663	432.890	370.355	81.296	−551.545	−522.089	20.978
1400	82.729	439.018	375.043	89.565	−552.817	−519.775	19.393
1500	82.782	444.728	379.501	97.841	−554.076	−517.371	18.016
1600	82.826	450.072	383.746	106.121	−555.323	−514.883	16.809
1700	82.862	455.094	387.797	114.406	−847.035	−497.965	15.301
1800	82.892	459.832	391.669	122.693	−846.762	−477.440	13.855
1900	82.918	464.314	395.375	130.984	−846.503	−456.929	12.562
2000	82.940	468.568	398.929	139.277	−846.263	−436.431	11.398
2100	82.959	472.615	402.343	147.572	−846.045	−415.945	10.346
2200	82.975	476.475	405.625	155.869	−845.853	−395.469	9.390
2300	82.990	480.163	408.786	164.167	−845.690	−375.001	8.517
2400	83.002	483.696	411.834	172.466	−845.561	−354.539	7.716
2500	83.013	487.084	414.777	180.767	−845.468	−334.082	6.980
2600	83.023	490.340	417.621	189.069	−845.416	−313.628	6.301
2700	83.032	493.474	420.373	197.372	−845.406	−293.174	5.672
2800	83.040	496.493	423.038	205.675	−845.441	−272.721	5.088
2900	83.047	499.407	425.621	213.980	−845.524	−252.265	4.544
3000	83.053	502.223	428.128	222.285	−845.656	−231.806	4.036
3100	83.059	504.946	430.562	230.590	−845.839	−211.342	3.561
3200	83.064	507.584	432.928	238.897	−846.074	−190.870	3.116
3300	83.069	510.140	435.230	247.203	−846.360	−170.391	2.697
3400	83.073	512.620	437.469	255.510	−846.700	−149.902	2.303
3500	83.077	515.028	439.651	263.818	−847.094	−129.403	1.931
3600	83.081	517.368	441.778	272.126	−847.541	−108.891	1.580
3700	83.084	519.644	443.851	280 434	−848.043	−88.366	1.248
3800	83.087	521.860	445.875	288.743	−848.599	−67.827	0.932
3900	83.090	524.018	447.851	297.052	−849.211	−47.272	0.633
4000	83.093	526.122	449.782	305.361	−849.878	−26.701	0.349
4100	83.095	528.174	451.669	313.670	−850.603	−6.113	0.078
4200	83.098	530.176	453.515	321.980	−851.384	14.494	−0.180
4300	83.100	532.132	455.320	330.290	−852.225	35.119	−0.427
4400	83.102	534.042	457.088	338.600	−853.084	55.762	−0.662
4500	83.104	535.910	458.819	346.910	−854.027	76.428	−0.887
4600	83.105	537.736	460.514	355.220	−855.035	97.116	−1.103
4700	83.107	539.524	462.177	363.531	−856.105	117.826	−1.309
4800	83.109	541.273	463.806	371.842	−857.240	138.560	−1.508
4900	83.110	542.987	465.405	380.153	−858.441	159.318	−1.698
5000	83.111	544.666	466.973	388.464	−859.711	180.102	−1.882
5100	83.113	546.312	468.513	396.775	−861.041	200.910	−2.058
5200	83.114	547.926	470.025	405.086	−862.454	221.746	−2.227
5300	83.115	549.509	471.509	413.398	−863.944	242.611	−2.391
5400	83.116	551.063	472.968	421.709	−865.513	263.504	−2.549
5500	83.117	552.588	474.402	430.021	−867.166	284.426	−2.701
5600	83.118	554.085	475.812	438.333	−868.904	305.380	−2.848
5700	83.119	555.557	477.198	446.645	−870.732	326.366	−2.991
5800	83.120	557.002	478.561	454.957	−872.653	347.383	−3.129
5900	83.121	558.423	479.903	463.269	−874.670	368.436	−3.262
6000	83.121	559.820	481.223	471.581	−876.786	389.523	−3.391

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

$S°(298.15\ K) = [117.2 \pm 4.2]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 984 \pm 15\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -524.26 \pm 2.1\ kJ·mol^{-1}$
$\Delta_{fus} H° = [39.330 \pm 4.2]\ kJ·mol^{-1}$

Enthalpy of Formation

The selected value for $\Delta_f H°(298.15\ K)$ is that given by NBS.[1] This value is derived from the solution calorimetric measurements of Finch *et al.*[2] Their enthalpies for the reaction of crystalline MgO with aqueous HBr and solution of anhydrous $MgBr_2$ in the same solvent are combined to give $\Delta_r H°(298.15\ K) = 7.77 \pm 0.40\ kcal·mol^{-1}$ for the process $MgO(cr) + 2\ HBr(aq) = MgBr_2(cr) + H_2O(l)$ When this result is combined with auxiliary data,[1,3-4] the selected value is obtained. This value is confirmed by an independent means. Bichowsky and Rossini[5] give the enthalpy of solution of $MgBr_2$ in 800 H_2O as $-43.3\ kcal·mol^{-1}$ based on measurements by Beketoff.[6] Correction of this value to 298.15 K and infinite dilution gives a value for $\Delta_{sol} H°$ which leads to $\Delta_f H°(298.15\ K) = -125.4\ kcal·mol^{-1}$ when combined with $\Delta_f H°(Mg^{+2}, aq, \infty, 298.15\ K) = -111.58\ kcal·mol^{-1}$[11] and $\Delta_f H°(Br^-, aq, \infty, 298.15\ K) = -29.039 \pm 0.035\ kcal·mol^{-1}$.[4]

Two emf studies[7,8] on the potential of the magnesium electrode in ether solution give results in disagreement with the calorimetric values. From these cell data we derive $\Delta_f H°(298\ 15\ K)$ values of $-118.8\ kcal·mol^{-1}$[7] and $-115.0\ kcal·mol^{-1}$.[8] These rather large discrepancies are taken as an indication that the electrodes are probably irreversible under these conditions. In fact one study[8] reported that from 10 to 20 hours were required before stable emf values were obtained.

Heat Capacity and Entropy

$C_p°$ at 298.15 K is obtained from the process $MgCl_2(cr) + 2\ NaBr(cr) = MgBr_2(cr) + 2\ NaCl(cr)$ by assuming $\Delta C_p°$ is zero. A comparison of the $C_p°$ value ($17.49\ cal·K^{-1}·mol^{-1}$) with those for other alkaline earth dihalides shows that it is reasonable. $C_p°$ data above 300 K are estimated by comparison with similar data for $MgCl_2$ and CaI_2.[3]

Several estimates[9-12] lying in the range 27–30 $cal·K^{-1}\ mol^{-1}$ for $S°(298.15\ K)$ have been reported. Available experimental data for several other alkaline earth dihalides suggest a value for $S°(298.15\ K)$ of $MgBr_2(cr)$ near 28 $cal·K^{-1}\ mol^{-1}$ ($117.152\ J·K^{-1}·mol^{-1}$). We tentatively adopt this value. It is also the value recommended by Kelley and King[10] and NBS.[1]

Fusion Data

The value of T_{fus} is that determined from cooling curves by Kellner.[13,14] The uncertainty in these measurements is probably near ±15 K. $\Delta_{fus} H°$ is calculated from a $\Delta_{fus} S° = 9.5\ cal·K^{-1}·mol^{-1}$ by multiplication of T_{fus}. $\Delta_{fus} S°$ is assumed the same as that for CaI_2[3] which also has the hexagonal CdI_2 structure.[15] Kelley[16] obtained a value of $\Delta_{fus} H°$ equal to 8.3 $kcal·mol^{-1}$ from an analysis of phase diagrams for the systems $MgBr_2$–MBr(M = Na, K)[14] and $MgBr_2$–LiBr.[17] However, he implied that the value was somewhat uncertain. Furthermore, it is noted that several $\Delta_{fus} H°$ values listed by Kelley for other alkaline earth dihalides deviate considerably (1–3 $kcal·mol^{-1}$) from those measured calorimetrically.[18] Thus, we prefer the estimated value at this time. (See also $MgBr_2(l)$ table Enthalpy of Formation Section).

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	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	73.161	117.152	117.152	0.	−524.255	−504.063	88.310
300	73.387	117.605	117.153	0.136	−524.306	−503.937	87.743
400	77.278	139.284	120.083	7.681	−553.796	−491.005	64.119
500	79.743	156.808	125.731	15.538	−552.296	−475.479	49.673
600	81.429	171.498	132.168	23.598	−550.723	−460.263	40.069
700	82.969	184.165	138.712	31.818	−549.114	−445.313	33.230
800	84.554	195.346	145.106	40.193	−547.480	−430.595	28.115
900	86.270	205.403	151.256	48.733	−545.822	−416.084	24.149
1000	88.136	214.586	157.136	57.450	−552.735	−401.046	20 948
1100	90.144	223.079	162.749	66.363	−551.036	−385.957	18.328
1200	92.257	231.013	168.111	75.483	−549.140	−371.032	16.151
1300	94.433	238.484	173.240	84.817	−547.036	−356.274	14.315
1400	96.567	245.560	178.155	94.367	−672.136	−338.518	12.630
1500	98.701	252.295	182.875	104.131	−668.270	−314.822	10.963

PREVIOUS: June 1966 CURRENT: June 1974

$S°(298.15\ K) = [150.500]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-490.408]\ kJ·mol^{-1}$

$T_{fus} = 984 \pm 15\ K$ $\Delta_{fus}H° = [39.330 \pm 4.2]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(984\ K)–H°(298.15\ K)$, between the crystal and liquid. The derived value is supported by results obtained from an equilibrium study[1] of the anion exchange reaction $0.5\ MgBr_2(l) + HCl(g) = 0.5\ MgCl_2(l) + HBr(g)$. A third law analysis of the K_p value reported for the equilibrium at 1073 K gives $\Delta_r H°(298.15\ K) = 0.05\ kcal·mol^{-1}$ which leads to $\Delta_f H°(l, 298.15\ K) = -117.2\ kcal·mol^{-1}$. In the same paper, Toguri *et al.*[1] reported similar data for the chloride–bromide salts of Ca, K, and Na. These results lead to $\Delta_f H°(298\ 15\ K)$ values for the molten bromides which show deviations from adopted JANAF values[2] of no more than $0.6\ kcal·mol^{-1}$. Thus, although the exact agreement in the $\Delta_f H°(298.15\ K)$ values for $MgBr_2(l)$ is fortuitous, it does tend to substantiate our thermal data.

Heat Capacity and Entropy

$C_p°$ for the liquid is estimated as $25.0\ cal·K^{-1}·mol^{-1}$ by analogy with measured $C_p°$ data for molten $CaBr_2$ and $SrBr_2$.[2] The value is taken to be constant above the assumed glass transition at 700 K. Below 700 K, $C_p°$ 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

Refer to the crystal table for details.

Vaporization Data

T_{vap} is the temperature at which $\Delta_r G° = 0$ at 1 bar for the process $MgBr_2(l) = MgBr_2(g)$. $\Delta_{vap}H°$ is the difference in the enthalpies of formation of the gas and liquid at T_{vap}.

References

[1]J. Toguri, H. Flood, and T. Forland, Acta Chem. Scand. **17**, 502 (1963).

[2]JANAF Thermochemical Tables: $CaBr_2(l)$ and $SrBr_2(l)$, 6–30–74, KBr(l), 3–31–67; NaBr(l), 6–30–64.

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	73.161	150.500	150.500	0.	−490.408	−480.158	84.122
300	73.387	150.954	150.502	0.136	−490.458	−480 094	83.592
400	77.278	172.633	153.431	7.681	−519.948	−470.497	61.441
500	79.743	190.156	159.080	15.538	−518.449	−458.306	47.879
600	81.429	204.846	165.516	23.598	−516.876	−446.424	38.865
700	82.970	217.516	172.060	31.819	−515.265	−434 809	32.446
700.000	82.970	217.516	172.060	31.819	GLASS <--> LIQUID		
700.000	104.600	217.516	172.060	31.819	TRANSITION		
800	104.600	231.484	178.635	42.279	−511.546	−423.571	27.656
900	104.600	243.804	185.205	52.739	−507.968	−412.790	23.958
1000	104.600	254.824	191.625	63.199	−513.139	−401.687	20.982
1100	104.600	264.794	197.831	73.659	−509.893	−390.699	18.553
1200	104.600	273.895	203.796	84.119	−506.655	−380.006	16.541
1300	104.600	282.268	209.514	94.579	−503.427	−369.583	14.850
1400	104.600	290.019	214.991	105.039	−627.616	−356.242	13.292
1500	104.600	297.236	220.237	115.499	−623.054	−337.017	11.736
1600	104.600	303.987	225.262	125.959	−618.502	−318.096	10.385
1700	104.600	310.328	230.082	136.419	−613.961	−299.460	9.201
1800	104.600	316.307	234.707	146.879	−609.434	−281.091	8.157
1900	104.600	321.962	239.152	157.339	−604.921	−262.972	7.230
2000	104.600	327.328	243.428	167.799	−600.426	−245.091	6.401

PREVIOUS: June 1966 CURRENT: June 1974

298.15 to 984 K crystal
above 984 K liquid

Refer to the individual tables for details.

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

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
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	73.161	117.152	117.152	0.	−524.255	−504.063	88.310
300	73.387	117.605	117.153	0.136	−524.306	−503.937	87.743
400	77.278	139.284	120.083	7.681	−553.796	−491.005	64.119
500	79.743	156.808	125.731	15.538	−552.296	−475.479	49.673
600	81.429	171.498	132.168	23.598	−550.723	−460.263	40.069
700	82.969	184.165	138.712	31.818	−549.114	−445.313	33.230
800	84.554	195.346	145.106	40.193	−547.480	−430.595	28.115
900	86.270	205.403	151.256	48.733	−545.822	−416.084	24.149
984.000	87.811	213.168	156.213	56.044	CRYSTAL <--> LIQUID TRANSITION		
984.000	104 600	253.137	156.213	95.373			
1000	104.600	254 824	157.778	97.047	−513.139	−401.687	20.982
1100	104.600	264.794	167.060	107.507	−509.893	−390.699	18.553
1200	104.600	273.895	175.590	117.967	−506.655	−380.006	16.541
1300	104.600	282.268	183.478	128.427	−503.427	−369.583	14.850
1400	104.600	290.019	190.815	138.887	−627.616	−356.242	13.292
1500	104 600	297.236	197.672	149.347	−623.054	−337.017	11.736
1600	104.600	303.987	204.108	159.807	−618.502	−318.096	10.385
1700	104.600	310.328	210.171	170.267	−613.961	−299.460	9.201
1800	104.600	316.307	215.903	180.727	−609.434	−281.091	8.157
1900	104.600	321.962	221.338	191.187	−604.921	−262.973	7.230
2000	104.600	327.328	226.504	201.647	−600.426	−245.091	6.401

PREVIOUS: CURRENT: June 1974

Magnesium Bromide ($MgBr_2$) IDEAL GAS $M_r = 184.113$ Magnesium Bromide ($MgBr_2$) $Br_2Mg_1(g)$

$S°(298\ 15\ K) = [301\ 0 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -288.4 \pm 10.5\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -302.9 \pm 10.5\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[179](1)
[70](2)
490(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point group: $[D_{\infty h}]$
Bond Distance: Mg–Br = 2.34 ± 0 03 Å
Bond Angle: Br–Mg–Br = [180]°
Rotational Constant: B = [0.019265] cm^{-1}

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ of the gas is obtained from that of the crystal by addition of $\Delta_{sub}H°(298\ 15\ K) = 52\ 9 \pm 2\ 0$ kcal mol^{-1} (221.334 ± 8.4 $kJ·mol^{-1}$) The selected value for the enthalpy of sublimation is derived from results of a mass spectrometric–Knudsen effusion study by Berkowitz and Marquart.[1] The presence of ~2% dimer in the vapor phase over the solid at near 800 K was revealed by the mass spectral results. Berkowitz and Marquart,[1] using $MgBr_2^+$–ion intensity as a measure of the monomer concentration, obtained a 2nd law $\Delta_{sub}H = 50.3$ $kcal·mol^{-1}$ at 751 K. This value when corrected to 298.15 K gives $\Delta_{sub}H°(298\ 15\ K) = 52.4\ kcal·mol^{-1}$ Absolute partial pressures were also determined at 798 and 842 K by integrating the ion current during complete volatilization of the sample. A 3rd law analysis of these two pressures gives a enthalpy of sublimation equal to 53 4 kcal mol^{-1} which is in good agreement with the value obtained from the ion intensities by the 2nd law. The drift in the 3rd law analysis is 1.0 $cal·K^{-1}·mol^{-1}$. The selected value of $\Delta_{sub}H°(298\ 15\ K)$ is an average of these two results.

Heat Capacity and Entropy

The bond length is from the electron–diffraction measurements of Akishin and Spirdonov.[3] Their diffraction patterns for $MgBr_2$ were satisfactorily explained on the basis of a linear model Klemperer *et al.*[4,5] have performed electronic quadrupole deflection experiments on several symmetrical triatomic dihalides in an attempt to determine which molecules possess permanent dipole moments Their results on the geometrics of the alkaline earth dihalides have been summarized by Hayes[6] who pointed out that the linear form is favored by the light metal–heavy halogen combination. Thus, one would expect $MgBr_2$ to be linear, and we adopt this configuration.

The antisymmetric stretching frequency ($\nu_3 = 490\ cm^{-1}$) has been observed in the infrared absorption spectrum of gaseous $MgBr_2$ by Randall *et al.*[7] The symmetric stretching (ν_1) and bending (ν_2) frequencies are calculated from force constants by the valence force method.[8] The observed ν_3 frequency leads to $k = 1.5 \times 10^5$ dynes/cm, or $\nu_1 = 179\ cm^{-1}$ A comparison of values for the ratio of the stretch to bend force constants for the linear molecules $MgCl_2$[9](ratio = 88)], $CaBr_2$[9](ratio = [100])], and $SrBr_2$[9](ratio = [100])] suggests a value near 100 for $MgBr_2$. This value for the ratio gives $k\delta/l^2 = 1.5 \times 10^3$ dynes/cm, or $\nu_2 = 70\ cm^{-1}$ Based on similar data for linear $BeBr_2$,[10] it is possible that the value of the ratio could be as low as 41. This ratio corresponds to a bending frequency of 109 cm^{-1}. We prefer the lower value of ν_2, since it is consistent with the observed value for [$MgCl_2$[9]($\nu_2 = 88\ cm^{-1}$)]. However, we do include in the uncertainty of the value for $S°(298\ 15\ K)$ the possibility that the higher value is correct. Brewer *et al* [2] used a value for the ratio of 10 and obtained $\nu_2 = 220\ cm^{-1}$. By comparison with the observed frequencies for $MgCl_2$ and [$BeBr_2$[10]($\nu_2 = 220\ cm^{-1}$)] it is unlikely that the value for $MgBr_2$ is this high. Krasnov and Svettsov[11] have reported $\nu_1 = 188\ cm^{-1}$ and $\nu_2 = 148\ cm^{-1}$ based on force constant correlations. The ground state is assumed to be singlet by analogy with that for $BaCl_2$.[9]

References

[1] J. Berkowitz and J. R. Marquart, J. Chem Phys. 37, 1853 (1962).
[2] L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Revs. 63, 111 (1963).
[3] P. A. Akishin and V. P. Spiridonov, Kristallografiya 2, 472 (1957).
[4] L. Wharton, R. A. Berg, and W. Klemperer, J. Chem. Phys. 39, 2023 (1963).
[5] A. Buchler, J. L. Stauffer, and W. Klemperer, J. Am. Chem. Soc. 86, 4544 (1964).
[6] E. F. Hayes, J. Phys. Chem. 70, 3740 (1966).
[7] S. P Randall, F. T. Greene, and J. L. Margrave, J. Phys. Chem. 63, 758 (1959).
[8] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, (1962).
[9] JANAF Thermochemical Tables: $MgCl_2$(g), 12–31–69, $CaBr_2$(g) and $SrBr_2$(g), 6–30–74; $BaCl_2$(g), 12–31–72.
[10] A. Snelson, J. Phys. Chem. 72, 250 (1968).
[11] K S. Krasnov and V I. Svettsov, Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol. 6, 167 (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	−15.012	−288.427	−288 427	INFINITE
100	49 669	241.523	351.095	−10 957	−287.807	−305.624	159.641
200	55.867	278.131	306.332	−5.640	−289.398	−322.911	84.336
250	57.579	290.793	301.998	−2.801	−290.546	−331.162	69.192
298.15	58 711	301 038	301.038	0.	−302.922	−337.555	59.138
300	58.747	301.401	301.039	0.109	−302.999	−337.769	58.811
350	59.557	310.521	301.757	3.067	−333.953	−341.862	51 020
400	60.134	318.514	303.363	6.061	−334.082	−342.984	44.789
450	60.555	325 622	305 448	9.078	−334.226	−344.088	39.941
500	60.870	332.019	307.791	12.114	−334.387	−345 175	36.060
600	61.299	343.158	312.784	18.224	−334.763	−347.299	30.235
700	61.568	352.629	317.817	24.369	−335.230	−349.353	26.069
800	61 747	360.863	322.694	30.535	−335.804	−351.332	22.940
900	61.872	368.143	327.347	36.716	−336.505	−353.233	20.501
1000	61.962	374.667	331.759	42.908	−345.943	−354.335	18.509
1100	62.030	380.576	335.932	49.108	−346.958	−355.125	16.863
1200	62.081	385.976	339.881	55.314	−347.975	−355.822	15.489
1300	62.122	390 946	343.620	61.524	−348.996	−356 435	14.322
1400	62.154	395.551	347.167	67.738	−477.432	−353.802	13.201
1500	62.180	399.841	350.538	73.954	−477.113	−344.982	12.013
1600	62.201	403.854	353 746	80.174	−476.801	−336.184	10.975
1700	62.219	407 626	356.805	86.395	−476.500	−327.404	10.060
1800	62.234	411.182	359.728	92 617	−476.210	−318 643	9.247
1900	62.247	414.548	362.526	98.841	−475.933	−309.896	8.520
2000	62.258	417 741	365.207	105.067	−475.672	−301.164	7 866
2100	62.267	420.779	367 782	111.293	−475.429	−292.445	7.274
2200	62.275	423.675	370.257	117.520	−475.205	−283.737	6.737
2300	62.282	426.444	372.640	123.748	−475.003	−275 038	6.246
2400	62.288	429.095	374.938	129.976	−474.822	−266.348	5 797
2500	62.294	431 637	377.155	136.205	−474.665	−257.665	5.384
2600	62.298	434 081	379 298	142 435	−474.532	−248 988	5.002
2700	62.303	436.432	381.371	148.665	−474.424	−240 315	4.649
2800	62.307	438.698	383.378	154.896	−474.339	−231 646	4.321
2900	62.310	440.884	385.324	161.126	−474.278	−222.980	4 016
3000	62.313	442 997	387.211	167.358	−474.241	−214.315	3.732
3100	62.316	445 040	389.044	173.589	−474.226	−205.651	3.465
3200	62.319	447.019	390.825	179.821	−474.233	−196.987	3.215
3300	62.321	448.936	392.557	186.053	−474.260	−188.323	2 981
3400	62.323	450.797	394.242	192.285	−474.307	−179.657	2.760
3500	62.325	452.603	395.884	198.517	−474.373	−170.990	2.552
3600	62.327	454.359	397.484	204.750	−474.458	−162.321	2.355
3700	62.329	456.067	399.045	210.983	−474.561	−153.649	2.169
3800	62.330	457.729	400.567	217.216	−474.681	−144 975	1.993
3900	62.332	459.348	402.054	223.449	−474.818	−136.296	1.825
4000	62.333	460.926	403.506	229.682	−474 972	−127.614	1.666
4100	62.334	462.465	404.925	235.915	−475.144	−118.928	1.515
4200	62.335	463.968	406.313	242.149	−475.333	−110.238	1.371
4300	62.336	465 434	407.671	248.382	−475.541	−101.543	1.233
4400	62.337	466 867	409.000	254.616	−475.767	−92 842	1.102
4500	62.338	468.268	410.302	260.850	−476 012	−84.137	0 977
4600	62.339	469.639	411.577	267.084	−476.278	−75.426	0.856
4700	62.340	470.979	412.827	273.318	−476.566	−66.708	0.741
4800	62.341	472.292	414.052	279.552	−476.876	−57.985	0.631
4900	62.341	473.577	415.253	285.786	−477.210	−49.254	0.525
5000	62.342	474.837	416.433	292.020	−477.570	−40.517	0.423
5100	62.343	476.071	417.590	298.254	−477.956	−31.772	0.325
5200	62.343	477.282	418.726	304.488	−478.370	−23.020	0.231
5300	62.344	478.469	419.842	310.723	−478.813	−14.258	0.141
5400	62.344	479 635	420.939	316.957	−479.287	−5.489	0.053
5500	62.345	480 779	422.016	323.192	−479.794	3.290	−0.031
5600	62.345	481.902	423.076	329.426	−480.334	12.078	−0.113
5700	62.346	483.005	424.118	335.661	−480.909	20.876	−0.191
5800	62.346	484.090	425.142	341.895	−481.522	29.684	−0.267
5900	62.346	485.155	426.150	348.130	−482.172	38.504	−0.341
6000	62.347	486.203	427.143	354.364	−482.862	47.334	−0 412

PREVIOUS. June 1974 (1 atm) CURRENT. June 1974 (1 bar)

$S°(298.15\ K) = [321.7 \pm 12.6]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 739.2 \pm 25.1\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [731.363]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Pi$	[25000]	4
$^2\Sigma$	[30000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[150](1)
[50](2)
[450](1)

Point Group: $[D_{\infty h}]$ $\sigma = 2$
Bond Distance: Mg–Br = [2.6] Å
Bond Angle: Br–Mg–Br = [180]°
Rotational Constant: B_o = [0.015605] cm^{-1}

Enthalpy of Formation

Berkowitz and Marquart[1] have reported the appearance potential of $MgBr_2^+$ as 10 6 ± 0.1$_5$ eV(245.6 kcal·mol^{-1}). Assuming this value refers to the direct ionization process $MgBr_2(g) + e^- = MgBr_2^+(g) + 2e^-$, we obtain $\Delta_f H°(MgBr_2^+, g, 0\ K) = 176\ 7 \pm 6.0$ kcal mol^{-1} by combining the appearance potential with $\Delta_f H°(MgBr_2, g, 0\ K) = -68.9 \pm 2.5$ kcal·mol^{-1}.[2] The former value corresponds to $\Delta_f H°(298.15\ K) = 174.8$ kcal mol^{-1} (731.363 kJ·mol^{-1}) which is adopted.

Heat Capacity and Entropy

A comparison of the dissociation energy, $\Delta_a H° = 91\ 0$ kcal·mol^{-1}, for $MgBr_2^+$ with that for $MgBr_2$,[2] $\Delta_a H° = 160.3$ kcal mol^{-1}, suggests the existence of somewhat weaker bonding in the ion relative to the molecule. Thus, one would expect the bond length in the ion to be greater than that for $MgBr_2$. We assume a 10% increase in r_e for the ion. The correlation diagrams of Walsh[3] predict a linear configuration for $MgBr_2^+$(fifteen valence electrons). This prediction is supported by the fact that several other fifteen valence electron molecules (BO_2, N_3, NCO, and NNO^+) are now known to be linear.[2] We adopt a linear configuration for the ion.

The vibrational frequencies are estimated to be slightly less than those for $MgBr_2$.[2] The ground state electronic configuration is assumed to be $^2\Pi$ by analogy with those for the isoelectronic molecules[2] BO_2, N_3, NCO, and N_2O^+. Two excited states are also included based on those observed for BO_2.[2] The enthalpy at 0 K is −15.441 kJ·mol^{-1}.

References

[1] J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962).
[2] JANAF Thermochemical Tables: $MgBr_2$(g), 6–30–74, BO_2(g), 6–30–68, CNO(g), N_2O^+(g), and N_3(g), 12–31–70.
[3] A. D. Walsh, J. Chem. Soc 1953, 2266.

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	−15.442	739.231		
100	51.289	261.045	372.577	−11.153			
200	56.811	298.524	327.095	−5.714			
250	58.322	311.375	322.708	−2.833			
298.15	59.303	321.737	321.737	0.	731.363	684.304	−119.887
300	59.334	322.104	321.738	0.110	731.325	684.012	−119.097
350	60.027	331.305	322.463	3.095	701.437	677.744	−101.148
400	60.514	339.354	324.082	6.109	702.368	674.296	−88.054
450	60.868	346.503	326.183	9.144	703.280	670.732	−77.857
500	61.131	352.931	328.542	12 194	704.174	667.067	−69.688
600	61.487	364.110	333.566	18.327	705.898	659.482	−57.413
700	61.710	373.607	338.625	24.487	707.527	651.616	−48.624
800	61.857	381.857	343.524	30.666	709.043	643.524	−42.018
900	61.960	389.149	348.196	36.857	710.431	635.249	−36.869
1000	62.034	395.681	352.624	43.057	703.079	627.540	−32.779
1100	62.090	401.596	356.811	49.264	704.150	619.935	−29.438
1200	62.132	407.001	360.772	55.475	705.217	612.232	−26.650
1300	62.165	411.975	364.522	61.690	706.279	604.440	−24.287
1400	62.191	416.583	368.078	67.908	579.926	599.734	−22.376
1500	62.213	420.875	371.456	74.128	582.327	601.064	−20.931
1600	62.230	424.891	374.672	80.350	584.720	602.236	−19.661
1700	62.245	428.664	377.738	86.574	587.103	603.257	−18.536
1800	62.257	432.222	380.667	92.799	589.474	604.139	−17.532
1900	62.267	435.588	383.470	99.025	591.831	604.889	−16.630
2000	62.276	438.782	386.156	105.252	594.173	605.516	−15.814
2100	62.284	441.821	388.735	111.480	596.496	606.026	−15.074
2200	62.290	444.719	391.214	117.709	598.800	606.426	−14.398
2300	62.296	447.488	393.601	123.938	601.083	606.721	−13.779
2400	62.302	450.139	395.902	130.168	603.343	606.918	−13.209
2500	62.306	452.682	398 123	136.398	605.580	607.021	−12.683
2600	62.311	455.126	400.269	142.629	607.793	607.035	−12.195
2700	62.315	457.478	402.344	148.861	609.982	606.964	−11.742
2800	62.320	459.744	404.354	155.092	612.146	606.812	−11.320
2900	62.324	461.931	406.302	161.325	614.287	606.584	−10.926
3000	62.329	464.044	408.192	167.557	616.404	606.282	−10.556
3100	62.335	466.088	410.027	173.791	618.500	605.910	−10.210
3200	62.341	468.067	411.810	180.024	620.574	605 471	−9.883
3300	62.348	469.986	413.544	186.259	622.627	604.967	−9.576
3400	62.355	471.847	415.231	192.494	624.662	604.401	−9.285
3500	62.364	473 655	416.875	198.730	626.677	603.776	−9 011
3600	62.374	475.412	418.476	204.967	628.676	603.094	−8.751
3700	62.386	477.121	420.038	211.205	630.657	602.356	−8.504
3800	62.399	478.785	421.563	217.444	632.622	601.564	−8.269
3900	62.414	480.406	423.051	223.685	634.571	600.721	−8.046
4000	62.431	481.986	424.504	229.927	636.504	599.829	−7.833
4100	62.450	483.528	425.925	236.171	638.422	598.888	−7.630
4200	62.471	485.033	427.315	242.417	640.324	597.901	−7.436
4300	62.494	486.503	428.674	248.665	642.209	596.868	−7.251
4400	62.519	487.940	430.005	254.916	644.079	595.793	−7.073
4500	62.547	489.346	431.308	261.169	645.932	594 674	−6.903
4600	62.577	490.721	432.585	267.425	647.766	593.515	−6.740
4700	62.610	492.067	433.836	273.685	649.583	592.316	−6.583
4800	62.645	493.385	435.063	279.947	651.380	591.078	−6.432
4900	62.683	494.677	436.266	286.214	653.157	589.804	−6.287
5000	62.723	495.944	437.447	292.484	654.912	588.493	−6.148
5100	62.765	497.187	438.607	298.758	656.644	587.148	−6.014
5200	62.810	498.406	439.745	305.037	658.353	585.768	−5.884
5300	62.857	499.603	440.863	311.320	660.038	584.356	−5.759
5400	62.907	500.778	441.962	317.609	661.696	582.913	−5.639
5500	62.959	501.933	443.042	323.902	663.327	581.439	−5.522
5600	63.013	503.068	444 103	330.201	664.930	579.935	−5.409
5700	63 069	504.184	445.148	336.505	666.503	578.403	−5.300
5800	63.127	505.281	446.175	342.814	668.044	576.844	−5.195
5900	63.188	506.361	447.186	349.130	669.553	575.259	−5.093
6000	63.250	507.423	448.181	355.452	671.029	573.648	−4.994

PREVIOUS. June 1974 (1 atm) CURRENT June 1974 (1 bar)

$S°(298.15\ K)$ = [124.7 ±] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = unknown

$\Delta_f H°(298.15\ K) = -202.9 \pm 25\ kJ·mol^{-1}$

Enthalpy of Formation

Shukurov *et al.*[1] (determined the enthalpies of combustion of $MoBr_2$(cr) and $MoBr_3$(cr)) Dellien *et al.*[2] used the combustion values of Shukurov to obtain $\Delta_f H°(MoBr_2, cr, 298.15\ K) = -54\ kcal·mol^{-1}$ and $\Delta_f H°(MoBr_3, cr, 298.15\ K) = -64\ kcal·mol^{-1}$. Oppermann[3] carried out equilibrium experiments on the mixed phases $MoBr_2$(cr) + $MoBr_3$(cr). Brewer[4] re-evaluated the data of Oppermann (see the discussion in the $MoBr_4$(g) table[5]) and supplemented the combustion data with other data on $MoBr_4$(cr). For this reason we believe Brewer's value of $\Delta_f H°(MoBr_2, cr, 298.15\ K) = -48.5 \pm 6\ kcal·mol^{-1}$ ($-202.924 \pm 25\ kJ·mol^{-1}$) to be the most reliable among all the data and is our adopted value. Note that the enthalpy of formation listed in NBS 270-4,[6] $\Delta_f H°(298.15\ K) = -62.4\ kcal·mol^{-1}$, is much more negative.

Heat Capacity and Entropy

Brewer[4] estimated $S°(298.15\ K) = 29.8 \pm 4\ cal·K^{-1}·mol^{-1}$ ($124.683 \pm 17\ J·K^{-1}·mol^{-1}$) and derived $C_p° = 18.30 + 2.50 \times 10^{-3}T$ $cal·K^{-1}·mol^{-1}$ (298-1353 K) from the heat capacities estimated by Opperman.[3] Other estimates are $C_p°(15\ K) = 17.1\ cal·K^{-1}·mol^{-1}$ from the ionic contributions of Kubaschewski and Unal[7] and $S°(298.15\ K) = 30.4\ cal·K^{-1}·mol^{-1}$ from the additive entropy constants of Stull and Prophet.[8] The heat capacity at 298.15 K listed in NBS 270-4[6] is $18.3\ cal·K^{-1}·mol^{-1}$.

Decomposition Data

T_{dcm} is the calculated temperature at which the pressure of $MoBr_4$(g) is one atmosphere for the reaction 2 $MoBr_2$(cr) = Mo(cr) + $MoBr_4$(g).

References

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[4] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, September 29, 1978; preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.

[5] JANAF Thermochemical Tables: $MoBr_4$(g), 9-30-78.

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[8] D. R. Stull and H. Prophet, Chap. 13 in "The Characterization of High Temperature Vapors" ed. by J. L. Margrave, John Wiley, (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
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	79.684	124.683	124.683	0.	−202.924	−186.189	32.620
300	79.705	125.176	124.685	0.147	−202.961	−186.085	32.400
400	80.751	148.249	127.824	8.170	−231.874	−174.412	22.776
500	81.797	166.381	133.785	16.298	−229.986	−160.265	16.743
600	82.843	181.387	140.504	24.530	−228.091	−146.499	12.754
700	83.889	194.235	147.284	32.866	−226.165	−133.052	9.928
800	84.935	205.506	153.871	41.308	−224.197	−119.884	7.828
900	85.981	215.570	160.177	49.853	−222.182	−106.965	6.208
1000	87.027	224.683	166.179	58.504	−220.118	−94.273	4.924
1100	88.073	233.027	171.882	67.259	−218.009	−81.790	3.884
1200	89.119	240.735	177.303	76.118	−215.860	−69.501	3.025
1300	90.165	247.909	182.461	85.083	−213.677	−57.393	2.306
1400	91.211	254.630	187.379	94.152	−211.468	−45.454	1.696
1500	92.257	260.958	192.075	103.325	−209.238	−33.674	1.173
1600	93.303	266.946	196.569	112.603	−206.997	−22.043	0.720
1700	94.349	272.634	200.878	121.986	−204.750	−10.552	0.324
1800	95.395	278.056	205.016	131.473	−202.508	0.807	−0.023

PREVIOUS. CURRENT: September 1978

$S°(298.15\ K)$ = [321.0 ± 8] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [179.2 ± 84] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [167.4 ± 84] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[1]
[243.10]	[3]
[669.60]	[5]
[1225.20]	[7]
[1873.80]	[9]
[11271]	[1]
[12510]	[3]
[12630]	[9]
[13201]	[11]
[13742]	[13]

Vibrational Frequencies and Degeneracies
ν_i, cm^{-1}
[300](1)
[60](2)
[300](1)

Ground State Quantum Weight: I σ = [2]
Point Group: [$D_{\infty h}$]
Bond Distance: Mo–Br = [2.42] Å
Bond Angle: Br–Mo–Br = [180]°
Rotational Constant: B_o = [0.018012] cm^{-1}

Enthaply of Formation

The adopted value of $\Delta_f H°(298.15\ K)$ = 40.0 ± 20 $kcal·mol^{-1}$ (167.360 ± 84 $kJ·mol^{-1}$) is that estimated by Brewer[1] using bonding models. The value is consistent with sublimation data for $MoBr_2$ at 1023 K and 1273 K reported by Schafer, *et al.*[2] Brewer gave no weight to the partial pressures of $MoBr_2$ obtained by Oppermann[3] by difference (see the discussion on the $MoBr_4$(g) table[4]). The value of $\Delta_f H°(0\ K)$ combined with JANAF data[4] for Mo(g) and Br(g) gives $\Delta_a H°(MoBr_2, g)$ = 171 ± 20 $kcal·mol^{-1}$ (715.5 ± 84 $kJ·mol^{-1}$). This yields a mean bond energy $\Delta_a H°(MoBr_2, g)/2$ = 85.5 $kcal·mol^{-1}$, somewhat higher than that found in $MoBr_4$(g), 76.0 $kcal·mol^{-1}$.[4]

Heat Capacity and Entropy

The linear structure of $MoBr_2$(g), bond length, and the ground state vibrational frequencies are estimates from Brewer.[1] The electronic contributions are assumed to be the same as the free ion, Mo^{++}, as suggested by Brewer.[1] All states up to 13,742 cm^{-1} as listed by Rico[5] are included in the calculation.

References

[1]L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication of September 29, 1978; preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[2]H. Schafer, T. Grofe, and M. Trenkel, J. Solid State Chem. 8, 14 (1973).
[3]H. Oppermann, Z. anorg. allg. Chem. 395, 249 (1973).
[4]JANAF Thermochemical Tables: Mo(g), 3–31–78, Br(g), 9–30–61, $MoBr_4$(g), 9–30–78.
[5]F. R. Rico, Anales. Real Soc. Espan. Fys. Quim., Ser. A, 61, 103 (1965).

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	−17.293	179.161	179.161	INFINITE
100	56.960	250.449	380.393	−12.994	180.175	161.218	−84.211
200	66.592	293.789	327.229	−6.688	179.738	142.360	−37.181
250	68.260	308.843	322.096	−3.313	179.179	133.075	−27.805
298.15	69.291	320.960	320.960	0.	167.360	125.575	−22.000
300	69.322	321.389	320.962	0.128	167.304	125.315	−21.819
350	70.005	332.131	321.809	3.613	136.924	119.974	−17.905
400	70.409	341.508	323.697	7.124	137.364	117.522	−15.347
450	70.590	349.813	326.147	10.650	137.784	115.017	−13.351
500	70.590	357.252	328.892	14.180	138.180	112.466	−11.749
600	70.206	370.094	334.722	21.223	138.887	107.254	−9.337
700	69.536	380.868	340.566	28.212	139.465	101.935	−7.606
800	68.771	390.104	346.195	35.127	139.906	96.541	−6.304
900	68.020	398.160	351.531	41.966	140.215	91.101	−5.287
1000	67.333	405.291	356.557	48.733	140.395	85.633	−4.473
1100	66.728	411.679	361.283	55.436	140.452	80.153	−3.806
1200	66.204	417.462	365.727	62.082	140.387	74.673	−3.250
1300	65.756	422.743	369.913	68.679	140.203	69.204	−2.781
1400	65.375	427.602	373.862	75.235	139.900	63.753	−2.379
1500	65.053	432.101	377.597	81.756	139.477	58.328	−2.031
1600	64.783	436.290	381.136	88.247	138.932	52.935	−1.728
1700	64.559	440.211	384.497	94.714	138.262	47.580	−1.462
1800	64.377	443.896	387.695	101.161	137.464	42.268	−1.227
1900	64.232	447.372	390.745	107.591	136.530	37.004	−1.017
2000	64.122	450.664	393.660	114.008	135.456	31.793	−0.830
2100	64.043	453.790	396.449	120.416	134.233	26.640	−0.663
2200	63.993	456.769	399.124	126.818	132.855	21.548	−0.512
2300	63.970	459.613	401.693	133.216	131.313	16.522	−0.375
2400	63.972	462.335	404.163	139.613	129.599	11.567	−0.252
2500	63.996	464.947	406.543	146.011	127.704	6.688	−0.140
2600	64.040	467.458	408.837	152.413	125.607	1.888	−0.038
2700	64.103	469.876	411.054	158.820	123.271	−2.827	0.055
2800	64.182	472.208	413.196	165.234	120.637	−7.451	0.139
2900	64.275	474.462	415.270	171.657	81.743	−11.924	0.215
3000	64.380	476.643	417.280	178.089	80.314	−15.129	0.263
3100	64.496	478.756	419.229	184.533	78.881	−18.287	0.308
3200	64.620	480.805	421.121	190.989	77.445	−21.399	0.349
3300	64.750	482.796	422.960	197.457	76.011	−24.465	0.387
3400	64.886	484.731	424.749	203.939	74.581	−27.489	0.422
3500	65.025	486.614	426.490	210.434	73.159	−30.470	0.455
3600	65.167	488.448	428.185	216.944	71.747	−33.411	0.485
3700	65.309	490.235	429.838	223.468	70.349	−36.312	0.513
3800	65.452	491.979	431.451	230.006	68.966	−39.177	0.539
3900	65.593	493.681	433.025	236.558	67.602	−42.005	0.563
4000	65.732	495.343	434.562	243.124	66.258	−44.798	0.585
4100	65.868	496.968	436.064	249.704	64.937	−47.558	0.606
4200	66.000	498.557	437.533	256.298	63.640	−50.286	0.625
4300	66.128	500.111	438.971	262.904	62.368	−52.984	0.644
4400	66.252	501.633	440.377	269.523	61.123	−55.652	0.661
4500	66.370	503.123	441.755	276.154	59.906	−58.292	0.677
4600	66.483	504.583	443.105	282.797	58.717	−60.905	0.692
4700	66.590	506.014	444.429	289.451	57.558	−63.493	0.706
4800	66.691	507.417	445.726	296.115	56.428	−66.057	0.719
4900	66.786	508.793	446.999	302.789	55.327	−68.597	0.731
5000	66.875	510.143	448.249	309.472	−537.129	−65.384	0.683
5100	66.958	511.468	449.475	316.163	−539.850	−55.922	0.573
5200	67.034	512.769	450.680	322.863	−542.688	−46.406	0.466
5300	67.105	514.047	451.864	329.570	−545.640	−36.834	0.363
5400	67.169	515.302	453.027	336.284	−548.707	−27.205	0.263
5500	67.227	516.535	454.170	343.004	−551.885	−17.519	0.166
5600	67.280	517.747	455.295	349.729	−555.175	−7.774	0.073
5700	67.327	518.938	456.401	356.460	−558.571	2.031	−0.019
5800	67.369	520.109	457.489	363.194	−562.074	11.896	−0.107
5900	67.405	521.261	458.561	369.933	−565.679	21.823	−0.193
6000	67.436	522.394	459.615	376.675	−569.388	31.812	−0.277

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

$S°(298.15\ K)$ = [348.949] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -468\ 33 \pm 3.77\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -486.35 \pm 3.77\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[182](1)	[134](1)
[120](1)	[188](1)
[207](1)	[228](1)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: [D_{2h}]
Bond Distance: Na–Br = [2.75] Å
Bond Angles: Na–Br–Na = [71]°; Br–Na–Br = [109]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [3.94920 × 10^{-112}] $g^3·cm^6$

Enthalpy of Formation

The temperature dependence of the equilibrium constants (1293–1434 K) for the reaction $(NaBr)_2(g) = 2NaBr(g)$ has been studied by Datz *et al.*[1] The dissociation energy ($\Delta_r E°$(1300 K) was evaluated to be 42.9 ± 1.3 $kcal·mol^{-1}$. The vapor mixture contains 37 to 17% of dimers in the temperature range of 1293 to 1434 K. Hence the vapor pressure data on NaBr(g) reported by the previous investigators were reexamined. In other words, the reported vapor pressures of NaBr(g) is the sum of the partial pressures of both the monomer (NaBr) and the dimer (Na_2Br_2). The partial pressures of Na_2Br_2(g) thus obtained were used to evaluate the enthaply of vaporization by both the 2nd and 3rd law methods. The values of $\Delta_f H°(Na_2Br_2, g, 298.15\ K)$ were then calculated. The results are as follows.

Source	Reaction	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°$(298.15 K)* kcal·mol^{-1}
Niwa[2]	$2NaBr(cr) \rightarrow Na_2Br_2(g)$	54.84	56.51	−117.08
Cogin and Kimball[3]	$2NaBr(cr) \rightarrow Na_2Br_2(g)$	56.69	56.80	−116.01
Mayer and Wintner[4]	$2NaBr(cr) \rightarrow Na_2Br_2(g)$	68.78	57.13	−115.63**
Ruff and Mugdan[5]	$2NaBr(l) \rightarrow Na_2Br_2(g)$	46.71	45.70	−116.00
Wartenberg and Albrecht[6]	$2NaBr(l) \rightarrow Na_2Br_2(g)$	46.77	45.64	−116.00
Bloom *et al.*[7]	$2NaBr(l) \rightarrow Na_2Br_2(g)$	51.17	45.49	−116.72**

*Based on the average of the 2nd and 3rd law values.
**Only the third law value being used.

The value of $\Delta_f H°(Na_2Br_2, g, 298.15\ K) = -116.24\ kcal·mol^{-1}$ (−486.348 $kJ·mol^{-1}$) adopted is the average of the six $\Delta_f H°(298.15\ K)$ values listed in the above table.

Heat Capacity and Entropy

Bond distance and angles were calculated based on the related data reported by Berkowitz.[8] The vibrational frequencies were calculated by Berkowitz,[9] from an assumed model. The ground state quantum weight was estimated. The principal moments of inertia are $I_A = 19.4713 \times 10^{-39}$, $I_B = 133.0124 \times 10^{-39}$, and $I_C = 152.4836 \times 10^{-39}$ $g·cm^2$.

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
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−19.383	−468.328	−468.328	INFINITE
100	63.244	268.362	417.381	−14.902	−469.320	−486.008	253.865
200	76.762	317.552	356.196	−7.729	−471.959	−501.707	131.032
250	78.921	334.937	350.262	−3.831	−473.526	−508.967	106.343
298.15	80.121	348.949	348.949	0.	−486.348	−514.324	90.108
300	80.157	349 445	348.950	0.148	−486.444	−514.498	89.582
350	80.925	361.863	349.929	4.177	−517.971	−517.428	77.222
400	81.432	372.704	352.113	8.236	−524.079	−516.883	67.498
450	81.785	382.317	354 945	12.317	−524.965	−515.930	59.888
500	82.039	390.948	358.121	16.413	−525.797	−514.881	53.789
600	82.373	405.937	364.879	24.635	−527.326	−512.551	44.622
700	82.576	418.652	371.675	32.884	−528.721	−509.977	38.055
800	82.708	429.687	378.252	41.148	−530.027	−507.210	33.117
900	82.799	439.435	384.519	49.424	−531.290	−504.281	29.268
1000	82.865	448.162	390.455	57.707	−532.555	−501.213	26.181
1100	82.913	456.062	396.066	65.996	−533.866	−498.016	23.649
1200	82.950	463.278	401.370	74.289	−728.786	−489.816	21.321
1300	82.978	469.919	406.391	82.586	−728.447	−469.916	18.881
1400	83.001	476.069	411.151	90.885	−728.114	−450.041	16.791
1500	83.020	481.796	415.672	99.186	−727.790	−430.190	14.981
1600	83.035	487.155	419.974	107.489	−727.473	−410.361	13.397
1700	83.047	492.189	424.076	115.793	−727.168	−390.550	12.000
1800	83.058	496.936	427.993	124.098	−726.875	−370.758	10.759
1900	83.066	501.427	431 741	132.404	−726.596	−350.981	9.649
2000	83.074	505.688	435.332	140.711	−726.335	−331.219	8.651
2100	83.081	509.741	438.780	149.019	−726.093	−311 469	7 747
2200	83.086	513.607	442.094	157.327	−725.873	−291.730	6.927
2300	83.091	517.300	445.284	165.636	−725.679	−272.001	6.177
2400	83.095	520.836	448.359	173.946	−725.511	−252.280	5.491
2500	83.099	524.229	451.326	182.255	−725.372	−232.565	4.859
2600	83.103	527.488	454 193	190.565	−725.265	−212.855	4.276
2700	83.106	530.624	456.967	198.876	−725.190	−193.148	3.737
2800	83.108	533.647	459.651	207.187	−725.150	−173.444	3.236
2900	83.111	536.563	462.254	215.498	−725.145	−153.740	2.769
3000	83.113	539.381	464.778	223.809	−725.176	−134.036	2.334
3100	83.115	542.106	467.229	232.120	−725.246	−114.330	1.926
3200	83.117	544.745	469.610	240.432	−725.353	−94.622	1.545
3300	83.118	547.302	471.926	248.743	−725.499	−74.909	1.186
3400	83.120	549.784	474.179	257.055	−725.685	−55.192	0.848
3500	83 121	552.193	476.374	265.367	−725.912	−35.468	0.529
3600	83.122	554.535	478.513	273.680	−726.182	−15.737	0.228
3700	83.124	556.812	480.598	281.992	−726.495	4.001	−0.056
3800	83.125	559.029	482.633	290.304	−726.855	23.749	−0.326
3900	83.126	561.188	484.620	298.617	−727.262	43.507	−0.583
4000	83.127	563.293	486.561	306.929	−727.719	63.276	−0.826
4100	83.127	565.346	488.457	315.242	−728.229	83.057	−1.058
4200	83.128	567.349	490.312	323.555	−728.791	102.851	−1.279
4300	83.129	569.305	492.126	331.868	−729.417	122.659	−1.490
4400	83.130	571.216	493.902	340.181	−730.022	142.476	−1.691
4500	83.130	573.084	495.641	348.494	−730.734	162.312	−1.884
4600	83.131	574.911	497.344	356.807	−731.527	182.166	−2.069
4700	83.131	576.699	499.014	365.120	−732.391	202.038	−2.245
4800	83.132	578.449	500.651	373.433	−733.329	221.929	−2.415
4900	83.132	580.163	502.256	381.746	−734.347	241.841	−2.578
5000	83.133	581.843	503.831	390.059	−735.434	261.773	−2.735
5100	83.133	583.489	505.377	398.373	−736.621	281.729	−2.885
5200	83.134	585.103	506.895	406.686	−737.902	301.708	−3.031
5300	83.134	586.687	508.385	415.000	−739.282	321.714	−3.171
5400	83.134	588.241	509.850	423.313	−740.764	341.747	−3.306
5500	83.135	589.766	511.289	431.626	−742.356	361.808	−3.436
5600	83.135	591.264	512.704	439.940	−744.060	381.899	−3.562
5700	83.135	592.736	514 095	448.253	−745.882	402.021	−3.684
5800	83.136	594.182	515.463	456.567	−747.827	422.176	−3.802
5900	83.136	595.603	516.809	464 881	−749.899	442.366	−3.916
6000	83.136	597.000	518.134	473.194	−751.786	462.556	−4.027

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

$\Delta_{at}H°(0\ K) = 358 \pm 5\ kJ·mol^{-1}$
$S°(298.15\ K) = 290.8 \pm 2\ J·K^{-1}·mol^{-1}$

$\Delta_fH°(0\ K) = 124\ 1 \pm 3.5\ kJ·mol^{-1}$
$\Delta_fH°(298.15\ K) = 107.6 \pm 3.5\ kJ·mol^{-1}$

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

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
526.1 (1)
180 (1)
623.4 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Br–O = 1.8429 Å
Bond Angle: Br–O–Br = 112.24°
Product of the Moments of Inertia. $I_AI_BI_C = 10238.8084 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

Thorn *et al.*[3] using experimental results from photoionization efficiency spectrum of Br_2O, along with the ionization and appearance energy, have derived a value of the enthalpy of formation $\Delta_fH(Br_2O, 0\ K) = 124.1 \pm 3.5\ kJ·mol^{-1}$, which we adopt.

There are three other related studies leading to an enthalpy of formation. Orlando and Burkholder[1] measured the equilibrium constant for the reaction: $Br_2O + H_2O = 2HOBr$. They determined $\Delta_rG°(298\ K) = 9.70\ kJ·mol^{-1}$. Using the thermal functions presented in this table and thermal functions for HOBr(g) given by JANAF,[2] we calculate $\Delta_fH°(Br_2O,g, 298.15) = 107.6 \pm 3.5\ kJ·mol^{-1}$. This value supports our adopted value. Assuming that the values $D_0°(ClO)$ and $\Delta_{at}H°(OClO,g)$ are reasonable, we would anticipate the ratio of the numbers (1.52) to apply for a similar relationship between BrO(g) and BrOBr(g). This would yield a value of 114 $kJ·mol^{-1}$ which is in good agreement with our adopted value. Using the estimation scheme of Novak[4] (in part based on ab initio calculations and an extended basis set), the enthalpy of formation was calculated to be $83 \pm 8\ kJ·mol^{-1}$ at 0 K.

Heat Capacity and Entropy

Mueller and Cohen,[5] from the microwave spectra of three isotopomers of BrOBr(g), have determined $r_o = 1.8429$ Å and ∠(BrOBr) = 112.24°, which we adopt. Supporting evidence was derived from bromine K-edge EXAFS study of Levason *et al.*[6] The structure of this molecule was bent with a Br–O–Br angle of 112 ± 2° and the Br–O bond length was 1.85 ± 0.01 Å. The bond angle is in good agreement with the value derived from matrix IR studies[7] where a value of 113° was estimated from isotope shifts. In comparison, Novak,[4] with the aid of ab initio calculations, determined a bond length of 1 809 Å and a bond angle of 115.7° The principal moments of inertia (in $g·cm^2$) are. $I_A = 2.5488 \times 10^{-39}$, $I_B = 62.1189 \times 10^{-39}$, and $I_C = 64.6677 \times 10^{-39}$.

The recommended vibrational frequencies (ν_1, ν_3) are those suggested by Jacox.[8] These results are based on the infrared spectra of the argon matrix isolated radical as studied by Tevault *et al.*,[9] Allen *et al.*,[7] and Levason *et al.*[6] A value of $\nu_2 = 197\ cm^{-1}$ reported in the solid IR spectra study of Campbell *et al.*[10] However, the Mueller and Cohen[5] study implied $\nu_2 = 180\ cm^{-1}$ (± 5). Lee,[11] using ab initio calculations – CCSD(T)–derived vibrational frequencies (513, 180 and 613 cm^{-1}) which are in reasonable agreement with our adopted values. Similar calculations by Lee yielded a structure in agreement with our recommendations (112.9° and 1.865 Å).

All specific studies (condensed or matrix)[5-12] yielded values for ν_1 and ν_3 which are in reasonable agreement. Although Tevault *et al.*[9] stated that the values for ν_1 and ν_3 reported by Campbell *et al.*[10] are reversed, this does not affect the thermal functions.

Anthar and Dostrovsky[13] measured the ultraviolet absorption spectra of Br_2O in CCl_4. A strong absorption band was observed at 2800 Å (35714 cm^{-1}). We assume this refers to the position of the first excited electronic state. This state is not included in the calculations.

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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	.000	.000	INFINITE	−12.399	124 100	124.100	INFINITE
50	34.529	217.773	432.252	−10.724	124.219	118.511	−123.808
100	38.480	242.978	331.921	−8.894	123.359	113.112	−59.083
150	41.918	259.228	305.126	−6.885	122.314	108.209	−37.682
200	45.264	271.753	295.272	−4.704	121.193	103.675	−27.077
250	48.075	282.168	291.638	−2.367	119.985	99.433	−20.775
298.15	50.168	290.823	290.823	.000	107.648	96.902	−16.977
300	50.238	291.133	290.824	.093	107.574	96.835	−16.861
400	53.068	306.013	292.833	5.272	76.787	99.594	−13.006
500	54.685	318.044	296.711	10.667	76.961	105.277	−10.998
600	55.664	328.108	301.128	16.188	77.183	110.920	−9.656
700	56.293	336.739	305.614	21.788	77.417	116.524	−8.695
800	56.717	344.285	309.986	27.440	77.648	122.095	−7.972
900	57.016	350.984	314.176	33.127	77.869	127.637	−7.408
1000	57.234	357.003	318 163	38.840	78.077	133.156	−6.955
1100	57.397	362.466	321.946	44.572	78.271	138.654	−6.584
1200	57.523	367.466	325.534	50.318	78.451	144.135	−6.274
1300	57.621	372.074	328.939	56.076	78.616	149.602	−6 011
1400	57.700	376.347	332.174	61.842	78.766	155.057	−5.785
1500	57.763	380.330	335.254	67.615	78.900	160.501	−5.589
1600	57.816	384.060	338.189	73.394	79.016	165.938	−5.417
1700	57.859	387.566	340.991	79.178	79.113	171.367	−5.265
1800	57.896	390.875	343.671	84.966	79.189	176.791	−5 130
1900	57.927	394.006	346.239	90.757	79.242	182.212	−5.009
2000	57.953	396 978	348.702	96.551	79.269	187.631	−4.900
2100	57.976	399.806	351.069	102.347	79.269	193.049	−4.802
2200	57.996	402.503	353.346	108.146	79.239	198.468	−4.712
2300	58.014	405.082	355.540	113.947	79.179	203.889	−4 630
2400	58.029	407.551	357.656	119.749	79.087	209.313	−4.556
2500	58.042	409.920	359.699	125.552	78.963	214.741	−4 487
2600	58.054	412.197	361.675	131.357	78.807	220.175	−4.423
2700	58.065	414.388	363.587	137.163	78.618	225.616	−4.365
2800	58.074	416.500	365.439	142.970	78.400	231.064	−4.311
2900	58.083	418.538	367.235	148.778	78.152	236.521	−4.260
3000	58.091	420.507	368.978	154.587	77.877	241.986	−4.213
3100	58.098	422.412	370.671	160.396	77.577	247.462	−4.170
3200	58.104	424.257	372.317	166.206	77.254	252.947	−4.129
3300	58.110	426.045	373.918	172.017	76.912	258 442	−4.091
3400	58.115	427.780	375 477	177.828	76.554	263.949	−4.055
3500	58.120	429.464	376.996	183.640	76.181	269.465	−4.022
3600	58.125	431.102	378.476	189.452	75.798	274.994	−3.990
3700	58.129	432.694	379.920	195.265	75.407	280.532	−3.960
3800	58.132	434.245	381.329	201.078	75.011	286.081	−3.932
3900	58.136	435.755	382.706	206.891	74.612	291.641	−3.906
4000	58.139	437.227	384.050	212.705	74.214	297.211	−3.881
4100	58.142	438.662	385.365	218.519	73.818	302.791	−3.858
4200	58.145	440.063	386.651	224.334	73.427	308.380	−3.835
4300	58.148	441.432	387.909	230.148	73.042	313.979	−3.814
4400	58.150	442.768	389.140	235.963	72.666	319.586	−3.794
4500	58.152	444.075	390.347	241.778	72.299	325.202	−3.775
4600	58.154	445.353	391.529	247.593	71.944	330.826	−3.757
4700	58.156	446.604	392.687	253.409	71.600	336.458	−3.739
4800	58.158	447.828	393.823	259.225	71.270	342.097	−3.723
4900	58.160	449.028	394.938	265.041	70.953	347.743	−3.707
5000	58.162	450.203	396.031	270.857	70.650	353.395	−3.692
5100	58.163	451.354	397 105	276.673	70.362	359.053	−3.677
5200	58.165	452.484	398.159	282.489	70.088	364.715	−3.664
5300	58.166	453.592	399.194	288.306	69.829	370.384	−3.650
5400	58.167	454.679	400.212	294.123	69.583	376.057	−3.638
5500	58.169	455.746	401.212	299.939	69.352	381.734	−3.625
5600	58.170	456.794	402.195	305.756	69.134	387.416	−3.614
5700	58 171	457.824	403.162	311.573	68.930	393.102	−3.602
5800	58.172	458.836	404.113	317.390	68.738	398.791	−3.591
5900	58.173	459.830	405 049	323.208	68.557	404 482	−3.581
6000	58.174	460.808	405.970	329.025	68.388	410.178	−3.571

PREVIOUS: CURRENT March 1996 (1 bar)

$S°(298.15\ K) = [312.7 \pm 2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [183.7 \pm 20]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [168 \pm 20]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
[$^3A''$]	0.0	[3]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
804 (1)
[150] (1)
236 (1)

Point Group: C_s $\sigma = 1$
Bond Distances: Br–O = [1.69] Å; Br–Br = [2.51] Å
Bond Angle: Br–Br–O = [113.1]°
Product of the Moments of Inertia: $I_A I_B I_C = [13784.9110 \times 10^{-117}]\ g^3 \cdot cm^6$

Enthalpy of Formation

For the four halogen oxide species, XXO(g) where X = F, Cl, Br, I, there is no experimental data related to the enthalpy of formation. Lee[1] determined the enthalpies of formation of many triatomic bromine compounds using a combination of theoretical isomeric, homodesmic and isodesmic reaction energies. The calculated results suggested that BrBrO is less stable than BrOBr by 14.6 kcal·mol^{-1} (61.1 kJ·mol) at 298.15 K.

Heat Capacity and Entropy

Lee,[1] using ab initio calculations–CCSD(T)–derived a bond angle of 113.1° and bond distances r(Br–Br) = 2.510 Å and r(Br–O) = 1.690 Å, which we adopt. The principal moments of inertia (in g·cm^2) are: $I_A = 4.7079 \times 10^{-39}$, $I_B = 51.8084 \times 10^{-39}$, and $I_C = 56.5163 \times 10^{-39}$.

The recommended vibrational frequencies are those suggested by Jacox.[2] These results are based on the infrared spectra of the argon matrix isolated radical as studied by Tevault *et al.*[3] ν_2 is estimated based on comparisons of the vibrational frequencies with ClOO. Lee,[1] using ab initio calculations, derived the vibrational frequencies to be 793, 153 and 215 cm^{-1}. These are in excellent agreement with our recommendations.

Tevault *et al.*[3] observed very intense bands at 804 and 236 cm^{-1} which appeared when Ar–Br_2–O_3 matrices were photolyzed with 632.8 nm light. The assignments for BrBrO were assumed to be $\nu_1 = 804\ cm^{-1}$ (Br–O stretch), $\nu_3 = 236\ cm^{-1}$ (Br–Br stretch) and the ν_2 value (the bending mode) was expected to be below 200 cm^{-1}.

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	−13.138	183.713	183.713	INFINITE
50	35.814	234.286	463.229	−11.447	183.848	177.315	−185.239
100	42.429	261.298	356.090	−9.479	183.126	171.047	−89.346
150	46.014	279.255	327.647	−7.259	182.292	165.183	−57.522
200	48.247	292.815	317.312	−4.899	181.349	159.619	−41.688
250	49.997	303.775	313.543	−2.442	180.262	154.309	−32.241
298.15	51.385	312.704	312.704	.000	168.000	150.730	−26.407
300	51.433	313.022	312.705	.095	167.928	150.623	−26.226
400	53.530	328.128	314.750	5.351	137.218	151.179	−19.742
500	54.868	340.228	318.676	10.776	137.422	154.646	−16.156
600	55.735	350.313	323.132	16.309	137.656	158.069	−13.761
700	56.316	358.951	327.647	21.913	137.895	161.453	−12.048
800	56.719	366.499	332.041	27.566	138.127	164.802	−10.760
900	57.008	373.197	336.249	33.253	138.347	168.123	−9.758
1000	57.222	379.215	340.250	38.965	138.554	171.420	−8.954
1100	57.384	384.677	344.044	44.696	138.747	174.698	−8.296
1200	57.509	389.676	347.642	50.441	138.925	177.958	−7.746
1300	57.608	394.283	351.054	56.197	139.089	181.204	−7.281
1400	57.687	398.555	354.297	61.962	139.238	184.438	−6.881
1500	57.752	402.537	357.381	67.734	139.371	187.662	−6.535
1600	57.805	406.266	360.321	73.512	139.486	190.877	−6.231
1700	57.849	409.772	363.128	79.295	139.582	194.086	−5.964
1800	57.887	413.080	365.812	85.081	139.657	197.290	−5.725
1900	57.918	416.210	368.383	90.872	139.708	200.490	−5.512
2000	57.946	419.182	370.849	96.665	139.735	203.689	−5.320
2100	57.969	422.010	373.219	102.461	139.734	206.886	−5.146
2200	57.989	424.707	375.498	108.259	139.704	210.085	−4.988
2300	58.007	427.285	377.694	114.059	139.643	213.285	−4.844
2400	58.023	429.754	379.812	119.860	139.550	216.488	−4.712
2500	58.037	432.123	381.858	125.663	139.426	219.697	−4.590
2600	58.049	434.400	383.835	131.467	139.269	222.910	−4.478
2700	58.060	436.591	385.749	137.273	139.080	226.131	−4.375
2800	58.070	438.702	387.602	143.079	138.861	229.359	−4.279
2900	58.079	440.740	389.400	148.887	138.613	232.595	−4.189
3000	58.087	442.709	391.144	154.695	138.337	235.841	−4.106
3100	58.094	444.614	392.838	160.504	138.037	239.096	−4.029
3200	58.101	446.459	394.485	166.314	137.714	242.361	−3.956
3300	58.107	448.246	396.088	172.124	137.372	245.636	−3.888
3400	58.112	449.981	397.647	177.935	137.013	248.922	−3.824
3500	58.117	451.666	399.167	183.747	136.640	252.219	−3.764
3600	58.122	453.303	400.648	189.559	136.256	255.527	−3.708
3700	58.126	454.896	402.093	195.371	135.865	258.845	−3.654
3800	58.130	456.446	403.503	201.184	135.469	262.175	−3.604
3900	58.134	457.956	404.880	206.997	135.070	265.514	−3.556
4000	58.137	459.428	406.225	212.811	134.671	268.864	−3.511
4100	58.140	460.863	407.540	218.624	134.275	272.224	−3.468
4200	58.143	462.264	408.827	224.438	133.884	275.593	−3.427
4300	58.146	463.632	410.085	230.253	133.499	278.972	−3.389
4400	58.148	464.969	411.318	236.068	133.122	282.359	−3.352
4500	58.150	466.276	412.524	241.883	132.756	285.755	−3.317
4600	58.153	467.554	413.707	247.698	132.400	289.158	−3.283
4700	58.155	468.805	414.866	253.513	132.056	292.570	−3.252
4800	58.157	470.029	416.002	259.329	131.726	295.989	−3.221
4900	58.158	471.228	417.117	265.144	131.409	299.415	−3.192
5000	58.160	472.403	418.211	270.960	131.106	302.846	−3.164
5100	58.162	473.555	419.285	276.776	130.817	306.284	−3.137
5200	58.163	474.684	420.340	282.593	130.543	309.727	−3.111
5300	58.165	475.792	421.376	288.409	130.284	313.176	−3.087
5400	58.166	476.880	422.393	294.226	130.038	316.629	−3.063
5500	58.167	477.947	423.394	300.042	129.807	320.086	−3.040
5600	58.168	478.995	424.377	305.859	129.589	323.548	−3.018
5700	58.170	480.025	425.345	311.676	129.384	327.013	−2.997
5800	58.171	481.036	426.296	317.493	129.192	330.482	−2.976
5900	58.172	482.031	427.232	323.310	129.012	333.954	−2.957
6000	58.173	483.008	428.154	329.127	128.842	337.429	−2.938

PREVIOUS: CURRENT: March 1996 (1 bar)

$S°(298.15\ K) = 161.13 \pm 2.1\ J·K^{-1}·mol^{-1}$
$T_{fus} = 644 \pm 5\ K$

$\Delta_f H°(0\ K) = -265.2 \pm 2.5\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -277.4 \pm 2.5\ kJ·mol^{-1}$
$\Delta_{fus} H° = 16.443 \pm 0.8\ kJ·mol^{-1}$

Enthaply of Formation

$\Delta_f H°(PbBr_2, cr, 298.15\ K) = -66.3 \pm 0.6\ kcal·mol^{-1}$ ($-277.399\ kJ·mol^{-1}$) is the rounded average of $-66.350\ kcal·mol^{-1}$ calorimetrically determined by Braune and Koref[1] at about 293.15 K and five other values obtained from a 2nd and 3rd law analysis of electromotive force data.[2,3,4] The auxiliary value $\Delta_f H°(AgBr, cr, 298.15\ K) = -23.99\ kcal·mol^{-1}$ [5] is used in the analysis.

Source	Reaction*	Data Points	T/K	$\Delta_f H°$(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} 2nd law	3rd law
Krahmer[2]	A	5	273–292	17.88 ± 0.06	18.52 ± 0.04	−2.2 ± 0.2	−65.86	−66.50
Cann and Sumner[3]	A	1	298		18.57			−66.57
Jahn–Held and Jellinek[4]	B	3	288–308	66.68 ± 0.06	66.09 ± 0.04	2.0 ± 0.2	−66.68	−66.09

*Reactions: (A) Pb(cr) + 2 AgBr(cr) = $PbBr_2$(cr) + 2 Ag(cr) (B) Pb(cr) + Br_2(l) = $PbBr_2$(cr)

Heat Capacity and Entropy

$C_p°$ (18.4–297.0 K) has been measured by Latimer and Hoenshel.[6] The enthalpy data of Ehrhardt (273–786 K)[7] and of Goodwin and Kalmus (298–860 K)[8] are discarded because the observed high T_{fus} shows their samples were not pure. (See melting data discussion.) Linsey[16] measured the enthalpy (39 points) of $PbBr_2$ in the range 319–424 K using an ice calorimeter. The heat capacity data of Latimer and Hoenshel[6] is smoothed graphically. The enthalpy data was analyzed by Linsey[16] to yield heat capacity values from 273–644 K. Both sets of heat capacity values are adjusted graphically in the region 200–400 K so as to yield a smooth curve in the vicinity of 298 K. The adjustments are quite small such that the resulting enthalpy at 600 K differs by about 7 cal·mol^{-1} from the smooth enthalpies reported by Linsey.[16] The data of Linsey[16] did not indicate any transitions other than the solid–liquid transition at 644 K.

Latimer and Hoenshel[6] obtained $S°(15.85\ K) = 2.4\ cal·K^{-1}·mol^{-1}$ after allowing for an approach to the T^3 rule. Kelley and King[10] later derived $S°(17.80\ K) = 1.64\ cal·K^{-1}·mol^{-1}$ from the same data; this value is adopted. Combining this with $S°(298.15;17.80) = 36.871\ cal·K^{-1}·mol^{-1}$ derived from the adopted $C_p°$ value gives $S°(298.15\ K) = 38.511 \pm 0.5\ cal·K^{-1}·mol^{-1}$ ($161.128\ J·K^{-1}·mol^{-1}$). A graphical extrapolation and integration of $C_p°$ gives $H°(17.80;0) = 0.0252\ kcal·mol^{-1}$. This value may not be entirely consistent with the adopted $S°(17.80\ K)$ value, but the error involved is undoubtedly small.

Fusion Data

The older reported values of T_{fus} have been summarized by Mellor.[11] Seven determinations fall in the 636–653 K range and four more range from 753 to 772 K. Included in the high melting range are $T_{fus} = 763$ K by Ehrhardt[7] and $T_{fus} = 761$ K by Goodwin and Kalmus.[8] Knowles,[12] suggested that contamination of the $PbBr_2$ by PbO probably caused the high melting temperatures. The enthalpy measurements of Ehrhardt[7] and of Goodwin and Kalmus[8] are therefore judged not to represent $PbBr_2$. More recently, Blanc and Petit[13] have reported $T_{fus} = 640$ K and $\Delta_{fus}H = 4.96\ kcal·mol^{-1}$ from a cryoscopic investigation. A visual polytherm technique was employed by Il'yasov[14] who found $T_{fus} = 649$ K. Cola *et al.*[15] determined $T_{fus} = 644$ K by differential thermal analysis and $\Delta_{fus}H° = 4.41 \pm 0.07\ kcal·mol^{-1}$ by differential scanning calorimetry. The enthalpy study by Linsey[16] gave $T_{fus} = 644$ K and $\Delta_{fus}H° = 3.93\ kcal·mol^{-1}$ ($16.443\ kJ·mol^{-1}$). We adopt these latter two values.

Sublimation Data

$\Delta_{sub}H°(298.15\ K) = 41.35\ kcal·mol^{-1}$ ($173.008\ kJ·mol^{-1}$) is the sum of the heat of fusion, the enthalpy difference of crystal and liquid between the melting point and 298.15 K, and $\Delta_{vap}H°(298.15\ K)$. See 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	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−19.235	−265.247	−265.247	INFINITE
100	68.199	79.592	229.504	−14.991	−265.562	−264.454	138.136
200	76.567	129.902	168.330	−7.686	−265.682	−263.324	68.773
298.15	79.578	161.128	161.128	0.	−277.399	−260.743	45.681
300	79.613	161.620	161.129	0.147	−277.442	−260.640	45.381
400	81.253	184.747	164.272	8.190	−306.608	−248.951	32.510
500	84.684	203.229	170.271	16.479	−304.824	−234.739	24.523
600	88.784	219.026	177.110	25.149	−302.762	−220.910	19.232
700	93.061	233.033	184.116	34.242	−305.230	−206.654	15.421
800	97.341	245.739	191.037	43.762	−302.480	−192.754	12.586
900	101.621	257.451	197.774	53.710	−299.281	−179.226	10.402
1000	105.901	268.380	204.294	64.086	−295.634	−166 078	8.675

PREVIOUS: March 1962 CURRENT: December 1973

$S°(298.15\ K) = [173.878]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 644 \pm 5\ K$

$\Delta_f H°(298.15\ K) = [-267\ 412]\ kJ\ mol^{-1}$
$\Delta_{fus} H° = 16.443 \pm 0.8\ kJ·mol^{-1}$

Enthaply of Formationo

$\Delta_f H°(PbBr_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(644\ K)-H°(298.15\ K)$, between the crystal and liquid. $\Delta_f H°(l)$ can also be obtained from a 2nd and 3rd law analysis of emf measurements for the cell reaction $Pb(l) + Br_2(g) = PbBr_2(l)$. Results from three investigations are tabulated below. The auxiliary values, $\Delta_f H°(Pb, l, 298.15\ K) = 1.025$ kcal·mol^{-1} [1] and $\Delta_f H°(Br_2, g, 298.15\ K) = 7.387$ kcal·mol^{-1}, are used. The average result or $\Delta_f H°(l, 298\ 15\ K)$ is $-63\ 80$ kcal·mol^{-1}, in good agreement with the adopted value.

Source	Data Points	T/K	$-\Delta_f H°(298.15\ K)$, kcal·mol 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law
Salstrom and Hildebrand[2]	16	711–849	73.60 ± 0.10	72.10 ± 0.13	1.9 ± 0.1	−65.19	−63.69
Lantratov and Shevlyakova[3]	1	862		72.36			−63.95
Bloom and Welch[4]	4	723–1000	74.22 ± 0.33	68.79 ± 1.63	6.3 ± 0.4	−65.80	−60.38

Heat Capacity and Entropy

Ehrhardt[5] and Goodwin and Kalmus[6] have reported enthalpy measurements in the liquid temperature range Their data are rejected because the high melting points observed indicated the samples were not entirely $PbBr_2$. See the $PbBr_2$(cr) table discussion. Bizouard and Paulty[7] have measured 26.3 ± 0.6 cal·K^{-1}·mol^{-1} for the heat capacity of the molten salt. Linsey[9] reported a heat capacity value of 26.8 cal·K^{-1}·mol^{-1} based on enthalpy measurements from T_{fus} to 924 K. This value is adopted and is assumed to represent the heat capacity up to 2000 K. A glass transition is assumed at 400 K below which the heat capacity is that of the crystal.

$S°(PbBr_2, l, 298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Vaporization Data

T_{vap} = 1185 K is calculated as the temperature at which $\Delta_r G° = 0$ for the reaction $PbBr_2(l) = PbBr_2(g)$ at one atm. $\Delta_{vap} H° = 28.23$ kcal·mol^{-1} (118.114 kJ·mol^{-1}) is calculated as the difference between $\Delta_f H°$ at T_{vap} for the gas and the liquid. Bloom and Anthony[8] found an average value of $\Delta_{vap} H° = 29.8 \pm 2.0$ kcal·mol^{-1} from mass spectrometric studies in the 660–735 K range The present table gives $\Delta_{vap} H°(700) = 34.50$ kcal·mol^{-1}.

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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							
100							
200							
298.15	79.580	173.878	173.878	0.	−267.412	−254.558	44.598
300	79.613	174.370	173.879	0.147	−267.455	−254 478	44.309
400	81.254	197.507	177.023	8.194	−296.617	−244 065	31.872
400 000	81.254	197.507	177.023	8 194	GLASS <--> LIQUID		
400.000	112 .131	197.507	177.023	8.194	TRANSITION		
500	112.131	222.528	183.715	19.407	−291.910	−231 474	24.182
600	112.131	242.972	191.939	30.620	−287.305	−219.820	19.137
700	112.131	260.257	200.496	41.833	−287.652	−208.133	15.531
800	112 131	275.230	208.923	53.046	−283.209	−197.076	12.868
900	112.131	288 437	217.038	64.259	−278.745	−186.577	10.829
1000	112.131	300.252	224.779	75.472	−274.261	−176.576	9.223
1100	112.131	310.939	232.134	86.685	−269.755	−167.026	7.931
1200	112.131	320.696	239.113	97.899	−265.228	−157.886	6.873
1300	112.131	329 671	245.739	109.112	−260.686	−149.125	5.992
1400	112.131	337.981	252.034	120.325	−256.145	−140.714	5.250
1500	112.131	345.717	258.025	131.538	−251.615	−132.627	4.618
1600	112.131	352.954	263.734	142.751	−247.104	−124 842	4 076
1700	112.131	359.752	269.184	153.964	−242.617	−117.338	3.605
1800	112 131	366.161	274.396	165.177	−238.159	−110.098	3.195
1900	112.131	372.223	279.386	176.390	−233.735	−103.104	2.835
2000	112.131	377.975	284.173	187.604	−229.347	−96.342	2.516

PREVIOUS: March 1962 CURRENT: December 1973

0	to	644 K	crystal
above		644 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°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−19.235	−265.247	−265.247	INFINITE
100	68.199	79.592	229.504	−14.991	−265.562	−264.454	138.136
200	76.567	129.902	168.330	−7.686	−265.682	−263.324	68.773
298.15	79.578	161.128	161.128	0.	−277.399	−260.743	45.681
300	79.613	161.620	161.129	0.147	−277.442	−260.640	45.381
400	81.253	184.747	164.272	8.190	−306.608	−248.951	32.510
500	84.684	203.229	170.271	16.479	−304.824	−234.739	24.523
600	88.784	219.026	177.110	25.149	−302.762	−220.910	19.232
644.000	90.667	225.375	180.193	29.097	CRYSTAL <--> LIQUID		
644.000	112.131	250.908	180.193	45.540	TRANSITION		
700	112.131	260.257	186.229	51.820	−287.652	−208.133	15.531
800	112.131	275.230	196.439	63.033	−283.209	−197.076	12.868
900	112.131	288.437	205.942	74.246	−278.745	−186.577	10.829
1000	112.131	300.252	214.792	85.459	−274.261	−176.576	9.223
1100	112.131	310.939	223.055	96.672	−269.755	−167.026	7.931
1200	112.131	320.696	230.791	107.885	−265.228	−157.886	6.873
1300	112.131	329.671	238.057	119.098	−260.686	−149.125	5.992
1400	112.131	337.981	244.901	130.312	−256.145	−140.714	5.250
1500	112.131	345.717	251.367	141.525	−251.615	−132.627	4.618
1600	112.131	352.954	257.493	152.738	−247.104	−124.842	4.076
1700	112.131	359.752	263.310	163.951	−242.617	−117.338	3.605
1800	112.131	366.161	268.847	175.164	−238.159	−110.098	3.195
1900	112.131	372.223	274.130	186.377	−233.735	−103.104	2.835
2000	112.131	377.975	279.180	197.590	−229.347	−96.342	2.516

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 339.39 \pm 2.9\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -87.99 \pm 6.3\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -104.39 \pm 6.3\ kJ\cdot mol^{-1}$

Vibrational Freqencies and Degeneracies ν, cm^{-1}
208 (1)
64 (1)
189 (1)

Ground State Quantum Weight : [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distance: Pb–Br = 2.6 ± 0.3 Å
Bond Angle: Br–Pb–Br = [95]°
Product of Moments of Inertia: $I_A I_B I_C = [6.47916 \times 10^{-112}]\ g^3\cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K) = -24.95 \pm 1.5\ kcal\cdot mol^{-1}$ ($-104.391\ kJ\cdot mol^{-1}$) is the sum of $\Delta_f H°$(l, 298.15 K) = $-63.913 \pm 0.8\ kcal\cdot mol^{-1}$ and $\Delta_{vap} H°$(l, 298.15 K) = $39.96\ kcal\cdot mol^{-1}$. The adopted enthaply of vaporization is from the 2nd and 3rd law analyses, tabulated below, of seven sets of liquid vapor pressure measurements, $PbBr_2(l) = PbBr_2(g)$. The overall average for $\Delta_{vap} H°(298.15\ K)$ is $39.23\ kcal\cdot mol^{-1}$. The average value of the 3rd law $\Delta_{vap} H°(298.15\ K)$ is $38.96\ kcal\cdot mol^{-1}$. This is in good agreement with both the 2nd and 3rd law values from the data of Wartenberg and Bosse.[1] The adopted enthalpy of formation for $PbBr_2(g)$ yields an atomization energy of $\Delta_a H° = 5.42$ eV for the process $PbBr_2(g) = Pb(g) + 2\ Br(g)$.

Source	Data Points	T/K	$\Delta_{vap} H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
Wartenberg and Bosse[1]	7*	1008–1191	38.05 ± 0.19	39.02 ± 0.12	0.9 ± 0.2
Volmer[2]	11	684–841	39.36 ± 0.11	38.93 ± 0.08	−0.6 ± 0.1
Greiner and Jellinek[3]	1	1043		38.90	
Jahn–Held and Jellinek[4]	3	1045–1153	41.85 ± 6.54	38.68 ± 0.73	−2.9 ± 5.9
Bloom, *et al.*[5]	Equation	796–1133	39.56 ± 0.48	38.81 ± 0.30	−0.8 ± 0.5
Murgulescu and Marta[6]	1	973		39.13	
Bloom and Hastie[7]	1	973		39.27	

*One point rejected by statistical test.

Heat Capacity and Entropy

Molecular dimensions are those given by Sutton.[8] Beattie and Perry[9] observed the frequencies $\nu_1 = 200\ cm^{-1}$ and $\nu_2 = 64\ cm^{-1}$ in a gas phase Raman study of $PbBr_2$ in the presence of excess bromine; the $PbBr_2$ spectrum was superimposed on the resonance fluorescence spectrum of Br_2. The matrix isolation laser Raman spectroscopic study by Ozin and Vander Voet[10] gave $\nu_1 = 208\ cm^{-1}$ and $\nu_3 = 189\ cm^{-1}$. Experimental conditions prevented observations below 90 cm^{-1} so ν_2 expected about 65 cm^{-1} was not confirmed. The principal moments of inertia are: $I_A = 46.2255 \times 10^{-39}$, $I_B = 97.5131 \times 10^{-39}$, and $I_C = 143.7386 \times 10^{-39}\ g\cdot cm^2$.

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^{-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	−14.989	−87.992	−87.992	INFINITE
100	49.793	280.145	388.803	−10.866	−88.428	−107.375	56.087
200	55.493	316.912	344.558	−5.529	−90.518	−125.561	32.793
250	56.408	329.404	340.321	−2.729	−91.839	−134 174	28.034
298.15	56.918	339.386	339.386	0.	−104.391	−140.883	24.682
300	56.933	339.739	339.388	0.105	−104.475	−141.109	24.569
350	57.259	348.541	340.082	2.961	−135.624	−145.497	21.714
400	57.474	356.202	341.629	5.829	−135.960	−146.885	19.181
450	57.624	362.981	343.632	8.707	−136.320	−148.229	17.206
500	57.732	369.058	345.876	11.591	−136.704	−149.532	15.622
600	57.873	379.597	350.644	17.372	−137.531	−152.022	13.235
700	57.960	388.525	355.434	23.164	−143.300	−153.568	11.459
800	58.016	396.269	360.065	28.963	−144.271	−154.968	10.118
900	58.054	403.104	364.475	34.766	−145.216	−156.248	9.068
1000	58.082	409.222	368.649	40.573	−146.138	−157.425	8.223
1100	58.103	414.759	372.593	46.383	−147.036	−158.509	7.527
1200	58.118	419.816	376.321	52.194	−147.911	−159.514	6.943
1300	58.131	424.468	379.848	58.006	−148.770	−160.446	6.447
1400	58.140	428.776	383.191	63.820	−149.628	−161.312	6.019
1500	58.148	432.788	386.365	69.634	−150.497	−162.116	5.645
1600	58.154	436.541	389.385	75.449	−151.384	−162.862	5.317
1700	58.160	440.067	392.264	81.265	−152.294	−163.551	5.025
1800	58.164	443.391	395.013	87.081	−153.234	−164.187	4.765
1900	58.168	446.536	397.642	92.898	−154.206	−164.769	4.530
2000	58.171	449.520	400.162	98.715	−155.215	−165.299	4.317
2100	58.174	452.358	402.581	104.532	−333.483	−158.662	3.947
2200	58.176	455.064	404.905	110.350	−334.182	−150.321	3.569
2300	58.178	457.650	407.143	116.167	−334.991	−141.946	3.224
2400	58.180	460.126	409.299	121.985	−335.912	−133.534	2.906
2500	58.182	462.501	411.380	127.803	−336.947	−125.080	2.613
2600	58.183	464.783	413.390	133.622	−338.096	−116.584	2.342
2700	58.185	466.979	415.335	139.440	−339.354	−108.040	2.090
2800	58.186	469.095	417.217	145.258	−340.719	−99.449	1.855
2900	58.187	471.137	419.042	151.077	−342.183	−90.806	1.636
3000	58.188	473.110	420.811	156.896	−343.740	−82.112	1.430
3100	58.188	475.018	422.529	162.715	−345.382	−73.364	1.236
3200	58.189	476.865	424.198	168.534	−347.100	−64.562	1.054
3300	58.190	478.656	425.822	174.352	−348.884	−55.705	0.882
3400	58.191	480.393	427 401	180.172	−350.726	−46.793	0.719
3500	58.191	482.080	428.940	185.991	−352.614	−37.827	0.565
3600	58.192	483.719	430.439	191.810	−354.541	−28.806	0.418
3700	58.192	485.313	431.900	197.629	−356.496	−19.730	0.279
3800	58.193	486.865	433.326	203.448	−358.471	−10.603	0.146
3900	58.193	488.377	434.719	209.267	−360.459	−1.422	0.019
4000	58.193	489.850	436.079	215.087	−362.450	7.809	−0.102
4100	58.194	491.287	437.408	220.906	−364.438	17.090	−0.218
4200	58.194	492.689	438.707	226.726	−366.418	26.420	−0.329
4300	58.194	494.059	439.979	232.545	−368.382	35.796	−0.435
4400	58.195	495.397	441.223	238.364	−370.327	45.218	−0.537
4500	58.195	496.705	442.441	244.184	−372.247	54.684	−0.635
4600	58.195	497.984	443.635	250.003	−374.139	64.193	−0.729
4700	58.195	499.235	444.805	255.823	−376.000	73.742	−0.820
4800	58.196	500.460	445.951	261.643	−377.826	83.330	−0.907
4900	58.196	501.660	447.076	267.462	−379.616	92.956	−0.991
5000	58.196	502.836	448.180	273.282	−381.368	102.618	−1.072
5100	58.196	503.988	449.263	279.101	−383.081	112.315	−1.150
5200	58.196	505.119	450.326	284.921	−384.754	122.045	−1.226
5300	58.197	506.227	451.370	290.741	−386.386	131.807	−1.299
5400	58.197	507.315	452.396	296.560	−387.977	141.599	−1.370
5500	58.197	508.383	453 405	302.380	−389.527	151.421	−1.438
5600	58.197	509.431	454.396	308.200	−391.036	161.269	−1.504
5700	58.197	510.461	455.370	314.019	−392.506	171.145	−1.568
5800	58.197	511.474	456.329	319.839	−393.937	181.046	−1.630
5900	58.197	512.468	457.272	325.659	−395.328	190.972	−1.691
6000	58.198	513.447	458.200	331.479	−396.682	200.920	−1.749

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

$S°(298.15\ K) = [305.22 \pm 2.13]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -37.9 \pm 16.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -52.3 \pm 16.7\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ, cm^{-1}	g_i
$[^1A_1]$	0	[1]
$[^3B_1]$	[20000]	[3]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
402 (1)
[120](1)
398.9(1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Si–Br = [2.19] Å
Bond Angle: Br–Si–Br = 109° ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = [4.91229 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The equilibrium reaction Si(cr) + $SiBr_4$(g) = 2 $SiBr_2$(g) was studied by Schafer *et al.*[1] and Wolf and Herbst.[2] Both investigators used a flow technique in an argon atmosphere. A 2nd and 3rd law analysis of their results (reported only in equation form) is summarized below. As in the case of $SiCl_2$,[3] there is acceptable agreement between these two studies. Using the mean $\Delta_f H°$(298.15 K) from the 3rd law results and auxiliary data,[3] we calculate and adopt $\Delta_f H°(298.15\ K) = -12.5\ kcal \cdot mol^{-1}$ (52.300 $kJ \cdot mol^{-1}$) for $SiBr_2$(g).

Source	T/K	$\Delta_f H°$(298.15 K), kcal·mol⁻¹ 2nd law	3rd law	Drift cal·K⁻¹·mol⁻¹
Schafer *et al.*[1]	1320–1475 K	71.61	73.26	1.18
Wolf and Herbst[2]	1200–1550 K	77.33	75.21	−1.54

The adopted enthalpy of formation leads to a $\Delta_{at} H°$ value which implies that the average bond energy is roughly 10% larger in $SiBr_2$(g) than in SiBr(g) or $SiBr_4$(g).[3]

Heat Capacity and Entropy

Maass, Hauge, and Margrave[4] observed the infrared spectra of $SiBr_2$ in nitrogen and argon matrices in the Si–Br stretching region. Attempts to observe the bending fundamental in the region between 90 cm^{-1} and 150 cm^{-1} were unsuccessful. Maass *et al.*[4] measured and assigned υ_1 and υ_3. The bond angle was calculated to be 109 ± 3° from the isotopic splittings due to three silicon isotopes. The authors also assumed $\upsilon_2 = 120\ cm^{-1}$. This bending frequency is consistent with the analogous $SiBr_2$ "bending mode" in $Si_1H_2Br_2$.[3] We adopt the frequencies and bond angles as suggested by Maass *et al.*[4]

We assume the Si–Br bond distance to be the same as that in SiH_2Br_2[3]. By observing the trends in SiF_2 and $SiCl_2$,[3] we assume a $^1A_1$ ground electronic state and a $^3B_1$ excited state at ~20000 cm^{-1}. Additional support for this assignment comes from the luminescense spectrum of a glow discharge in $SiBr_4$ vapors observed by Kuznetsova and Kuzyokov.[5] They states that the complex spectral structure of the 16800–23500 cm^{-1} band could be attributed to the oscillation and deformation of the nonlinear $SiBr_2$ molecule. The inclusion of this triplet electronic state increases the entropy by 0.0004 $cal \cdot K^{-1}\ mol^{-1}$ at 3000K. The principal moments of inertia are: $I_A = 6.4154 \times 10^{-39}$, $I_B = 84.3558 \times 10^{-39}$, and $I_C = 90.7711 \times 10^{-39} g \cdot cm^2$.

References

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[2]E. Wolf and C. Herbst, Z. anorg allg. Chem. **347**, 113 (1966).
[3]JANAF Thermochemical Tables: $SiBr_4$(g), SiBr(g), and SiH_2Br_2(g), 12–31–76; Si(g), 3–31–67; Br(g), 6–30–74, $SiCl_2$(g) and SiF_2(g), 12–31–77
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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	−13.368	−37.941	−37.941	INFINITE
100	41.529	252.970	349.983	−9.701	−37.333	−56.862	29.702
200	49.762	284.529	310.029	−5.100	−38.812	−75.900	19.823
250	52.126	295.906	306.100	−2.549	−39.926	−85.050	17.770
298.15	53.637	305.225	305.225	0.	−52.300	−92.311	16.173
300	53.684	305.557	305.226	0.099	−52.378	−92.559	16.116
350	54.738	313.916	305.884	2.811	−83.351	−97.553	14.559
400	55.473	321.276	307.357	5.568	−83.511	−99.571	13.003
450	56.003	327.843	309.275	8.355	−83.689	−101.568	11.790
500	56.395	333.764	311.433	11.166	−83.882	−103.545	10.817
600	56.923	344.097	316.040	16.834	−84.310	−107.438	9.353
700	57.251	352.898	320.693	22.544	−84.786	−111.255	8.302
800	57.468	360.558	325.208	28.280	−85.311	−115.001	7.509
900	57.619	367.336	329.519	34.035	−85.882	−118.679	6.888
1000	57.728	373.413	333.610	39.803	−86.499	−122.290	6.388
1100	57.809	378.919	337.483	45.580	−87.162	−125.838	5.976
1200	57.871	383.952	341.148	51.364	−87.868	−129.323	5.629
1300	57.919	388.586	344.621	57.154	−88.619	−132.747	5.334
1400	57.958	392.879	347.917	62.947	−89 417	−136.112	5.078
1500	57.989	396.879	351 049	68 745	−90.263	−139.418	4.855
1600	58.014	400.623	354.032	74.545	−91.158	−142.666	4.658
1700	58.036	404.140	356.877	80.348	−142.281	−145.410	4.468
1800	58.054	407.458	359.596	86.152	−143.051	−145.572	4.224
1900	58.070	410.597	362.198	91.958	−143.833	−145.691	4.005
2000	58.084	413.576	364.693	97.766	−144.630	−145.768	3.807
2100	58.098	416.411	367.089	103.575	−145.445	−145.805	3.627
2200	58.111	419.114	369.393	109.385	−146.278	−145.803	3.462
2300	58.125	421.697	371.611	115.197	−147.131	−145.762	3.310
2400	58.140	424.171	373.750	121.010	−148.005	−145.684	3.171
2500	58.157	426.545	375.815	126.825	−148.900	−145.569	3.041
2600	58.178	428.826	377.810	132.642	−149.816	−145.418	2.921
2700	58.202	431.022	379.740	138.461	−150.752	−145.231	2.810
2800	58.230	433.139	381.610	144.283	−151.707	−145.009	2.705
2900	58.264	435.183	383.422	150.107	−152.679	−144.752	2.607
3000	58.304	437.159	385.181	155.936	−153.665	−144.462	2.515
3100	58.351	439.072	386.888	161.768	−154 664	−144.139	2.429
3200	58.405	440.925	388.548	167.606	−155.672	−143.784	2.347
3300	58.466	442.723	390.163	173.449	−156.685	−143.396	2.270
3400	58.536	444 470	391 735	179.299	−157.700	−142.979	2.197
3500	58.614	446.168	393.266	185.157	−158 715	−142.531	2.127
3600	58.701	447.820	394 758	191.023	−543.876	−131.593	1.909
3700	58 797	449.430	396.214	196.897	−544.464	−120.133	1.696
3800	58.901	450 999	397.635	202.782	−545.041	−108.657	1.494
3900	59.014	452.530	399.023	208.678	−545.605	−97.166	1.301
4000	59.136	454.026	400.380	214.585	−546.152	−85.660	1.119
4100	59.266	455.488	401.706	220.505	−546.678	−74.141	0.945
4200	59.405	456.918	403.004	226.439	−547.181	−62.610	0 779
4300	59.551	458.317	404.274	232.387	−547.657	−51.067	0.620
4400	59.704	459.688	405.518	238.349	−548.104	−39.513	0.469
4500	59.864	461.031	406.736	244.328	−548.519	−27 949	0.324
4600	60.031	462.349	407 931	250.322	−548.901	−16.377	0 186
4700	60.203	463.642	409.103	256.334	−549.248	−4.797	0.053
4800	60.380	464.911	410.252	262.363	−549.557	6.791	−0.074
4900	60.562	466.158	411.381	268.410	−549.829	18.384	−0.196
5000	60.749	467.383	412.488	274.476	−550.061	29.983	−0.313
5100	60.938	468.588	413.577	280.560	−550.253	41.586	−0.426
5200	61 131	469.773	414.646	286.663	−550.405	53.192	−0.534
5300	61.325	470.940	415.697	292.786	−550.515	64.801	−0.639
5400	61.522	472.088	416.731	298.929	−550.584	76.412	−0.739
5500	61 719	473.219	417.748	305.091	−550.611	88.023	−0.836
5600	61.917	474.332	418.748	311.272	−550.597	99.634	−0.929
5700	62.114	475.430	419.733	317.474	−550.542	111.245	−1.019
5800	62.311	476.512	420 703	323.695	−550.446	122.854	−1.106
5900	62.507	477.579	421.658	329.936	−550.311	134 462	−1.190
6000	62.702	478.631	422.598	336.197	−550.135	146.067	−1.272

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

$S°(298\ 15\ K) = 143.4 \pm 4.2\ J\ K^{-1}\cdot mol^{-1}$
$T_{trs} = 918\ K$
$T_{fus} = 930\ K$

$\Delta_f H°(O\ K) = -704.96 \pm 1.7\ kJ\cdot mol^{-1}$
$\Delta_f H°(298\ 15\ K) = -717.97 \pm 1.7\ kJ\cdot mol^{-1}$
$\Delta_{trs} H° = 12.217 \pm 0.21\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = 10.125 \pm 0.21\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The selected value for $\Delta_f H°$ is derived from results of solution calorimetric measurements in aqueous acids performed by Ehrlich *et al.*[1] Their results on the enthalpy of solution of Sr(cr) and $SrBr_2$(cr) in HBr 555 H_2O are combined with data for HBr(aq)[2, 3] in a thermochemical cycle to give $\Delta_f H°(SrBr_2, cr, 298.15\ K) = -171.6 \pm 0\ 4\ kcal\cdot mol^{-1}$ ($-717.974 \pm 1.7\ kJ\cdot mol^{-1}$). In the same paper, Ehrlich *et al* [1] reported similar results for three (Ca, Sr, and Ba) of the alkaline earth dichlorides; these results have been the basis for adopted JANAF enthalpies of formation[4] for these dichlorides.

Independent values for $\Delta_f H°$ can be obtained from measurements of the enthalpy of solution of $SrBr_2$(cr) in aqueous solution[5-7] as summarized by Bichowsky and Rossini.[8] Combining these results with $\Delta_f H°(Sr^{+2}, \infty\ aq, 298.15\ K) = -130.45\ kcal\cdot mol^{-1}$ [9] and $\Delta_f H°(Br^-, \infty\ aq, 298.15\ K) = -29.039 \pm 0.036\ kcal\cdot mol^{-1}$,[2] we derive $\Delta_f H°$ values for $SrBr_2$(cr) in $kcal\cdot mol^{-1}$ of -171.5,[5] -172.2,[6] and -171.6.[7] Deviations from our adopted value are at worst only 0.6 $kcal\ mol^{-1}$, and the results of two studies[5,7] provide additional support for the selected value of $\Delta_f H°$. Also, our value for $\Delta_f H°$ is essentially that ($-171\ 5\ kcal\ mol^{-1}$) selected by NBS.[9]

Heat Capacity and Entropy

$C_p°$ data below 300 K are based primarily on the adiabatic calorimetry (60–302 K) of Taylor and Smith.[10] These $C_p°$ data show an unusual leveling off at near 18.0 $cal\cdot K^{-1}\cdot mol^{-1}$ above 245 K. We adopt their $C_p°$ data in the temperature range 60–245 K, values above 245 K are estimated by comparison with similar data for $SrCl_2$ and $BaCl_2$.[4] Our value for $C_p°$ at 298.15 K (18.37 $cal\cdot K^{-1}\cdot mol^{-1}$) is roughly 0.4 $cal\cdot K^{-1}\cdot mol^{-1}$ higher than the measured value of Taylor and Smith.[10] Huttig and Slonim[11] have reported mean heat capacity values over three temperature intervals (85–198, 196–271, and 276–368 K). Their measurements suggest a slightly higher value (18.8 $cal\cdot K^{-1}\cdot mol^{-1}$) for $C_p°$ at 298.15 K than is adopted.

Taylor and Smith[10] reported $S°(298.15\ K) = 32.29\ cal\cdot K^{-1}\ mol^{-1}$ based on $S°(60\ K) = 6.68\ cal\cdot K^{-1}\ mol^{-1}$ obtained from Debye–Einstein functions which represented their $C_p°$ data to only ±1.8 percent from 60 to 100 K. A comparison of their extrapolated $C_p°$ data with those which have been measured for $SrCl_2$, $BaCl_2$, and CaI_2[4] indicates that the values for $SrBr_2$ decrease much more rapidly with temperature below 50 K than would be expected. We have made our own extrapolation to 0 K for $SrBr_2$ by comparison with the measured data for $SrCl_2$ (7.4 to 60 K), $BaCl_2$(6 to 60 K), and CaI (13.1 to 60 K) Our extrapolation gives $S°(60\ K) = 8.7\ cal\cdot K^{-1}\cdot mol^{-1}$, or $S°(298.15\ K) = 34.28\ cal\cdot K^{-1}\cdot mol^{-1}$ (143.438 $J\cdot K^{-1}\cdot mol^{-1}$) based on the adopted $C_p°$ data (60–300 K). Our value for $S°(298.15\ K)$ is consistent with the estimates of 35 $cal\cdot K^{-1}\cdot mol^{-1}$ [12] and 33.8 $cal\cdot K^{-1}\cdot mol^{-1}$,[13] suggesting a possible uncertainty of ±1 $cal\cdot K^{-1}\cdot mol^{-1}$ in the adopted value.

Taylor and Smith[10] measured relative enthalpy data (293–902 K) on a portion of the same sample used for their $C_p°$ measurements. This sample was reported to contain less than 0.1% oxide and was investigated in a Bunsen ice calorimeter. Our analysis of their relative enthalpies by curve fitting techniques reveals the existence of considerable scatter in the data, and no weight is given to their results. The average deviation of 36 points in a Shomate type fit is 2.5%; the maximum deviation is −9.3% at 397 K. Also, these workers[10] were apparently unaware of the transition in $SrBr_2$ at 918 K, since their data set contains only two enthalpy points between 902–927 K. Relative enthalpies have also been measured by Dworkin and Bredig,[14] and the results were reported in graphical form. The short temperature interval (846–902 K) over which these measurements were made for the α phase preclude derivation of accurate heat capacities. Dworkin and Bredig[14] also reported in the same paper enthalpy data for three (Ca, Sr, and Ba) of the alkaline earth dichlorides. A comparison of these enthalpies with those adopted by JANAF[4] indicates that their results are probably reliable to better than ±2%. We adopt their measured value for $H°(918;298.15) = 12.37\ kcal\cdot mol^{-1}$ of the α phase at the transition temperature. $C_p°$ values (300–918 K) are then estimated by comparison with those for $SrCl_2$ and $BaCl_2$.[4] These estimates are made so as to reproduce as closely as possible the adopted enthalpy at 918 K. Our estimated $C_p°$ data give a value of $H°(918;298\ 15) = 12.35\ kcal\cdot mol^{-1}$ which agrees with the measured value of Dworkin and Bredig to within 20 calories. The enthalpies of Taylor and Smith[10] are roughly 2.5% higher than the adopted values at temperatures near the transition. $C_p°$ data for the β phase (918–930 K) are taken from Dworkin and Bredig[14] and extrapolated above the melting point.

TransitionData

Existence of two forms of $SrBr_2$ has been shown by thermal analysis[15-18] and drop calorimetry.[14] Values of T_{trs}reported are 915 K,[15-16] 920 K,[17] 919 K,[18] and 918 K.[14] We adopt the last value which is based on the drop calorimetry of Dworkin and Bredig.[14] Several other investigators[10,19-21] have mistakenly interpreted the transition as due to melting.

$\Delta_{trs} H°$ of 2.92 $kcal\cdot mol^{-1}$ (12.217 $kJ\cdot mol^{-1}$) is derived from the enthalpy data of Dworkin and Bredig.[14]

FusionData

Refer to the liquid table for details.

SublimationData

$\Delta_{sub} H°(298.15\ K)$ is calculated as the difference in the adopted gas and crystal enthalpies of formation at 298.15 K.

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

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
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	−18.064	−704.960	−704.960	INFINITE
100	64.337	64.952	209.316	−14.436	−705.626	−703.931	367.696
200	73.645	113.388	150.374	−7.397	−705.976	−702.127	183.377
298.15	76.853	143.438	143.438	0.	−717.974	−698.755	122.419
300	76.902	143.913	143.439	0 142	−718.022	−698.636	121.643
400	79.036	166.337	146 482	7.942	−747.431	−686.047	89.589
500	80.835	184.166	152.295	15.935	−745.957	−670.871	70.085
600	82.676	199.060	158.881	24.107	−744.434	−655.995	57.109
700	84.893	211.966	165.563	32.482	−742.832	−641.381	47.860
800	87.571	223 468	172.094	41.099	−741.107	−627.004	40.939
900	91.002	233.971	178.394	50.020	−739.825	−612 781	35.565
918.000	91.717	235.781	179.501	51.664	ALPHA <--> BETA		
918.000	115.060	249.098	179.501	63.890	TRANSITION		
930.000	115.060	250.593	180.409	65.271	---- BETA <--> LIQUID ----		
1000	115.060	258.943	185.617	73.325	−723.327	−599.967	31.339
1100	115.060	269 909	192.790	84.831	−726.540	−587.492	27 898
1200	115.060	279.920	199.640	96.337	−722.773	−575.018	25.030
1300	115.060	289.130	206.174	107.843	−719.013	−562.857	22.616
1400	115.060	297.657	212.408	119.349	−715.263	−550.986	20.558
1500	115.060	305.595	218.359	130.855	−711.522	−539.383	18.783

PREVIOUS: CURRENT. June 1974

Continued on page 548

$S°(298.15\ K)$ = [154.843] $J·K^{-1}·mol^{-1}$
T_{fus} = 930 K

$\Delta_f H°(298.15\ K)$ = [−705.098] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 10.125 ± 0.21 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(SrBr_2, l)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(930\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ for the liquid in the temperature range 600–3000 K is assumed constant at 27.818 $cal·K^{-1}·mol^{-1}$. This value is based on JANAF curve fits (deviations ±0.1%) of the relative enthalpies (931–1002 K) reported by Dworkin and Bredig.[1] Taylor and Smith[2] have also reported enthalpies (927–1118 K) for the liquid. These results suggest a somewhat higher value (28.36 $cal·K^{-1}·mol^{-1}$) for $C_p°$; however, the data are considered less reliable. (See $SrBr_2$(cr) table for further discussion). The average deviation of the data of Taylor and Smith[2] from our adopted enthalpies is ±0.4%; the maximum deviation is 1.2% at 1067 K. A glass transition is assumed at 600 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 observed by Dworkin and Bredig[1] from drop calorimetry. Other reported values for T_{fus} are 926 K,[3] 931 K,[4] 924 K,[5] and 928 K.[6] Four other investigators[2, 7–10] have reported values of T_{fus} near 916 K, but they have mistakenly interpreted the transition in $SrBr_2$ as that due to melting.

$\Delta_{fus}H°$ is calculated as the difference in the enthalpies of the liquid and β phase at T_{fus}. The enthalpy of the liquid at T_{fus} is based on JANAF curve fits of the enthalpy data reported by Dworkin and Bredig.[1] We adopted their measured value of 15.6 $kcal·mol^{-1}$ for $H°(930; 298.15)$ of the β phase at T_{fus}. A cryoscopic[4] determination of $\Delta_{fus}H°$ gave 2.6 ± 1.3 $kcal·mol^{-1}$which agrees well with the adopted calorimetric value. Taylor and Smith[2] reported a calorimetric value of $\Delta_{fus}H°$ = 5.25 $kcal·mol^{-1}$; however, this value also includes the heat of transition. Addition of our values for $\Delta_{trs}H°$ and $\Delta_{vap}H°$ gives 5.34 $kcal·mol^{-1}$.

Vaporization Data

T_{vap} is the temperature at which $\Delta_r G°$ for the process $SrBr_2(l) = SrBr_2(g)$ approaches zero. $\Delta_{vap}H°$ is the difference in the heats of formation of the gas and liquid at T_{vap}. Peterson and Hutchinson[10] obtained T_{vap} = 2318 K from vapor pressure measurements on the liquid (1114–1304 K). However, the value is based on a rather long extrapolation and is probably uncertain to at least ±100 K.

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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							
100							
200							
298.15	76.852	154.843	154.843	0.	−705.098	−689.280	120.759
300	76.902	155.319	154.845	0.142	−705.146	−689.181	119.997
400	79.036	177.742	157.888	7.942	−734.555	−677.733	88.503
500	80.835	195.571	163.701	15.935	−733.082	−663.697	69.336
600	82.678	210.471	170.287	24.110	−731.556	−649.963	56.584
600.000	82.678	210.471	170.287	24.110	GLASS <-- -> LIQUID TRANSITION		
600.000	116.391	210.471	170.287	24.110			
700	116.391	228.413	177.342	35.749	−726.689	−636.751	47.515
800	116.391	243.955	184.719	47.388	−721.942	−624.228	40.758
900	116.391	257.664	192.077	59.027	−717.941	−612.220	35.532
1000	116.391	269.926	199.260	70.667	−713.110	−600.733	31.379
1100	116.391	281.020	206.196	82.306	−716.190	−589.363	27.987
1200	116.391	291.147	212.860	93.945	−712.289	−578.006	25.160
1300	116.391	300.463	219.245	105.584	−708.397	−566.974	22.781
1400	116.391	309.089	225.358	117.223	−704.513	−556.241	20.754
1500	116.391	317.119	231.211	128.862	−700.640	−545.785	19.006
1600	116.391	324.630	236.817	140.501	−696.776	−535.587	17.485
1700	116.391	331.687	242.193	152.140	−829.838	−524.451	16.114
1800	116.391	338.339	247.351	163.779	−824.139	−506.652	14.703
1900	116.391	344.632	252.307	175.418	−818.460	−489.169	13.448
2000	116.391	350.602	257.074	187.057	−812.806	−471.984	12.327
2100	116.391	356.281	261.664	198.696	−807.183	−455.081	11.320
2200	116.391	361.695	266.089	210.335	−801.596	−438.446	10.410
2300	116.391	366.869	270.359	221.974	−796.053	−422.063	9.585
2400	116.391	371.823	274.484	233.613	−790.561	−405.921	8.835
2500	116.391	376.574	278.473	245.252	−785.127	−390.006	8.149
2600	116.391	381.139	282.335	256.891	−779.761	−374.307	7.520
2700	116.391	385.532	286.076	268.530	−774.471	−358.813	6.942
2800	116.391	389.764	289.704	280.169	−769.265	−343.514	6.408
2900	116.391	393.849	293.225	291.809	−764.152	−328.399	5.915
3000	116.391	397.795	296.645	303.448	−759.140	−313.459	5.458

PREVIOUS: CURRENT: June 1974

Strontium Bromide ($SrBr_2$) CRYSTAL(I–II)-LIQUID

0	to	918 K	crystal, I
918	to	930 K	crystal, II
above		930 K	liquid

Refer to the individ ual tables for details.

M_r = 247.428 Strontium Bromide ($SrBr_2$) Br_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°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−18.064	−704.960	−704.960	INFINITE
100	64.337	64.952	209.316	−14.436	−705.626	−703.931	367.696
200	73.645	113.388	150.374	−7.397	−705.976	−702.127	183.377
298.15	76.853	143.438	143.438	0.	−717.974	−698.755	122.419
300	76.902	143.913	143.439	0.142	−718.022	−698.636	121.643
400	79.036	166.337	146.482	7.942	−747.431	−686.047	89.589
500	80.835	184.166	152.295	15.935	−745.957	−670.871	70.085
600	82.676	199.060	158.881	24.107	−744.434	−655.995	57.109
700	84.893	211.966	165.563	32.482	−742.832	−641.381	47.860
800	87.571	223.468	172.094	41.099	−741.107	−627.004	40.939
900	91.002	233.971	178.394	50.020	−739.825	−612.781	35.565
918.000	91.717	235.781	179.501	51.664	ALPHA <– –> BETA TRANSITION		
918.000	115.060	249.098	179.501	63.890			
930.000	115.060	250.593	180.409	65.271	BETA <– –> LIQUID TRANSITION		
930.000	116.391	261.480	180.409	75.396			
1000	116.391	269.926	186.383	83.543	−713.108	−600.732	31.379
1100	116.391	281.020	194.490	95.182	−716.189	−589.362	27.986
1200	116.391	291.147	202.129	106.822	−712.288	−578.005	25.160
1300	116.391	300.463	209.340	118.461	−708.396	−566.973	22.781
1400	116.391	309.089	216.160	130.100	−704.512	−556.240	20.754
1500	116.391	317.119	222.626	141.739	−700.639	−545.784	19.006
1600	116.391	324.630	228.769	153.378	−696.775	−535.586	17.485
1700	116.391	331.687	234.618	165.017	−829.837	−524.450	16.114
1800	116.391	338.339	240.197	176.656	−824.138	−506.651	14.703
1900	116.391	344.632	245.530	188.295	−818.459	−489.168	13.448
2000	116.391	350.602	250.635	199.934	−812.805	−471.983	12.327
2100	116.391	356.281	255.532	211.573	−807.182	−455.080	11.320
2200	116.391	361.695	260.235	223.212	−801.595	−438.445	10.410
2300	116.391	366.869	264.760	234.851	−796.052	−422.062	9.585
2400	116.391	371.823	269.118	246.490	−790.560	−405.920	8.835
2500	116.391	376.574	273.322	258.129	−785.126	−390.005	8.149
2600	116.391	381.139	277.382	269.768	−779.760	−374.306	7.520
2700	116.391	385.532	281.307	281.407	−774.470	−358.812	6.942
2800	116.391	389.764	285.105	293.046	−769.264	−343.513	6.408
2900	116.391	393.849	288.785	304.685	−764.151	−328.398	5.915
3000	116.391	397.795	292.353	316.324	−759.139	−313.458	5.458

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K) = [323.4 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -392.1 \pm 12.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -407.1 \pm 12.6\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[157](1)
[37](2)
[263](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Sr–Br = 2.82 ± 0.03 Å
Bond Angle: Br–Sr–Br = 180°
Rotational Constant: $B_0 = 0.013265\ cm^{-1}$

Enthalpy of Formation

Peterson and Hutchison[1,2] have measured vapor pressures (1114–1304 K) for liquid $SrBr_2$ by the Knudsen effusion method. Results of 2nd and 3rd law analysis of these pressures are tabulated below. We assume that the dibromide monomer was the only vapor species present. Mass spectra for some of the other alkaline earth dihalides[3] indicate that the saturated vapor consist predominantly of the metal dihalide monomer which agrees with predictions which were made by Brewer *et al.*[4] for the dihalide molecules. Included in the table is a value for $\Delta_f H°$ derived from a 3rd law analysis of a single vapor pressure point determined by Stock and Heynemann[5] and tabulated by Brewer *et al.*[4]

Source	Reaction[a]	Data Points	T/K	$\Delta_f H°$(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}
1,2	A	13[b]	1147–1304	69.9	71.24 ± 0.86	1.1 ± 2.5	97.3 ± 2.5
4,5	A	1	1040		66.9		101.6

[a]Reaction: (A) SrBr (l) = SrBr (g); [b]Two points rejected due to failure of a statistical test.

The value $\Delta_f H°(SrBr_2, g, 298.15\ K) = -97.3 \pm 3.0\ kcal^{-1} \cdot mol^{-1}$ ($-407.103 \pm 12.6\ kJ \cdot mol^{-1}$) is preferred here rather than an average (−99.5 kcal·mol^{-1}) of the two results, since it is impossible to assess the reliability of the measurement by Stock and Heynemann.[5] However, our value does compare favorably with that (−98.0 kcal·mol^{-1}) selected by NBS.[6]

Heat Capacity and Entropy

The value of the bond length is that measured by Akishin and Spiridonov[7] in a high–temperature electron diffraction study. Electron diffraction patterns[7] for $SrBr_2$ were satisfactorily explained on the basis of a linear model (180° ± 10°). Later studies by Wharton *et al.*,[8] using electric deflection of molecular beams to detect dipole moments, showed no polarity in the $SrBr_2$ molecule, this is most reasonably explained by a linear and centrosymmetric configuration.

Few infrared spectral studies[9–11] have been reported for the gaseous alkaline earth dibromides The antisymmetric stretch (ν_3) and bending (ν_2) frequencies for BeBr ν_2 were observed by Snelson[9] in a neon matrix. Baikov[10] observed a band at 330 ± 5 cm^{-1} in the high–temperature infrared spectra of $CaBr_2$ vapor and assigned this band to ν_3. In a similar study on $MgBr_2$(g) by Randall *et al.*[11] ν_3 was observed at 490 cm^{-1} The only frequencies available for SrBr ν_2 are estimates[4,10,12] which have been obtained by force constant calculations. The adopted vibrational frequencies are derived from force constants estimated by the valence force method.[13] A comparison of values for the ratio of the stretching force constants for diatomic and triatomic strontium fluorides (ratio = 1.33)[3] and chlorides (ratio = 1.15)[3] suggests a value of near unity for the ratio of the bromides. Therefore, the stretching force constant for $SrBr_2$ is taken equal to that for SrBr($k = 1.154 \times 10^5$ dynes/cm).[4] Our values for ν_1 and ν_3 compare favorably with those estimated by a similar procedure[4] (ν_1 = 156 cm and ν_3 = 262 cm^{-1}) and with those given by Krasnov and Svettsov[12] (ν_1 = 158 cm^{-1} and ν_3 = 265 cm^{-1}). The estimated frequencies of Baikov[10] are roughly 12% lower than ours. A comparison of values for the ratio of the stretch to bend force constants for the bent molecules SrF_2(ratio = 50)[3] and $SrCl_2$(ratio = 78)[3] suggests a value near 100 for $SrBr_2$. Brewer[4] used this same value in his force constant calculations. This value for the ratio gives $k\delta/l^2 = 1.154 \times 10^3$ dynes/cm, or ν_2 = 37 cm^{-1}. A comparison of similar data for the linear molecule $BeBr_2$[9] indicates that the value of the ratio could be as low as 41. This leads to a ν_2 = 58 cm^{-1} which is in excellent agreement with the value (56 cm^{-1} recommended by Krasnov and Svettsov.[12] We prefer the lower value of ν_2 at this time but include in the uncertainty ±2.0 cal·K^{-1}·mol^{-1} assigned to the value of $S°$(298.15 K) the possibility that the higher value is the correct one The singlet ground state is assigned by analogy with that for $BaCl_2$.[3] Our adopted functions agree with those tabulated by Brewer *et al.*[4] to within 0.1 cal·K^{-1}·mol^{-1} in the range 298–2000 K.

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	−16.092	−392.118	−392.118	INFINITE
100	53.702	259.975	376.278	−11.630	−391.949	−409.756	214.035
200	59.338	299.377	328.945	−5.914	−393.621	−426.971	111.513
250	60.331	312.735	324.413	−2.920	−394.746	−435.188	90.928
298.15	60.896	323.413	323.413	0.	−407.103	−441.544	77.357
300	60.913	323.790	323.415	0.113	−407.180	−441.757	76.917
350	61.279	333.209	324.158	3.168	−438.128	−445.818	66.535
400	61.523	341.409	325.813	6.239	−438.263	−446.908	58.360
450	61.693	348.666	327.957	9.319	−438.425	−447.979	52.000
500	61.817	355.173	330.358	12.407	−438.614	−449.031	46.910
600	61.979	366.459	335.463	18.598	−439.073	−451.073	39.269
700	62.079	376.021	340.591	24.801	−439.642	−453.029	33.805
800	62.144	384.315	345.550	31.012	−440.323	−454.897	29.702
900	62.188	391.637	350.272	37.229	−441.744	−456.600	26.500
1000	62.220	398.191	354.742	43.449	−442.331	−458.220	23.935
1100	62.244	404.123	358.965	49.673	−450.827	−459.414	21.816
1200	62.262	409.539	362.958	55.898	−452.340	−460.128	20.029
1300	62.276	414.523	366.735	62.125	−453.860	−460.715	18.512
1400	62.288	419.139	370.315	68.353	−455.388	−461.185	17.207
1500	62.297	423.437	373.715	74.583	−456.923	−461.546	16 072
1600	62.304	427.458	376.950	80.813	−458.469	−461.804	15.076
1700	62.310	431.235	380.033	87.043	−596.940	−460.785	14.158
1800	62.315	434.797	382.977	93.275	−596.648	−452.784	13.139
1900	62.320	438.166	385.794	99.506	−596.377	−444.799	12.228
2000	62.323	441.363	388.493	105.739	−596.130	−436.828	11 409
2100	62.327	444.404	391.084	111.971	−595.913	−428.868	10.668
2200	62.329	447.303	393.574	118.204	−595.732	−420.918	9.994
2300	62.332	450.074	395.971	124.437	−595.595	−412.976	9.379
2400	62.334	452.727	398.281	130.670	−595.508	−405.038	8.815
2500	62.336	455.271	400.510	136.904	−595.480	−397.102	8.297
2600	62.338	457.716	402.663	143.137	−595.520	−389.167	7.818
2700	62.339	460.069	404.746	149.371	−595.635	−381.228	7.375
2800	62.340	462.336	406.763	155.605	−595.834	−373.284	6.964
2900	62.342	464.524	408.717	161.839	−596.125	−365.330	6.580
3000	62.343	466.637	410.613	168.074	−596.519	−357.366	6.222
3100	62.344	468.681	412.453	174.308	−597.021	−349.386	5.887
3200	62.345	470.661	414.241	180.542	−597.641	−341.388	5.573
3300	62.345	472.579	415.980	186.777	−598.385	−333.369	5.277
3400	62.346	474.440	417.672	193.011	−599.259	−325.326	4.998
3500	62.347	476.248	419.320	199.246	−600.270	−317.254	4.735
3600	62.347	478.004	420.926	205.481	−601.423	−309.152	4.486
3700	62.348	479.712	422.492	211.715	−602.720	−301.016	4.250
3800	62.348	481.375	424.020	217.950	−604.165	−292.843	4.025
3900	62.349	482.994	425.511	224.185	−605.759	−284.630	3.812
4000	62.349	484.573	426.968	230.420	−607.504	−276.374	3.609
4100	62.350	486 113	428.392	236.655	−609.398	−268.072	3.415
4200	62.350	487.615	429.784	242.890	−611.437	−259.723	3.230
4300	62.351	489.082	431.146	249.125	−613.623	−251.324	3.053
4400	62.351	490.516	432.479	255.360	−615.951	−242.871	2.883
4500	62.351	491.917	433.785	261.595	−618.416	−234.365	2.720
4600	62.352	493.287	435.063	267.830	−620.948	−225.807	2.564
4700	62.352	494.628	436.316	274.066	−623.651	−217.188	2.414
4800	62.352	495.941	437.545	280.301	−626.467	−208.510	2.269
4900	62.352	497.227	438.750	286.536	−629.391	−199 773	2.130
5000	62.353	498.486	439.932	292.771	−632.409	−190.975	1.995
5100	62.353	499.721	441.092	299.006	−635.497	−182.118	1.865
5200	62.353	500.932	442.231	305.242	−638.685	−173.197	1.740
5300	62.353	502.120	443.350	311.477	−641.944	−164.214	1.618
5400	62.353	503.285	444.449	317.712	−645.266	−155.169	1.501
5500	62.353	504.429	445.530	323.948	−648.643	−146.063	1.387
5600	62.354	505.553	446.591	330.183	−652.065	−136.894	1.277
5700	62.354	506.656	447.636	336.418	−655.524	−127.664	1.170
5800	62.354	507.741	448.662	342.654	−659.013	−118.373	1.066
5900	62.354	508.807	449.673	348.889	−662.314	−109.045	0.965
6000	62.354	509.855	450.667	355.125	−665.808	−99.639	0.867

PREVIOUS. June 1974 (1 atm) CURRENT: June 1974 (1 bar)

Continued on page 548

$S°(298.15\ K) = [108.4 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = unknown

$\Delta_f H°(298.15\ K) = -405.43 \pm 20.9\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of $TiBr_2$ crystal is derived from the data of Hall and Blocher[1] for the reaction $2\ TiBr_3(cr) = TiBr_4(g) + TiBr_2(cr)$. 2nd and 3rd law analyses of these data are not useful because of the formation of solid solutions in the above process. Hall and Blocher[1] obtained a value of $\Delta_r H°(800\ K)$ of 31.3 $kcal·mol^{-1}$ for the reaction by integrating the incremental Gibbs energy changes over varying compositions of the solid solutions. The corresponding $\Delta_r H°(298.15\ K)$ and $\Delta_f H°(298.15\ K)$ are calculated as 34.6 $kcal·mol^{-1}$ and −96.9 $kcal·mol^{-1}$ (−405.430 $kJ·mol^{-1}$), respectively, using auxiliary JANAF enthalpy of formation and enthalpy data.

Heat Capacity and Entropy

The heat capacity of $TiBr_2(cr)$ was estimated by Kell.ey[2] The value of $S°(298.15\ K)$ is estimated from that of $TiCl_2(cr)$ and the difference between ionic entropy contribution of Cl^- and Br^-.

Sublimation Data

The enthalpy sublimation of $TiBr_2(cr)$ is taken as the difference in the enthalpies of formation of $TiBr_2(cr)$ and $TiBr_2(g)$ at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta_r G° = 0$ for the reaction $TiBr_2(cr)$ $TiBr_2(g)$. The enthalpy of formation of $TiBr_2(g)$, upon which these quantities depend, is an estimated quantity.

References

[1]E. H. Hall and J. M. Blocher, Jr., J. Phys. Chem. 63, 1525 (1959).
[2]K. K. Kelley, U.S. Bur. Mines Bull. 584, 232 pp. (1960).

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	78.688	108.366	108.366	0	−405 430	−383.188	67.133
300	78.709	108.852	108.367	0 146	−405 471	−383.050	66.695
400	79.856	131.653	111.468	8 074	−434.636	−369.491	48.251
500	81.002	149.595	117.362	16.117	−433.025	−353 391	36.919
600	82.149	164.465	124.008	24.274	−431.412	−337.615	29.392
700	83.295	177.214	130.719	32.546	−429.767	−322.112	24.036
800	84.441	188.412	137.245	40.933	−428.057	−306.849	20.035
900	85.588	198.424	143.496	49.435	−426.311	−291.802	16.936
1000	86 734	207.501	149.450	58.051	−424.590	−276.950	14.466
1100	87.881	215.821	155.110	66.782	−422.957	−262.266	12.454
1200	89.027	223.517	160 494	75.627	−425.398	−247.606	10.778
1300	90.174	230.688	165 621	84.587	−423.219	−232.878	9.357
1400	91.320	237.413	170.511	93.662	−421.013	−218.319	8.146
1500	92.466	243.752	175.185	102.851	−418.793	−203.919	7.101

PREVIOUS. June 1964 CURRENT: June 1968

$S°(298.15\ K) = [308.7 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-164.9 \pm 20.9]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-179.1 \pm 20.9]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequences and Degeneracies ν, cm^{-1}
[160](1)
[105](2)
[333](1)

Ground State Quantum Weight: [3] $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distance: Ti–Br = [2.4] Å
Bond Angle: Br–Ti–Br = [180°]
Rotational Constant: $B_0 = [0.018314]\ cm^{-1}$

Enthalpy of Formation

The enthalpy of formation of $TiBr_2(g)$ is calculated from the estimated Ti–Br bond energy. The bond energy is estimated as being the same as the average Ti–Cl bond energy of $TiCl_2(g)$. This estimate is used because the measured average bond energies of $TiBr_3(g)$ and $TiCl_3(g)$ and those of $TiBr_4(g)$ and $TiCl_4(g)$ are very nearly equal.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiCl_2(g)$, $TiCl_4(g)$ and $TiBr_4(g)$. The vibrational frequencies are estimated from a valence force field model. The force constant k is estimated as 1.2 millidynes $Å^{-1}$, and the constant k_δ/l^2 is assumed to be 0.06 millidynes $Å^{-1}$. These values are derived by a correlation with other dihalides.

The electronic levels are assumed to be the same as $TiCl_2(g)$. The levels of $TiCl_2(g)$ are estimated by assuming that they correspond to the inverted states of $NiCl_2(g)$.[1] The linear configuration is adopted since experimental evidence indicates that other transition metal dihalides are linear.[2–5]

References

[1] C. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966).
[2] R. A. Berg and O. Sinanoglu, J. Chem. Phys. 32, 1082 (1960).
[3] J. T. Hougen, G. E. Leroi and T. C. James, J. Chem. Phys. 34, 1670 (1961).
[4] G. E. Leroi, T. C. James, J. T. Hougen and W. Klemperer, J. Chem. Phys. 36, 2879 (1962).
[5] A. Buchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. 40, 3471 (1964).

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
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−15.127	−164.863	−164.863	INFINITE
100	49.952	247.576	360.164	−11.259	−164.348	−182.895	95.535
200	57.678	285.140	314.116	−5.795	−165.703	−201.001	52.496
250	59.160	298.185	309.669	−2.871	−166.758	−209.710	43.816
298.15	60.026	308.685	308.685	0.	−179.075	−216.558	37.940
300	60.052	309.056	308.686	0.111	−179.151	−216.791	37.747
350	60 624	318.359	309.419	3.129	−210.070	−221.365	33.037
400	61.009	326.481	311.055	6.170	−210.185	−222.971	29.117
450	61.281	333.684	313.177	9.228	−210.326	−224.561	26.066
500	61.479	340.151	315.556	12.297	−210.490	−226.134	23.624
600	61.741	351.385	320.619	18.459	−210.873	−229.228	19.956
700	61.904	360.916	325.712	24.642	−211.317	−232.253	17.331
800	62.016	369.189	330.641	30.839	−211.798	−235.211	15.358
900	62.109	376.499	335.338	37.045	−212.346	−238.106	13.819
1000	62.204	383.048	339.788	43.260	−213.026	−240.933	12.585
1100	62.319	388.982	343.994	49.486	−213.898	−243.684	11.572
1200	62.466	394.410	347.973	55 725	−218.946	−246.226	10.718
1300	62.655	399.417	351.740	61.981	−219.471	−248.478	9.984
1400	62.887	404.069	355.313	68.258	−220.063	−250.688	9.353
1500	63.163	408.417	358.710	74.560	−220 730	−252.853	8.805
1600	63.478	412.503	361.946	80.892	−221.482	−254.970	8.324
1700	63.825	416.362	365.034	87.256	−222.330	−257.038	7.898
1800	64.198	420.020	367.988	93.657	−223.287	−259.052	7.518
1900	64.587	423.502	370.819	100.097	−224.365	−261.010	7.176
2000	64.986	426.825	373.537	106.575	−240.264	−262.455	6.855
2100	65.387	430.005	376.151	113.094	−242.373	−263.512	6.555
2200	65 784	433.056	378.669	119.653	−244 462	−264.470	6.279
2300	66.171	435 989	381.097	126.250	−246.533	−265.333	6.026
2400	66.546	438.813	383.444	132.886	−248.588	−266.106	5.792
2500	66.904	441.537	385.713	139.559	−250.630	−266.794	5.574
2600	67.246	444 168	387 911	146.267	−252.659	−267.401	5.372
2700	67.568	446 712	390.042	153.007	−254.677	−267.929	5.183
2800	67.872	449.175	392.110	159 780	−256.686	−268.384	5.007
2900	68.157	451.561	394.119	166.581	−258.685	−268.766	4.841
3000	68.425	453.876	396.073	173.410	−260.675	−269.080	4.685
3100	68.675	456 124	397.974	180.266	−262.655	−269.327	4.538
3200	68.911	458.308	399.826	187 145	−264.625	−269.511	4.399
3300	69.132	460.432	401.630	194.047	−266.583	−269.633	4.268
3400	69.341	462.499	403.390	200.971	−268.530	−269 696	4.143
3500	69.538	464.512	405 108	207 915	−270.462	−269 703	4.025
3600	69.726	466.474	406.785	214.878	−272.378	−269.654	3.913
3700	69 904	468.387	408 424	221.860	−683.375	−261.763	3.695
3800	70.074	470.253	410.027	228.859	−684.021	−250.360	3.441
3900	70.238	472.075	411.595	235.874	−684.701	−238.939	3.200
4000	70.395	473.856	413.129	242.906	−685.412	−227.500	2.971
4100	70.547	475.596	414 632	249.953	−686 152	−216.044	2.752
4200	70.694	477.298	416.103	257.015	−686.917	−204.568	2.544
4300	70.836	478.963	417.546	264.092	−687.705	−193.075	2.345
4400	70.974	480.593	418.960	271.183	−688.512	−181.562	2.155
4500	71 108	482.189	420.348	278.287	−689.335	−170 031	1 974
4600	71.237	483.754	421.709	285 404	−690.172	−158.482	1.800
4700	71.362	485.287	423.046	292.534	−691.020	−146.915	1.633
4800	71 484	486 791	424.358	299.676	−691.876	−135.329	1.473
4900	71.601	488.266	425.647	306.831	−692.739	−123 725	1.319
5000	71.714	489.713	426.914	313.996	−693.605	−112.104	1.171
5100	71.822	491.135	428.160	321.173	−694.473	−100.465	1.029
5200	71.926	492.530	429.384	328.361	−695.340	−88.810	0.892
5300	72.026	493.901	430.588	335.558	−696.205	−77.137	0.760
5400	72.120	495.249	431.773	342.766	−697.067	−65.448	0.633
5500	72.210	496.573	432.940	349.982	−697.924	−53.744	0.510
5600	72.294	497.875	434.088	357.207	−698.774	−42.024	0.392
5700	72.373	499 155	435.218	364.441	−699.616	−30.289	0.278
5800	72.447	500.414	436.331	371.682	−700.449	−18.539	0.167
5900	72.516	501.653	437.428	378.930	−701.273	−6.775	0 060
6000	72.579	502.873	438.508	386.185	−702.086	5.003	−0.044

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

Zirconium Bromide ($ZrBr_2$) CRYSTAL $M_r = 251.028$

$S°(298.15\ K) = [115.9 \pm 13]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [900]\ K$

$\Delta_f H°(0\ K) =$ Unknown
$\Delta_f H°(298.15\ K) = [-404.6 \pm 42]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [62.760 \pm 42]\ kJ·mol^{-1}$

Enthalpy of Formation

The value of $\Delta_f H°(ZrBr_2, cr, 298.15\ K) = -96.7\ kcal\ mol^{-1}$ $(-404.593\ kJ·mol^{-1})$ is calculated from the estimated $\Delta_{sub} H°(298.15\ K) = 55 \pm 5\ kcal·mol^{-1}$ for $ZrBr_2(cr) \rightarrow ZrBr_2(g)$, using $\Delta_f H°(ZrBr_2, g, 298.15\ K) = -41.7\ kcal·mol^{-1}$.[1] The estimated $\Delta_{sub} H°(298\ 15\ K)$ is obtained as an average of the enthalpies of sublimation at 298°K for $CrBr_2$, $MnBr_2$, $CoBr_2$ and $NiBr_2$ given by Brewer, Somayajulu and Brackett[2] and $TiBr_2$ and $FeBr_2$ listed in JANAF tables.[1]

Heat Capacity and Entropy

The heat capacities of $ZrBr_2(cr)$ are estimated from $TiBr_2(cr)$,[1] based on the assumption $C_p°(ZrBr_2) = C_p°(TiBr_2) + 3/2\ R\ln[A_r\ of\ Zr)/(A_r\ of\ Ti)]$. The entropy, $S°(298.15\ K) = 27.7\ cal·K^{-1}·mol^{-1}$ $(115.897\ J·K^{-1}·mol^{-1})$ is estimated in a similar manner based on $TiCl_2(cr)$[1] and $TiBr_2(cr)$.[1]

Fusion Data

The enthalpy of fusion is roughly estimated, so that the entropy of vaporization is about 20 $cal·K^{-1}\ mol^{-1}$ The melting point was estimated by Brewer.[3]

References

[1]JANAF Thermochemical Tables. $ZrBr_2(g)$, 6–30–70; $TiBr_2(cr)$, $FeBr_2(cr)$, 9–30–66;$TiCl_2(cr)$, 12–31–68.
[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 Book Company, New York, (1949).

Zirconium Bromide ($ZrBr_2$) $Br_2Zr_1(cr)$

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	86.722	115.897	115.897	0.	−404.593	−382.178	66.956
300	86.743	116.433	115.898	0.160	−404.619	−382 039	66.519
400	87.889	141.545	119.315	8.892	−432.927	−368.554	48.128
500	89.036	161.280	125.803	17.738	−430.397	−352.753	36.852
600	90.182	177.614	133.116	26.699	−427.847	−337.464	29.379
700	91.328	191.602	140.495	35 775	−425.276	−322.603	24.073
800	92.475	203.872	147.666	44.965	−422.688	−308.111	20.118
900	93.621	214.830	154.530	54.270	−420.095	−293.945	17.060
900 000	93 621	214.830	154.530	54.270	--- CRYSTAL <--> LIQUID ---		
1000	94.768	224.753	161.064	63.689	−417.506	−280.067	14.629
1100	95 914	233.839	167.273	73.223	−414.926	−266 448	12.653
1200	97 060	242.234	173.174	82.872	−416.071	−252.842	11 006
1300	98.207	250.048	178.791	92.635	−412.977	−239.365	9 618
1400	99.353	257.368	184.145	102.513	−409.819	−226.128	8.437
1500	100.500	264.262	189.258	112.506	−406.609	−213 119	7.421

PREVIOUS: March 1962 CURRENT: June 1970

$S°(298.15\ K) = [184.024]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-342.333]\ kJ·mol^{-1}$
$T_{fus} = [900]\ K$ $\Delta_{fus}H° = [62.760 \pm 42]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(ZrBr_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(900\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is 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

Refer to the crystal table for details.

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change approaches zero for the process $ZrBr_2(l) \rightarrow ZrBr_2(g)$ at one bar. The difference between $\Delta_f H°$ for ZrBr(l) and $ZrBr_2(g)$ at T_{vap} is $\Delta_{vap}H°$.

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	91.002	184.024	184.024	0.	−342.333	−340.230	59.607
300	91.002	184.587	184.026	0.168	−342.351	−340.217	59.237
400	91.002	210.767	187.596	9.269	−370.290	−333.606	43.565
500	91.002	231.074	194.336	18.369	−367.506	−324.760	33.927
600	91.002	247.665	201.884	27.469	−364.817	−316.464	27.551
700	91.002	261.693	209.452	36.569	−362.222	−308.612	23.029
800	91.002	273.845	216.758	45.669	−359.724	−301.125	19.661
900	91.002	284.563	223.708	54.770	−357.335	−293.945	17.060
1000	91.002	294.151	230.282	63.870	−355.065	−287.025	14.993
1100	91.002	302.825	236.488	72.970	−352.919	−280.325	13.312
1200	91.002	310.743	242.351	82.070	−354.613	−273.594	11.909
1300	91.002	318.027	247.896	91.170	−352.182	−266.942	10.726
1400	91.002	324.771	253.149	100.271	−349.802	−260 475	9.718
1500	91.002	331.049	258.136	109.371	−347.484	−254.175	8.851
1600	91.002	336.923	262.878	118.471	−345.240	−248.028	8.097
1700	91.002	342.440	267.398	127.571	−343.081	−242.019	7.436
1800	91.002	347.641	271.713	136.671	−341.020	−236.134	6.852
1900	91.002	352.561	275.839	145.772	−339.070	−230.361	6.333
2000	91.002	357.229	279.793	154.872	−337.242	−224.687	5.868

PREVIOUS: March 1962 CURRENT: June 1970

298.15	to	900 K	crystal
above		900 K	liquid

Refer to the individual tables for details.

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

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
		J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
298.15	86.722	115.897	115.897	0.	−404.593	−382.178	66.956
300	86.743	116.433	115.898	0.160	−404.619	−382.039	66.519
400	87.889	141.545	119.315	8.892	−432.927	−368.554	48.128
500	89.036	161.280	125.803	17.738	−430.397	−352.753	36.852
600	90.182	177.614	133.116	26.699	−427.847	−337 464	29.379
700	91.328	191.602	140.495	35.775	−425.276	−322.603	24.073
800	92.475	203.872	147.666	44.965	−422.688	−308.111	20.118
900	93.621	214.830	154.530	54.270	−420.095	−293.945	17.060
900.000	93.621	214.830	154.530	54.270	____ CRYSTAL <--> LIQUID ____		
900.000	91.002	284.563	154.530	117.030	TRANSITION		
1000	91.002	294.151	168.022	126.130	−355.065	−287.025	14.993
1100	91.002	302.825	179.888	135.230	−352.919	−280.325	13.312
1200	91.002	310.743	190.468	144.330	−354.613	−273.594	11.909
1300	91.002	318.027	200.004	153.430	−352.182	−266.942	10.726
1400	91.002	324.771	208.678	162.531	−349.802	−260.475	9.718
1500	91.002	331.049	216.629	171.631	−347.484	−254.175	8.851
1600	91.002	336.923	223.966	180.731	−345.240	−248.028	8.097
1700	91.002	342.440	230.774	189.831	−343.081	−242.019	7.436
1800	91.002	347.641	237.124	198.931	−341.020	−236.134	6.852
1900	91.002	352.561	243.071	208.032	−339.070	−230.361	6.333
2000	91.002	357.229	248.663	217.132	−337.242	−224.687	5.868

PREVIOUS: CURRENT: June 1970

$S°(298.15\ K) = [316.8 \pm 13]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-160.0 \pm 42]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-174.5 \pm 42]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
[160](1)
[84](2)
[265](1)

Ground State Quantum Weight: [3] σ = [2]
Point Group: [$D_{\infty h}$]
Bond Distance: Zr–Br = [2.47] Å
Bond Angle: Br–Zr–Br = [180]°
Rotational Constant, B_0 = [0.017290] cm^{-1}

Enthalpy of Formation

$\Delta_f H°(ZrBr_2, g, 298.15\ K) = -41.7\ kcal·mol^{-1}(-174.473\ kJ·mol^{-1})$ is derived from the estimated $\Delta_f H°(298.15\ K) = 243.5 \pm 10\ kcal·mol^{-1}$ for $ZrBr_2(g \rightarrow Zr(g) + 2\ Br(g))$. The value of $\Delta_f H°(298.15\ K)$ is twice the average bond dissociation energy, $\Delta_{at}H°(298.15\ K)/2 = 121.75\ kcal·mol^{-1}$, which is calculated from the proportion of the average bond dissociation energies at 298.15 K for $ZrBr_2/TiBr_2 = ZrBr_4/TiBr_4$. The average bond dissociation energies at 298.15 K, $\Delta_{at}H°(ZrBr_4)/4 = 102.2\ kcal·mol^{-1}$, $\Delta_{at}H°(TiBr_4)/4 = 87.9\ kcal·mol^{-1}$, and $\Delta_{at}H°(TiBr_2)/2 = 104.6\ kcal·mol^{-1}$, are all calculated from JANAF $\Delta_f H°(298.15\ K)$ for $ZrBr_4(g)$, $TiBr_4(g)$, $TiBr_2(g)$, Zr(g), Ti(g), and Br(g).

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the transition metal dihalides are generally linear[1–5] even though a few fluorides are bent.[6] The bond distance is assumed to be the same as that in $ZrBr_4(g)$ which was estimated as 2.47 Å by Godnev *et al.*[7]

The vibrational frequencies are calculated from a valence force field model. The stretching force constant is estimated to be 1.2 millidyne $Å^{-1}$ and the bending force constant 0.06 millidyne $Å^{-1}$. These values are derived from force constants of transition metal dihalides listed by Brewer, Somayajulu and Brackett.[8] The electronic levels and quantum weights are estimated to be the same as those of gaseous $TiCl_2$.[9]

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[9] JANAF Thermochemical Tables: $TiCl_2$(g), 12-31-68.

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	−15.564	−160.030	−160.030	INFINITE
100	52.080	254.108	369.245	−11.514	−159.659	−178.280	93.124
200	58.882	292.867	322.284	−5.883	−161.123	−196.402	51.295
250	60.034	306.143	317.773	−2.908	−162.179	−205.105	42.854
298.15	60.685	316.777	316.777	0.	−174.473	−211.951	37.133
300	60.704	317.152	316.778	0.112	−174.547	−212.183	36.944
350	61.125	326.544	317.519	3.159	−205.422	−216.760	32.350
400	61.404	334.725	319.169	6.222	−205.477	−218.376	28.517
450	61.599	341.970	321.308	9.298	−205.547	−219.984	25.535
500	61.741	348.468	323.705	12.381	−205.634	−221.584	23.149
600	61.927	359.742	328.799	18.566	−205.860	−224.754	19.567
700	62.042	369.298	333.920	24.765	−206.166	−227.880	17.005
800	62.123	377.588	338.871	30.973	−206.560	−230.956	15.080
900	62.193	384.909	343.588	37.189	−207.056	−233.977	13.580
1000	62.273	391.465	348.053	43.412	−207.663	−236.936	12.376
1100	62.375	397.405	352.274	49.644	−208.385	−239.830	11.389
1200	62.514	402.838	356.265	55.888	−212.935	−242.431	10.553
1300	62.695	407.849	360.042	62.148	−213.344	−244.872	9.839
1400	62.922	412.503	363.625	68.429	−213.783	−247.281	9.226
1500	63.194	416.853	367.030	74.734	−214.260	−249.658	8.694
1600	63.505	420.941	370.273	81.069	−214.782	−252.001	8.227
1700	63.849	424.802	373.368	87.436	−215.356	−254.310	7.814
1800	64.219	428.461	376.328	93.840	−215.992	−256.583	7.446
1900	64.607	431.944	379.165	100.281	−216.701	−258.819	7.115
2000	65.003	435.268	381.887	106.761	−217.493	−261.016	6.817
2100	65.403	438.449	384.505	113.282	−218.380	−263.170	6.546
2200	65.798	441.501	387.027	119.842	−240.697	−264.535	6.281
2300	66.184	444.434	389.460	126.441	−242.227	−265.584	6.032
2400	66.558	447.259	391.810	133.078	−243.741	−266.567	5.802
2500	66.916	449.983	394.082	139.752	−245.242	−267.487	5.589
2600	67.256	452.614	396.283	146.461	−246.730	−268.348	5.391
2700	67.578	455.159	398.417	153.202	−248.208	−269.151	5.207
2800	67.881	457.622	400.488	159.975	−249.676	−269.900	5.035
2900	68.165	460.009	402.499	166.778	−251.134	−270.596	4.874
3000	68.432	462.324	404.455	173.608	−252.583	−271.243	4.723
3100	68.683	464.572	406.358	180.464	−254.023	−271.841	4.580
3200	68.918	466.757	408.212	187.344	−255.453	−272.393	4.446
3300	69.139	468.881	410.018	194.247	−256.871	−272.900	4.320
3400	69.347	470.948	411.780	201.171	−258.276	−273.365	4.200
3500	69.544	472.961	413.499	208.116	−259.668	−273.788	4.086
3600	69.731	474.923	415.178	215.080	−261.044	−274.172	3.978
3700	69.909	476.836	416.819	222.062	−262.403	−274.518	3.875
3800	70.079	478.702	418.423	229.061	−263.742	−274.828	3.778
3900	70.243	480.525	419.992	236.077	−265.061	−275.102	3.685
4000	70.400	482.305	421.528	243.110	−266.357	−275.343	3.596
4100	70.551	484.046	423.032	250.157	−267.629	−275.552	3.511
4200	70.698	485.747	424.505	257.220	−268.876	−275.730	3.429
4300	70.840	487.413	425.948	264.297	−270.095	−275.879	3.351
4400	70.978	489.043	427.364	271.388	−271.287	−275.999	3.277
4500	71.111	490.639	428.752	278.492	−272.449	−276.093	3.205
4600	71.240	492.204	430.115	285.610	−273.581	−276.162	3.136
4700	71.366	493.737	431.452	292.740	−274.682	−276.206	3.070
4800	71.487	495.241	432.765	299.883	−836.689	−264.610	2.880
4900	71.604	496.716	434.056	307.037	−837.379	−252.684	2.694
5000	71.717	498.164	435.323	314.203	−838.054	−240.745	2.515
5100	71.825	499.585	436.569	321.380	−838.713	−228.792	2.343
5200	71.929	500.981	437.795	328.568	−839.354	−216.827	2.178
5300	72.028	502.352	439.000	335.766	−839.976	−204.849	2.019
5400	72.123	503.699	440.186	342.974	−840.578	−192.860	1.866
5500	72.212	505.023	441.352	350.190	−841.160	−180.859	1.718
5600	72.296	506.325	442.501	357.416	−841.720	−168.849	1.575
5700	72.376	507.606	443.632	364.649	−842.258	−156.828	1.437
5800	72.449	508.865	444.746	371.891	−842.773	−144.799	1.304
5900	72.518	510.104	445.843	379.139	−843.265	−132.761	1.175
6000	72.581	511.323	446.924	386.394	−843.733	−120.714	1.051

PREVIOUS: June 1970 (1 atm) CURRENT June 1970 (1 bar)

$S°(298.15\ K) = 348.05 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-276.5 \pm 17]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-302.9 \pm 17]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2239.2(1)	774. (2)
362. (1)	483.5(2)
168.5 (1)	116.8(2)

Ground State Quantum Weight. [1] $\sigma = 3$

Point Group C_{3v}

Bond Distances. Si–H = 1.494 Å; Si–Br = 2.170 Å

Bond Angles: H–Si–Br = 107.51°; Br–Si–Br = 111.36°

Product of the Moments of Inertia: $I_A I_B I_C = 1.31228 \times 10^{-111}\ g \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298\ 15\ K)$ is estimated by linear interpolation between the values[1] of $SiBr_4(g)$ and $SiH_4(g)$. In adopting linear estimate for SiH_nBr_{4-n} (n=1,2,3), we dismiss the solution calorimetry of Wolf *et al.*[2] because of possible negative bias. These authors reported $\Delta_f H°(g, 298.15\ K) = -69.3 \pm 2.0\ kcal \cdot mol^{-1}$ derived from enthalpies of solution in dilute aqueous NaOH. Wagman *et al.*[3] changed this value to $-75.9\ kcal \cdot mol^{-1}$ due to revised auxiliary data, especially $\Delta_f H°$ of $Na_2SiO_3(cr)$ and $Na_2SiO_3(sln)$ The calorimetric result is 3.5 $kcal \cdot mol^{-1}$ more negative than our linear estimate. This could imply a cubic variation of $\Delta_f H°(Si_1H_nBr_{4-n})$ with n, such as we adopt for the chlorosilanes.[1] We tentatively reject this hypothesis ecause the solution results[2] for $SiHCl_3(g)$, $SiCl_4(g)$, $SiBr_4(l)$ and $SiI_4(cr)$ are also more negative than our adopted values.[1] It is conceivable that the hydrolysis reactions did not proceed to equal degrees in the different calorimetric studies. We conclude, as did Hunt and Sirtl,[4] that the available data justify only linear interpolation of $\Delta_f H°$.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Mitzlaff *et al.*[5] for eight isotopic forms of $SiHBr_3$ and $SiDBr_3$ Structural parameters are presumably substitutional (r_s) values. The principal moments of inertia are: $I_A = I_B = 87.7371 \times 10^{-39}$ and $I_C = 170.4749 \times 10^{-39}\ g\ cm^2$. Vibrational frequencies are from gas–phase infrared spectra of Buerger and Cichon.[6] Assignments are based on band contour analysis and are consistent with Shimanouchi's values[7] derived from liquid–phase Raman spectra.[8]

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_3Br and SiH_2Cl_2.[1]

References

[1]JANAF Thermochemical Tables. Br_4Si(l, g), Br_2H_2Si(g), BrH_3Si(g), ClH_3Si(g), Cl_2H_2Si(g), Cl3HSi(g)12–31–76, H_4Si(g), I_4Si(cr) 6–30–76.

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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	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0	0.	INFINITE	−17.823	−276.529	−276.529	INFINITE
100	53.723	275.599	411 866	−13.627	−278.288	−292.351	152.709
200	69.766	318.044	355.097	−7.411	−281.949	−305.058	79.673
250	75.812	334.287	349.349	−3.765	−284 076	−310.594	64.895
298.15	80.410	348.049	348.049	0.	−302.922	−313.530	54.929
300	80.565	348.547	348.051	0.149	−303.046	−313.595	54.602
350	84.261	361.256	349.046	4.273	−349.657	−312.784	46.681
400	87.163	372.704	351.299	8.562	−349.928	−307.498	40.155
450	89.488	383.109	354.265	12.980	−350.126	−302.181	35.076
500	91.398	392 640	357.632	17.504	−350.263	−296.846	31.011
600	94.380	409.581	364.914	26.800	−350.386	−286.148	24.911
700	96.632	424.307	372.370	36.356	−350.355	−275.443	20.554
800	98.399	437.330	379 691	46.111	−350.214	−264.749	17.286
900	99.818	449.004	386.755	56.024	−349.996	−254.079	14.746
1000	100.970	459.583	393.518	66.065	−349.728	−243.435	12.716
1100	101.915	469.252	399.969	76.211	−349.433	−232.820	11.056
1200	102.697	478.155	406.119	86.443	−349.127	−222.232	9.674
1300	103.348	486.401	411.981	96.746	−348.825	−211.670	8.505
1400	103.894	494.081	417.574	107.109	−348.541	−201.131	7.504
1500	104.356	501.265	422.917	117.522	−348.284	−190.611	6.638
1600	104.748	508.013	428.026	127.978	−348.064	−180.106	5.880
1700	105.085	514.373	432.920	138.470	−398.065	−169.168	5.198
1800	105.374	520.388	437.614	148.993	−397.709	−155.714	4.519
1900	105.625	526.092	442.122	159.544	−397.368	−142.279	3.912
2000	105.844	531.516	446.457	170.117	−397.047	−128.861	3.366
2100	106.036	536.685	450.632	180.712	−396.751	−115.459	2.872
2200	106.205	541.622	454.656	191.324	−396.484	−102.071	2.423
2300	106.354	546.346	458.541	201.952	−396.249	−88.694	2.014
2400	106.486	550.875	462.294	212.594	−396.049	−75.326	1.639
2500	106.604	555.225	465.925	223.249	−395.884	−61.966	1.295
2600	106.710	559.408	469.441	233.914	−395.757	−48.612	0.977
2700	106.805	563.437	472.848	244.590	−395.666	−35.263	0.682
2800	106.891	567.323	476.153	255.275	−395.610	−21.916	0.409
2900	106.968	571.075	479.362	265.968	−395.589	−8.570	0.154
3000	107.039	574.703	482.480	276.669	−395.600	4.776	−0.083
3100	107.103	578.213	485.512	287.376	−395.640	18.122	−0.305
3200	107.161	581.615	488.462	298.089	−395.706	31.470	−0.514
3300	107.214	584.913	491.335	308.808	−395.794	44.821	−0.709
3400	107.263	588.115	494.135	319.532	−395.901	58.175	−0.894
3500	107.308	591.224	496.864	330.260	−396.023	71.531	−1.068
3600	107.350	594.248	499.528	340.993	−780.307	95.353	−1.384
3700	107.388	597.190	502.128	351.730	−780.033	119.673	−1.689
3800	107.423	600.054	504.667	362.471	−779.765	143.986	−1.979
3900	107.456	602.845	507.149	373.215	−779.497	168.291	−2.254
4000	107.486	605.566	509.575	383.962	−779.228	192.590	−2.515
4100	107.515	608.220	511.949	394.712	−778.952	216.882	−2.763
4200	107.541	610.812	514.272	405.465	−778.667	241.167	−2.999
4300	107.566	613.342	516.547	416.220	−778.371	265.446	−3.225
4400	107.589	615.815	518.775	426.978	−778.059	289.717	−3.439
4500	107.610	618.234	520.958	437.738	−777.731	313.981	−3.645
4600	107.630	620.599	523.099	448.500	−777.384	338.237	−3.841
4700	107.649	622.914	525.198	459.264	−777.015	362.486	−4.029
4800	107.667	625.180	527.258	470.030	−776.625	386.727	−4.208
4900	107.684	627.401	529.279	480.797	−776.210	410.959	−4.381
5000	107.699	629.576	531.263	491.566	−775.771	435.183	−4.546
5100	107.714	631.709	533.212	502.337	−775.305	459.397	−4.705
5200	107.728	633.801	535.126	513.109	−774.813	483.602	−4.858
5300	107.742	635.853	537.007	523.883	−774.294	507.798	−5.005
5400	107.754	637.867	538.856	534.657	−773.748	531.983	−5.146
5500	107.766	639.844	540.675	545.433	−773.173	556.158	−5.282
5600	107.777	641.786	542.463	556.211	−772.571	580.322	−5.413
5700	107.788	643.694	544.222	566.989	−771.941	604.476	−5.539
5800	107.798	645.569	545.953	577.768	−771.283	628.617	−5.661
5900	107.808	647.412	547.658	588.548	−770.598	652.748	−5.779
6000	107 817	649.224	549.335	599.330	−769.884	676.866	−5.893

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

$S°(298.15\ K) = [174.5 \pm 17]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -283.7 \pm 25\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Shukurov *et al.*[1] determined the enthalpy of combustion of $MoBr_3(cr)$. Dellien *et al.*[2] obtained $\Delta_f H°(298.15\ K) = -64 \pm 5\ kcal \cdot mol^{-1}$ from the calorimetric result. Brewer[3] re-examined the equilibrium measurements of Oppermann[4] on the mixed solids $MoBr_2 + MoBr_3$ (see the discussion on the $MoBr_4(g)$ table[5]) and obtained $\Delta_f H°(298.15\ K) = -67.8 \pm 6\ kcal \cdot mol^{-1}(-283.675 \pm 25\ kJ \cdot mol^{-1})$ which is the value adopted here.

Heat Capacity and Entropy

Brewer[3] estimated $S°(298.15\ K) = 41.7 \pm 4\ cal \cdot K^{-1} \cdot mol^{-1}(174.473 \pm 17\ J \cdot K^{-1} \cdot mol^{-1})$ and derived $C_p° = 24.14 + 3.50 \times 10^{-3} T\ cal \cdot K^{-1} \cdot mol^{-1}(298\text{–}963\ K)$ from the heat capacities estimated by Opperman.[4] Other estimates are $S°(298.15\ K) = 40.9\ cal \cdot K^{-1} \cdot mol^{-1}$ from the additive entropy constants of Stull and Prophet[6] and $C_p°(298.15\ K) = 23.3\ cal \cdot K^{-1} \cdot mol^{-1}$ from the ionic contributions of Kubaschewski and Unal.[7] We adopt the estimates of Brewer.[3]

Decomposition Data

T_{dcm} is the calculated temperature at which $\Delta_r G° = 0$ for the reaction $2\ MoBr_3(cr) = MoBr_2(cr) + MoBr_4(g)$ at one bar.

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[3] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, September 29, 1978; preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.

[4] H. Oppermann, Z. anorg. allg. Chem. *395*, 249 (1973).

[5] JANAF Thermochemical Tables: $MoBr_4(g)$, 9–30–78.

[6] D. R. Stull and H. Prophet, in "The Characterization of High–Temperature Vapors," J. L. Margrave (ed.), John Wiley, (1967).

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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
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	105.370	174.473	174.473	0.	−283.675	−259.095	45.392
300	105.395	175.125	174.475	0.195	−283.734	−258.942	45.086
400	106.859	205.645	178.626	10.808	−327.297	−241.576	31.547
500	108.324	229.648	186.514	21.567	−324.624	−220.454	23.031
600	109.788	249.527	195.406	32.472	−321.915	−199.874	17.401
700	111.253	266.561	204.383	43.524	−319.143	−179.752	13.413
800	112.717	281.512	213.108	54.723	−316.294	−160.032	10.449
900	114.181	294.873	221.464	66.068	−313.362	−140.675	8.165
1000	115.646	306.979	229.420	77.559	−310.344	−121.648	6.354
1100	117.110	318.070	236.982	89.197	−307.244	−102.928	4.888
1200	118.575	328.322	244.171	100.981	−304.066	−84.494	3.678
1300	120.039	337.871	251.016	112.912	−300.817	−66.327	2.665
1400	121.503	346.821	257.543	124.989	−297.504	−48.414	1.806
1500	122.968	355.254	263.778	137.213	−294.134	−30.739	1.070

PREVIOUS: CURRENT: September 1978

$S°(298.15\ K) = [375.0 \pm 8]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [13.1 \pm 33]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-8.4 \pm 33]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[3505.43]	[2]
[10860.95]	[4]
[11062]	[4]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[170](1)	[260](2)
[95](1)	[90](2)

Point Group: [D_{3h}] $\sigma = [6]$

Bond Distance: Mo–Br = [2.42] Å

Bond Angle: Br–Mo–Br = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [3.16715 \times 10^{-111}]\ g^3·cm^6$

Enthalpy of Formation

The adopted value of $\Delta_f H°(298.15\ K) = -2.0 \pm 8\ kcal·mol^{-1}$ ($-8.368 \pm 33\ kJ·mol^{-1}$) is that estimated by Brewer[1] who used bonding models to estimate the enthalpy of formation of MoBr(g), $MoBr_2$(g), and $MoBr_3$(g). The value of $\Delta_f H°(0\ K)$ combined with JANAF data[2] for Mo(g) and Br(g) leads to $\Delta_{at}H°(MoBr_3, g) = 238.6 \pm 8\ kcal·mol^{-1}$. The mean bond energy $\Delta_{at}H°(MoBr_3, g)/3 = 79.5 \pm 3\ kcal·mol^{-1}$ compared to $\Delta_{at}H°(MoBr_4, g)/4 = 76.0\ kcal·mol^{-1}$.[4] The enthalpy of formation of $MoBr_4$(g) is based on the experimental measurements of Oppermann,[3] providing some confidence in the estimate of Brewer.

Heat Capacity and Entropy

Brewer[1] used a slight modification of the vibrational frequencies and internuclear distance estimated by Lofgren.[4] The Mo–Br distance was taken as 2.42 Å. Drake and Rosenblatt[5] predicted that $MoBr_3$ would be planar. The electronic contributions are taken to be the same as those for MoF_3(g)[2] which are estimated from TaO(g).[2] The principal moments of inertia are $I_A = I_B = 116.5591 \times 10^{-39}$ g cm^2 and $I_C = 233.1183 \times 10^{-39}$ g·cm^2.

References

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[2]JANAF Thermochemical Tables: $MoBr_4$(g) and MoF_3(g), 9–30–78; TaO(g), 12–31–73, Br(g), 9–30–61, Mo(g), 3–31–78.

[3]H. Oppermann, Z. anorg. allg. Chem. 395, 249 (1973).

[4]N. L. Lofgren, private communication to L. Brewer, (1967).

[5]M. C. Drake and G. M. Rosenblatt, paper 388, The Electrochemical Society, Atlanta, Georgia, (October, 1977).

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	−19.910	13.071	13.071	INFINITE
100	65.839	293.440	443.828	−15.039	13.261	−7.303	3.815
200	77.191	343.488	382.257	−7.754	11.352	−27.224	7.110
250	79 157	360.945	376.306	−3.840	9.924	−36.710	7.670
298.15	80.270	374.990	374.990	0.	−8.368	−43.572	7.634
300	80.303	375.487	374.992	0.149	−8.474	−43.790	7.625
350	81.025	387.924	375.972	4.183	−54.628	−47.145	7.036
400	81.509	398.777	378.159	8.247	−54.551	−46.082	6.018
450	81.853	408.398	380.995	12.332	−54.493	−45.027	5.227
500	82.117	417.036	384.174	16.431	−54.453	−43.977	4.594
600	82.533	432.046	390.939	24.664	−54.416	−41.886	3.647
700	82.916	444.797	397.745	32.937	−54.423	−39.798	2.970
800	83.325	455.895	404.335	41.248	−54.462	−37.706	2.462
900	83.766	465.735	410.621	49.603	−54.520	−35.609	2.067
1000	84.222	474.584	416.582	58.002	−54.594	−33.504	1.750
1100	84.672	482.633	422.226	66.447	−54.686	−31.390	1.491
1200	85.099	490.019	427.572	74.936	−54.804	−29.267	1.274
1300	85.491	496.846	432.642	83.466	−54.956	−27.133	1.090
1400	85.845	503.195	437.457	92.033	−55.153	−24.986	0.932
1500	86.161	509.128	442.039	100.633	−55.406	−22.823	0.795
1600	86.445	514.698	446.408	109.264	−55.726	−20.641	0.674
1700	86.703	519.947	450.581	117.921	−56.125	−18.436	0.566
1800	86.943	524.909	454.574	126.604	−56.615	−16.206	0.470
1900	87.172	529.616	458.401	135.310	−57.207	−13.945	0.383
2000	87.395	534.093	462.074	144.038	−57.914	−11.650	0.304
2100	87.617	538.363	465.606	152.789	−58.746	−9.317	0.232
2200	87.841	542.444	469.007	161.562	−59.714	−6.941	0.165
2300	88.067	546.354	472.285	170.357	−60.832	−4.518	0.103
2400	88.297	550.106	475.450	179.175	−62.108	−2.043	0.044
2500	88.531	553.716	478.509	188.016	−63.556	0.489	−0.010
2600	88.766	557.192	481.469	196.881	−65.196	3.083	−0.062
2700	89.001	560.547	484.336	205.770	−67.068	5.743	−0.111
2800	89.235	563.788	487.116	214.681	−69.233	8.479	−0.158
2900	89.464	566.923	489.814	223.616	−107.653	11.347	−0.204
3000	89.688	569.960	492.435	232.574	−108.604	15.467	−0.269
3100	89.904	572.905	494.984	241.554	−109.558	19.618	−0.331
3200	90.110	575.762	497.464	250.555	−110.511	23.800	−0.388
3300	90.305	578.538	499.879	259.576	−111.461	28.012	−0.443
3400	90.487	581.237	502.232	268.615	−112.406	32.253	−0.496
3500	90.656	583.862	504.527	277.673	−113.343	36.521	−0.545
3600	90.810	586.418	506.766	286.746	−114.269	40.816	−0.592
3700	90.949	588.908	508.953	295.834	−115.182	45.137	−0.637
3800	91.072	591.335	511.089	304.935	−116.079	49.481	−0.680
3900	91.180	593.702	513.177	314.048	−116.958	53.850	−0.721
4000	91.272	596.012	515.219	323.171	−117.817	58.241	−0.761
4100	91.350	598.267	517.218	332.302	−118.655	62.652	−0.798
4200	91.412	600.469	519.174	341.440	−119.470	67.084	−0.834
4300	91.459	602.620	521.089	350.584	−120.260	71.535	−0.869
4400	91.493	604.723	522.966	359.731	−121.026	76.005	−0.902
4500	91.513	606.780	524.806	368.882	−121.765	80.491	−0.934
4600	91.521	608.791	526.610	378.034	−122.477	84.994	−0.965
4700	91.517	610.759	528.380	387.186	−123.162	89.511	−0.995
4800	91.502	612.686	530.116	396.337	−123.820	94.043	−1.023
4900	91.476	614.573	531.820	405.486	−124.450	98.589	−1.051
5000	91.441	616.420	533.494	414.632	−716.437	108.878	−1.137
5100	91.397	618.231	535.138	423.774	−718.691	125.407	−1.284
5200	91.345	620.005	536.753	432.911	−721.065	141.980	−1.426
5300	91.285	621.744	538.340	442.042	−723.555	158.601	−1.563
5400	91.219	623.450	539.900	451.168	−726.162	175.270	−1.695
5500	91.147	625.123	541.435	460.286	−728.882	191.988	−1.823
5600	91.069	626.765	542.944	469.397	−731.715	208.756	−1.947
5700	90.987	628.376	544.429	478.500	−734.658	225.577	−2.067
5800	90.900	629.958	545.890	487.594	−737.709	242.448	−2.183
5900	90.810	631.511	547.328	496.680	−740.864	259.375	−2.296
6000	90.716	633.036	548.744	505.756	−744.125	276.355	−2.406

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

$S°(298.15\ K) = 359.83\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-362.5]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-389.1]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
118 (2)	340 (1)
173 (1)	488 (2)
267 (2)	1261 (1)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: P–O = 1.41 ± 0.07 Å; P–Br = 2.06 ± 0.03 Å
Bond Angle: Br–P–Br = 108° ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = 1.11121 \times 10^{-111}\ g^3·cm^6$

Enthalpy of Formation

The $\Delta_f H°(POBr_3, g, 298.15\ K)$ is calculated from the enthalpy of formation of the crystal and the enthalpy of sublimation. The enthalpy of sublimation is obtained by combining the $\Delta_{vap}H°$ and an estimated $\Delta_{fus}H°$. The enthalpy of formation of the crystal is derived from the enthalpies observed for the reaction: $POBr_3(cr) + (n+3)H_2O(l) \rightarrow [H_3PO_4 + 3\ HBr]\ in\ nH_2O(l)$. The data used in these calculations may be summarized as follows:

Data	Source
$\Delta_f H°(H_3PO_4, aq, 298.15\ K)$	Obtained graphically from Holmes[1]
$\Delta_f H°(HBr, aq, 298.15\ K)$	Obtained graphically from[2]
$\Delta_f H°(H_2O, l, 298.15\ K) = -68.3174\ kcal·mol^{-1}$	Obtained from[2]
$\Delta_f H°(POBr_3, cr, 298.15\ K) = -109.1\ kcal\ mol^{-1}$	Recalculated from data of Charnley and Skinner[3]
$\Delta_{fus}H°(298.15\ K) = [3\ 7]\ kcal·mol^{-1}$	Estimated from comparison with $POCl_3$
$\Delta_{vap}H°(298.15\ K) = [12.1]\ kcal·mol^{-1}$	Estimated from the $\Delta_{vap}H°$ at T_{vap}(10.6 kcal·mol^{-1} at 464.9 K). Δ_{vap}H was calculated from a least squares treatment of the vapor pressure data of Driel[4]

Heat Capacity and Entropy

The molecular constants used were calculated from electron diffraction measurements by Secrist and Brockway.[5] The principal moments of inertia are: $I_A = I_B = 86.8222 \times 10^{-39}\ g·cm^2$ and $I_C = 147.4125 \times 10^{-39}\ g·cm^2$.

From the Raman spectra of $POBr_3$ the vibrational frequencies were measured and assigned by Gerding and Driel.[6] The Raman spectra was studied and the vibrational frequencies were listed by Delwaulle and Francois.[7]

References

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[2] U S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
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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	.000	.000	INFINITE	−19.850	−362.496	−362.496	INFINITE
100	59.241	277.279	432.506	−15.523	−364.698	−373.915	195.313
150	71.868	303.845	385.347	−12.225	−366.394	−378.155	131.685
200	80.331	325.763	367.792	−8.406	−368.652	−381.805	99.717
250	85.998	344.337	361.291	−4.239	−370.529	−384.880	80.416
298.15	89.862	359.832	359.832	.000	−389.112	−385.496	67.537
300	89.989	360.388	359.834	.166	−389.227	−385.473	67.117
350	92.960	374.494	360.941	4.743	−436.299	−382.228	57.044
400	95.267	387.063	363.435	9.451	−436.399	−374.496	48.904
450	97.107	398.394	366.700	14.262	−436.425	−366.756	42.572
500	98.602	408.706	370.393	19.156	−436.394	−359.016	37.506
600	100.851	426.894	378.334	29.136	−436.206	−343.555	29.909
700	102.423	442.566	386.417	39.304	−435.905	−328.136	24.486
800	103.555	456.320	394.313	49.606	−435.533	−312.765	20.421
900	104.391	468.568	401.895	60.005	−435.115	−297.444	17.263
1000	105.022	479.601	409.123	70.477	−434.668	−282.171	14.739
1100	105.508	489 634	415.993	81.005	−434.202	−266.944	12.676
1200	105.890	498.832	422.519	91.576	−497.298	−250.681	10.912
1300	106.194	507.320	428.719	102.180	−496.044	−230.181	9.249
1400	106.441	515.199	434.618	112.813	−494.795	−209.777	7.827
1500	106.643	522.550	440.238	123.467	−493.556	−189.462	6.598
1600	106.810	529.438	445.600	134.140	−492.331	−169.229	5.525
1700	106.950	535.917	450.724	144.828	−491.124	−149.072	4.580
1800	107.069	542.034	455.629	155.529	−489.938	−128.986	3.743
1900	107.170	547.826	460.330	166.241	−488.778	−108.964	2.996
2000	107.257	553.325	464.844	176.963	−487.647	−89.003	2.325
2100	107.332	558.560	469.183	187.692	−486.549	−69.098	1 719
2200	107.398	563.555	473.360	198.429	−485 488	−49.244	1.169
2300	107.455	568.330	477.386	209.172	−484 466	−29.438	.669
2400	107.506	572.904	481.271	219.920	−483.485	−9.676	.211
2500	107.551	577.294	485.025	230.673	−482.546	10.047	−.210
2600	107.590	581.513	488.655	241.430	−481.650	29.733	−.597
2700	107.626	585.574	492.170	252.191	−480.795	49.385	−.955
2800	107 658	589.489	495.576	262.955	−479.980	69.006	−1.287
2900	107.687	593.267	498.880	273.722	−479.205	88.599	−1.596
3000	107.712	596.918	502.088	284.492	−478.465	108.166	−1.883
3100	107.736	600.450	505.204	295.264	−477.758	127.709	−2.152
3200	107 757	603.871	508.234	306.039	−477.080	147.228	−2.403
3300	107.777	607.187	511.183	316.816	−476.427	166.728	−2.639
3400	107.795	610 405	514.054	327.594	−475.796	186.208	−2.861
3500	107.811	613.530	516.852	338.375	−475.182	205.669	−3.069
3600	107.826	616.567	519.580	349.157	−474.580	225.114	−3.266
3700	107.840	619.522	522.241	359.940	−473.987	244.542	−3.452
3800	107.853	622.398	524.839	370.725	−473.399	263.954	−3.628
3900	107.864	625.200	527.377	381.510	−472.811	283.350	−3.795
4000	107.875	627.931	529.856	392.297	−472.221	302.731	−3.953
4100	107.885	630.595	532.281	403.085	−471.624	322.098	−4.104
4200	107.895	633.195	534.653	413.874	−471.017	341.449	−4.247
4300	107.904	635.733	536.974	424.664	−470.399	360.787	−4.383
4400	107.912	638.214	539.247	435.455	−469.765	380.109	−4.512
4500	107.920	640.639	541.473	446.247	−469.115	399 417	−4.636
4600	107.927	643.011	543.655	457.039	−468.446	418.710	−4.755
4700	107.933	645.333	545.794	467.832	−467.756	437.989	−4.868
4800	107.940	647.605	547.891	478.626	−467.045	457.253	−4.976
4900	107.946	649.831	549.949	489.420	−466.311	476.502	−5.080
5000	107.951	652.012	551.969	500.215	−465.553	495.735	−5.179
5100	107.957	654.149	553.951	511.010	−464.772	514.954	−5.274
5200	107.962	656.246	555.898	521.806	−463.966	534.155	−5.366
5300	107.966	658.302	557.811	532.603	−463.135	553.343	−5.454
5400	107.971	660.320	559.691	543.399	−462.281	572.514	−5.538
5500	107.975	662.302	561.539	554.197	−461.402	591.668	−5.619
5600	107.979	664.247	563.355	564.994	−460.500	610.807	−5.697
5700	107.983	666.158	565.142	575.792	−459.574	629.929	−5.773
5800	107.986	668.036	566.900	586.591	−458.627	649.035	−5.845
5900	107.989	669.882	568.630	597.390	−457.657	668.123	−5.915
6000	107.993	671 697	570.333	608.189	−456.667	687.197	−5.983

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

$S°(298.15\ K) = 348.234\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -121.7 \pm 6.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -146.0 \pm 6.3\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
392 (1)	392.2 (2)
161.3 (1)	115.7 (2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distance: P–Br = 2.20 ± 0.03 Å
Bond Angle: Br–P–Br = 106° ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = 1.18987 \times 10^{-111}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation of PBr gas from white (α) phosphorus, −34.9 kcal·mol^{-1}, was obtained by Charnley and Skinner.[1] To obtain their value (−34.9 kcal·mol^{-1}), Charnley and Skinner[1] measured the enthalpy of formation of the liquid, and combined it and their estimate of the liquid enthalpy with the enthalpy of vaporization (9.5 kcal·mol^{-1}) calculated by Driel and Gerding.[2] For the liquid enthalpy of formation Charnley and Skinner[1] observed the $\Delta_f H° = -67.2 \pm 0.6$ kcal·mol^{-1} for $PBr_3(l) + (n+3)H_2O(l) \rightarrow [H_3PO_3 + 3HBr]$ in $nH_2O(l)$. Driel and Gerding[2] measured the vapor pressure over $PBr_3(l)$ and calculated the enthalpy of vaporization with the aid of a modified Claperyron equation. The uncertainties on the enthalpy of formation are estimates.

Heat Capacity and Entropy

Williams and Gordy[3] have reported moments of inertia from the microwave spectrum of PBr_3. From this data Whiffen[4] has calculated the selected molecular constants. The principal moments of inertia are $I_A = I_B = 85.2188 \times 10^{-39}$ g cm^2 and $I_C = 163.8427 \times 10^{-39}$ g◀cm^2.

Lister and Sutton[5] have reported P–Br = 2.23 ± 0.04 Å and the angle Br–P–Br = 100 ± 2. Swingle[6] has measured P–Br = 2.18 ± 0.03 Å and the angle Br–P–Br = 101.5 ± 1.5. Swingle's data as well as that of Lister and Sutton were obtained by electron diffraction. The 106° angle was selected since 101.5° and 100° give imaginary force constants with the ranges allowed for the type A, 392 cm^{-1} frequency and the form of the potential function assumed by Davis and Oetjen.[7]

The vibrational frequencies were measured and assigned in the infrared by Davis and Oetjen.[7] Raman measurements and assignments by Cabannes and Rausset[8] were also listed by Delwaulle.[9] The Raman assignments were as follows: type A, 380 cm^{-1} and 162 cm^{-1} and type E, 400 cm^{-1} and 116 cm^{-1}.

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	−17.753	−121.651	−121.651	INFINITE
100	54.768	275.812	411.024	−13.521	−122.496	−140.231	73.249
200	69.764	319.032	355.025	−7.199	−125.788	−156.943	40.989
250	73.619	335.046	349.473	−3.607	−127.512	−164.539	34.378
298.15	76.033	348.234	348.234	0.	−146.022	−169.530	29.701
300	76.108	348.704	348.235	0.141	−146.135	−169.675	29.543
350	77.770	360.569	349.168	3.990	−193.196	−170.981	25.518
400	78.922	371.034	351.260	7.909	−193.338	−167.797	21.912
450	79.748	380.380	353.986	11.877	−193.449	−164.598	19.106
500	80.357	388.815	357.054	15.881	−193.537	−161.387	16.860
600	81.176	403.545	363.610	23.961	−193.669	−154.944	13.489
700	81.683	416.099	370.234	32.105	−193.764	−148.482	11.080
800	82.018	427.029	376.665	40.292	−193.840	−142.007	9.272
900	82.250	436.704	382.809	48.506	−193.904	−135.525	7.866
1000	82.417	445.379	388.640	56.739	−193.964	−129.035	6.740
1100	82.542	453.240	394.161	64.988	−194.023	−122.539	5.819
1200	82.637	460.427	399.388	73.247	−257.656	−114.959	5.004
1300	82.711	467.044	404.341	81.514	−256.947	−103.097	4.142
1400	82.771	473.176	409.041	89.789	−256.250	−91.288	3.406
1500	82.818	478.888	413.509	98.068	−255.566	−79.529	2.769
1600	82.858	484.234	417.764	106.352	−254.896	−67.816	2.214
1700	82.890	489.259	421.824	114.639	−254.243	−56.143	1.725
1800	82.918	493.997	425.703	122.930	−253.610	−44.508	1.292
1900	82.941	498.481	429.416	131.223	−252.999	−32.908	0.905
2000	82.960	502.736	432.977	139.518	−252.414	−21.340	0.557
2100	82.977	506.784	436.396	147.815	−251.856	−9.800	0.244
2200	82.992	510.644	439.684	156.113	−251.329	1.714	−0.041
2300	83.005	514.334	442.850	164.413	−250.835	13.205	−0.300
2400	83.016	517.867	445.903	172.714	−250.374	24.675	−0.537
2500	83.026	521.256	448.849	181.016	−249.948	36.126	−0.755
2600	83.035	524.512	451.697	189.319	−249.558	47.561	−0.956
2700	83.043	527.646	454.453	197.623	−249.201	58.982	−1.141
2800	83.050	530.667	457.121	205.928	−248.877	70 390	−1.313
2900	83.057	533.581	459.707	214.233	−248.585	81.788	−1.473
3000	83.062	536.397	462.217	222.539	−248.320	93.175	−1.622
3100	83.067	539.121	464 654	230.846	−248.081	104.554	−1.762
3200	83 072	541.758	467.023	239.153	−247.864	115.926	−1.892
3300	83.076	544.314	469.326	247.460	−247.666	127.291	−2.015
3400	83.080	546.794	471.568	255.768	−247.481	138.651	−2.130
3500	83.084	549.203	473.752	264.076	−247.307	150.005	−2.239
3600	83.087	551.543	475.881	272.385	−247.139	161.355	−2.341
3700	83.090	553.820	477.957	280.694	−246.974	172.700	−2.438
3800	83.093	556.036	479.982	289.003	−246.806	184.039	−2.530
3900	83.096	558.194	481.960	297.312	−246.634	195.375	−2.617
4000	83.098	560.298	483.893	305.622	−246.453	206.707	−2.699
4100	83.100	562.350	485.781	313.932	−246.260	218.033	−2.778
4200	83.102	564.353	487.628	322.242	−246.052	229.355	−2.852
4300	83.104	566.308	489.435	330.552	−245.826	240.671	−2.924
4400	83.106	568.219	491.204	338.863	−245.580	251.983	−2.991
4500	83.108	570.086	492.936	347.174	−245.312	263.288	−3.056
4600	83.109	571.913	494.634	355.485	−245.019	274.587	−3.118
4700	83.111	573.700	496.297	363.796	−244.700	285.879	−3.177
4800	83.112	575.450	497.928	372.107	−244.354	297.165	−3.234
4900	83.113	577.164	499.527	380.418	−243.979	308.442	−3.288
5000	83.115	578.843	501.097	388.729	−243.574	319.712	−3.340
5100	83.116	580.489	502.638	397.041	−243.139	330.974	−3.390
5200	83.117	582.103	504.150	405.353	−242.673	342.226	−3.438
5300	83.118	583.686	505.636	413.664	−242.176	353.470	−3.484
5400	83.119	585.240	507.096	421.976	−241.647	364.704	−3.528
5500	83.120	586.765	508.531	430.288	−241.087	375.927	−3.570
5600	83.121	588.262	509.941	438.600	−240.494	387.140	−3.611
5700	83.121	589.734	511.328	446.912	−239.871	398.343	−3.650
5800	83.122	591.179	512.692	455.224	−239.215	409.533	−3.688
5900	83.123	592.600	514.035	463.537	−238.529	420.713	−3.725
6000	83.124	593.997	515.356	471.849	−237.812	431.880	−3.760

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

$S°(298.15\ K) = 372.828\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-238.2]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-263.6]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
299 (1)
438 (2)
718 (1)
115 (2)
165 (1)
179 (2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: P–Br = 2.13 ± 0.03 Å; P–S = 1.89 ± 0.06 Å
Bond Angle: Br–P–Br = 106° ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = 1.94531 \times 10^{-111}\ g^3·cm^6$

Enthalpy of Formation

The $\Delta_f H°(PSBr_3, g, 298.15\ K)$ was calculated from the $\Delta_f H°(POBr_3, g, 298.15\ K)$ and estimated strengths for P–S and P–O bonds.

The difference in the P–S and P–O bond strengths was assumed to be the same for $POF_3 - PSF_3$ and $POBr_3 - PSBr_3$. For the P–S bond strength in PSF_3, Henderson and Scheffee[1] estimated 91 kcal from a consideration of unpublished data. The P–O bond was estimated to be 115 kcal by Neale and Williams[2] and Neale *et al.*[3]

Auxiliary data for $POBr_3(g)$, O(g), and S(g) are from the JANAF tables.[4]

Heat Capacity and Entropy

The molecular constants were determined from electron diffraction data by Secrist and Brockway.[5] The principal moments of inertia are: $I_A = I_B = 112.5445 \times 10^{-39}$ g cm^2 and $I_C = 153.5823 \times 10^{-39}$ g·cm^2.

The vibrational frequencies obtained from the Raman spectra of $PSBr_3$ were reported 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	.000	.000	INFINITE	−21.191	−238.247	−238.247	INFINITE
100	65.087	284.297	450.202	−16.591	−239.413	−256.745	134.110
150	77.458	313.212	399.905	−13.004	−240.831	−265.111	92.320
200	85.612	336.689	381.258	−8.914	−242.994	−272.953	71.288
250	91.175	356.429	374.371	−4.486	−244.900	−280.228	58.550
298.15	94.934	372.828	372.828	.000	−263.592	−284.875	49.909
300	95.055	373.415	372.829	.176	−263.712	−285.007	49.624
350	97.818	388.287	373.998	5.001	−310.964	−285.923	42.672
400	99.831	401.487	376.624	9.945	−313.512	−282.235	36.856
450	101.330	413.336	380.056	14.976	−314.485	−278.276	32.301
500	102.468	424.074	383.930	20.072	−315.483	−274.196	28.645
600	104.045	442.907	392.234	30.404	−316.948	−265.793	23.139
700	105.051	459.026	400.652	40.862	−318.077	−257.175	19.191
800	105.728	473.101	408.847	51.403	−319.008	−248.409	16.219
900	106.204	485.583	416.693	62.001	−372.945	−238.454	13.840
1000	106.551	496.792	424.152	72.640	−372.457	−223.537	11.676
1100	106.810	506.960	431.225	83.309	−371.967	−208.668	9.909
1200	107.010	516.262	437.929	94.000	−435.055	−192.766	8.391
1300	107.166	524.834	444.289	104.709	−433.807	−172.626	6.936
1400	107.291	532.781	450.329	115.432	−432.579	−152.582	5.693
1500	107.392	540.187	456.076	126.167	−431.373	−132.624	4.618
1600	107.475	547.120	461.552	136.910	−430.192	−112.746	3.681
1700	107.544	553.638	466.779	147.661	−429.038	−92.941	2.856
1800	107.602	559.787	471.777	158.419	−427.914	−73.204	2.124
1900	107.652	565.606	476.563	169.181	−426.823	−53.527	1.472
2000	107.694	571.129	481.155	179.949	−425.767	−33.907	.886
2100	107.730	576.384	485.565	190.720	−424.747	−14.340	.357
2200	107.762	581.397	489.808	201.495	−423.767	5.180	−.123
2300	107.789	586.187	493.895	212.272	−422.826	24.657	−.560
2400	107.813	590.775	497.837	223.052	−421.928	44.093	−.960
2500	107.835	595.177	501.643	233.835	−421.070	63.493	−1.327
2600	107.854	599.407	505.322	244.619	−420.254	82.859	−1.665
2700	107.871	603.477	508.883	255.405	−419.477	102.195	−1.977
2800	107.886	607.401	512.332	266.193	−418.738	121.502	−2.267
2900	107.899	611.187	515.676	276.982	−418.035	140.784	−2.536
3000	107.912	614.845	518.921	287.773	−417.365	160.042	−2.787
3100	107.923	618.384	522.072	298.565	−416.724	179.279	−3.021
3200	107.933	621.810	525.136	309.358	−416.109	198.494	−3.240
3300	107.942	625.132	528.116	320.151	−415.516	217.692	−3.446
3400	107.950	628.354	531.017	330.946	−414.941	236.871	−3.639
3500	107.958	631.483	533.843	341.741	−414.380	256.034	−3.821
3600	107.965	634.525	536.598	352.538	−413.829	275.181	−3.993
3700	107.972	637.483	539.285	363.334	−413.284	294.312	−4.155
3800	107.978	640.363	541.907	374.132	−412.741	313.429	−4.308
3900	107.983	643.167	544.467	384.930	−412.197	332.532	−4.454
4000	107.988	645.901	546.969	395.728	−411.649	351.621	−4.592
4100	107.993	648.568	549.415	406.528	−411.093	370.695	−4.723
4200	107.998	651.170	551.807	417.327	−410.527	389.756	−4.847
4300	108.002	653.712	554.147	428.127	−409.948	408.804	−4.966
4400	108.006	656.195	556.438	438.927	−409.353	427.838	−5.079
4500	108.009	658.622	558.682	449.728	−408.742	446.858	−5.187
4600	108.012	660.996	560.881	460.529	−408.112	465.865	−5.290
4700	108.016	663.319	563.036	471.331	−407.461	484.857	−5.389
4800	108.019	665.593	565.149	482.132	−406.789	503.836	−5.483
4900	108.021	667.820	567.221	492.934	−406.095	522.800	−5.573
5000	108.024	670.003	569.255	503.737	−405.377	541.750	−5.660
5100	108.026	672.142	571.252	514.539	−404.636	560.685	−5.743
5200	108.029	674.239	573.212	525.342	−403.870	579.605	−5.822
5300	108.031	676.297	575.138	536.145	−403.080	598.511	−5.899
5400	108.033	678.316	577.030	546.948	−402.265	617.401	−5.972
5500	108.035	680.299	578.889	557.751	−401.426	636.276	−6.043
5600	108.037	682.245	580.718	568.555	−400.562	655.136	−6.111
5700	108.039	684.158	582.516	579.359	−399.673	673.980	−6.176
5800	108.040	686.037	584.284	590.163	−398.761	692.807	−6.239
5900	108.042	687.884	586.025	600.967	−397.825	711.620	−6.300
6000	108.043	689.699	587.738	611.771	−396.866	730.416	−6.359

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

$S°(298.15\ K) = [351.77 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-179.1 \pm 63]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-201.7 \pm 63]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[362] (1)
[168] (1)
[483.5](2)
[116.8](2)

Ground State Quantum Weight: [2] $\sigma = [3]$

Point Group: [C_{3v}]

Bond Distance: Si–Br = [2.17] Å

Bond Angle: Br–Si–Br = [111.36]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.29082 \times 10^{111}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation of $SiBr_3(g)$ is based on an assumed average bond energy of 78 ± 5 kcal·mol^{-1}.[1] This average bond energy is that of $SiBr_4(g)$, i.e. $\Delta_a H°(SiBr_4, g)/4$. The rationale for this assumption is based on the same relationship existing for the silicon chloride and fluoride species.[1]

Heat Capacity and Entropy

The molecular structure is assumed to be identical to the $SiBr_3$ group in $SiHBr_3$.[1] From this structure we estimate the following principal moments of inertia: $I_A = I_B = 87.0168 \times 10^{-39}$, and $I_C = 170.479 \times 10^{-39}$ g·cm^2. The vibrational requencies are assumed to be those of the $SiBr_3$ group in $SiHBr_3(g)$.

Reference

[1]JANAF Thermochemical Tables: $SiCl_3(g)$ and $SiF_3(g)$, 12–31–77; $SiBr_4(g)$ and $SiHBr_3(g)$, 12–31–76.

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	−17.370	−179.082	−179.082	INFINITE
100	53.692	281.244	412.980	−13.174	−179.341	−199.005	103.950
200	67.782	323.273	358.414	−7.028	−181.727	−217.822	56.889
250	71.881	338.868	352.988	−3.530	−183.302	−226.671	47.360
298.15	74.578	351.774	351.774	0.	−201.694	−232.894	40.802
300	74.663	352.236	351.776	0.138	−201.803	−233.087	40.584
350	76.584	363.898	352.692	3.922	−248.029	−235.764	35.186
400	77.944	374.218	354.750	7.787	−247.995	−234.014	30.559
450	78.934	383.459	357.436	11.710	−247.958	−232.268	26.961
500	79.673	391.816	360.463	15.676	−247.921	−230.527	24.083
600	80.677	406.438	366.941	23.698	−247.855	−227.055	19.767
700	81.305	418.925	373.497	31.799	−247.809	−223.592	16.685
800	81.723	429.811	379.871	39.952	−247.794	−220.134	14.373
900	82.014	439.454	385.966	48.140	−247.815	−216.675	12.576
1000	82.224	448.107	391.754	56.352	−247.874	−213.213	11.137
1100	82.381	455.951	397.240	64.583	−247.974	−209.742	9.960
1200	82.501	463.125	402.435	72.827	−248.116	−206.260	8.978
1300	82.595	469.732	407.361	81.082	−248.302	−202.765	8.147
1400	82.670	475.856	412.038	89.346	−248.536	−199.254	7.434
1500	82.731	481.562	416.485	97.616	−248.818	−195.724	6.816
1600	82.780	486.903	420.721	105.892	−249.152	−192.174	6.274
1700	82.822	491.923	424.763	114.172	−299.718	−188.154	5.781
1800	82.856	496.658	428.627	122.456	−299.935	−181.586	5.269
1900	82.886	501.138	432.326	130.743	−300.171	−175.004	4.811
2000	82.911	505.390	435.874	139.033	−300.429	−168.410	4.398
2100	82.932	509.436	439.281	147.325	−300.712	−161.802	4.025
2200	82.951	513.294	442.559	155.619	−301.023	−155.180	3.684
2300	82.967	516.982	445.715	163.915	−301.365	−148.543	3.374
2400	82.982	520.514	448.758	172.212	−301.739	−141.891	3.088
2500	82.994	523.901	451.697	180.511	−302.145	−135.222	2.825
2600	83.006	527.157	454.537	188.811	−302.584	−128.537	2.582
2700	83.016	530.289	457.285	197.112	−303.056	−121.834	2.357
2800	83.025	533.309	459.946	205.414	−303.559	−115.113	2.147
2900	83.033	536.222	462.527	213.717	−304.091	−108.373	1.952
3000	83.040	539.037	465.030	222.021	−304.650	−101.615	1.769
3100	83.047	541.760	467.462	230.325	−305.232	−94.838	1.598
3200	83.053	544.397	469.825	238.630	−305.835	−88.041	1.437
3300	83.058	546.953	472.124	246.936	−306.455	−81.225	1.286
3400	83.063	549.432	474.361	255.242	−307.088	−74.391	1.143
3500	83.068	551.840	476.541	263.548	−307.729	−67.538	1.008
3600	83.072	554.180	478.665	271.855	−692.528	−50.205	0.728
3700	83.076	556.457	480.737	280.163	−692.761	−32.359	0.457
3800	83.079	558.672	482.759	288.470	−692.993	−14.508	0.199
3900	83.082	560.830	484.733	296.778	−693.220	3.350	−0.045
4000	83.086	562.934	486.662	305.087	−693.438	21.214	−0.277
4100	83.088	564.985	488.547	313.396	−693.643	39.082	−0.498
4200	83.091	566.988	490.391	321.705	−693.833	56.956	−0.708
4300	83.093	568.943	492.195	330.014	−694.003	74.834	−0.909
4400	83.096	570.853	493.961	338.323	−694.153	92.716	−1.101
4500	83.098	572.720	495.691	346.633	−694.278	110.601	−1.284
4600	83.100	574.547	497.385	354.943	−694.378	128.488	−1.459
4700	83.102	576.334	499.046	363.253	−694.450	146.377	−1.627
4800	83.103	578.084	500.675	371.563	−694.493	164.268	−1.788
4900	83.105	579.797	502.272	379.874	−694.505	182.159	−1.942
5000	83.107	581.476	503.839	388.184	−694.487	200.050	−2.090
5100	83.108	583.122	505.378	396.495	−694.436	217.940	−2.232
5200	83.109	584.736	506.889	404.806	−694.353	235.829	−2.369
5300	83.111	586.319	508.372	413.117	−694.238	253.716	−2.501
5400	83.112	587.872	509.830	421.428	−694.089	271.601	−2.627
5500	83.113	589.397	511.263	429.739	−693.907	289.482	−2.749
5600	83.114	590.895	512.672	438.050	−693.693	307.360	−2.867
5700	83.115	592.366	514.057	446.362	−693.446	325.234	−2.980
5800	83.116	593.812	515.420	454.674	−693.168	343.103	−3.090
5900	83.117	595.232	516.760	462.985	−692.859	360.967	−3.196
6000	83.118	596.629	518.080	471.297	−692.518	378.825	−3.298

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

$S°(298.15\ K) = 176.4 \pm 3.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 179.9\ K$

$\Delta_f H°(0\ K) = -531.6 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -550.2 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of $TiBr_3$(cr) is based on the vapor pressure data reported by Hall and Blocher[1] for the process $1/2Hg_2Br_2(cr) + TiBr_3(cr) = TiBr_4(g) + Hg(l)$ over the temperature range 430 to 546 K. 2nd and 3rd law analyses of these data give values for the enthalpy of reaction of 24.2 ± 0.3 and 24.4 $kcal \cdot mol^{-1}$, respectively, for seventy three points, with ten points rejected due to failure of a statistical test. The 3rd law drift in the data is calculated as 0.6 ± 0.8 $cal \cdot K^{-1} mol^{-1}$. The 3rd law value of 24.4 $kcal \cdot mol^{-1}$ is combined with the JANAF enthalpies of formation of $TiBr_4$(g) and $HgBr_2$(cr) to obtain the adopted enthalpy of formation, $\Delta_f H°$(cr, 298.15 K) = −131.5 ± 2.0 $kcal \cdot mol^{-1}$ (−550.196 ± 8.4 $kJ \cdot mol^{-1}$).

Heat Capacity and Entropy

The heat capacity and entropy of $TiBr_3$(cr) have been measured over the temperature range 51 to 800 K by King *et al.*[2] Heat capacities above 800 K are estimated from graphical extrapolation. The value of $S°(298.15\ K)$ is derived from these data, based on $S°(51\ K) = 8.60$ $cal \cdot K^{-1} \cdot mol^{-1}$. The value of $S°(51\ K)$ is estimated from a Debye–Einstein extrapolation of the measured heat capacities, the equation being $C_p° = D(70.0/T) + E(120/T) + 2E(306/T)$. It is assumed that all electronic entropy is contained within the measured and extrapolated heat capacities.

Transition Data

A second order transition at 179.9 K was observed by King *et al.*[2] The heat capacity at this temperature is in excess of 56.1 $cal \cdot K^{-1} \cdot mol^{-1}$. King *et al.*[2] measured the value of $H°(188\ K) - H°(160\ K)$ as 0.773 $kcal \cdot mol^{-1}$.

Sublimation Data

The enthalpy of sublimation is calculated from the enthalpies of formation of $TiBr_3$(cr) and $TiBr_3$(g) at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta_r G = 0$ for the process $TiBr_3(cr) = TiBr_3(g)$ at one bar.

References

[1] E. H. Hall and J. M Blocher, Jr., J Electrochem. Soc. 105, 40 (1958).
[2] E. G. King, W W. Weller, A. U. Christensen and K K. Kelley, U. S. Bur. Mines RI 5799, (1961).

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	−22.970	−531.572	−531.572	INFINITE
100	70.655	74.136	264.466	−19.033	−532.385	−530.896	277.312
200	97.818	137.244	185.506	−9.652	−532.274	−529.251	138.226
298.15	101.705	176.443	176.443	0.	−550.196	−525.561	92.076
300	101.776	177.073	176.445	0.188	−550.264	−525.408	91.482
400	105.818	206.789	180.471	10.527	−594.259	−507.949	66.331
500	114.709	231.322	188.246	21.538	−591.526	−486.673	50.842
600	125.507	253.176	197.274	33.541	−587.928	−466.024	40.571
700	137.210	273.423	206.722	46.691	−583.274	−446.060	33.285
800	147.277	292.463	216.262	60.961	−577.557	−426.837	27.870
900	151.879	310.075	225.722	75.918	−571.237	−408.372	23.701
1000	156.673	326.329	234.980	91.349	−564.588	−390.630	20.404
1100	161.084	341.471	243.980	107.240	−557.687	−373.567	17.739
1200	165.111	355.663	252.702	123.553	−554.556	−357.021	15.541
1300	168.755	369.025	261.141	140.250	−546.541	−340.883	13.697
1400	172.015	381.653	269.302	157.291	−538.272	−325.372	12.140
1500	174.891	393.621	277.195	174.640	−529.802	−310.459	10.811

PREVIOUS: June 1964 CURRENT: June 1968

$S°(298.15\ K) = [359.1 \pm 5.0]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -351.4 \pm 10.5\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -374.9 \pm 10.5\ kJ·mol^{-1}$

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	
υ, cm^{-1}	υ, cm^{-1}
[380](1)	[427](2)
[162](1)	[103](2)

Point Group: C_{3v} $\sigma = 3$
Bond Distance: Ti–Br = [2.4] Å
Bond Angle: Br–Ti–Br = [100]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.72305 \times 10^{-111}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation of $TiBr_3(g)$ is calculated from the enthalpy of sublimation of $TiBr_3(cr)$. A tentative equation for the vapor pressure of $TiBr_3(cr)$ was reported by Hall and Blocher.[1] 2nd and 3rd law analyses of the equation over the temperature range 700 to 900 K give values of $\Delta_{sub}H°(298.15\ K)$ of 45.2 and 41.9 $kcal·mol^{-1}$, respectively, with a 3nd law drift of $-4.2\ cal·K^{-1}·mol^{-1}$. The chosen value of $\Delta_f H°(298.15\ K)$, $-89.6 \pm 2.5\ kcal·mol^{-1}$ ($-374.886 \pm 10.5\ kJ\ mol^{-1}$), is based on the 3rd law $\Delta_{sub}H°(298.15\ K)$.

Heat Capacity and Entropy

The interatomic distance is estimated from those of $TiCl_4$, $TiCl_3$ and $TiBr_4$. The pyramidal bond angle is estimated assuming that $TiBr_3(g)$ is similar to the group V trihalides. The principal moments of inertia are: $I_A = I_B = 98.0035 \times 10^{-39}\ g\ cm^2$ and $I_C = 179.3970 \times 10^{-39}\ g·cm^2$. 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}.[2]

References

[1] E. H. Hall and J. M Blocher, J. Phys. Chem. 63, 1525 (1959).
[2] C. E. Moore, U. S. Nat. Bur. Stand., Circ. 467, (1949).

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	−18.122	−351.415	−351.415	INFINITE
100	55.060	285.335	423.540	−13.820	−351.863	−371.494	194.048
200	71.226	328.902	366.106	−7.441	−354.752	−390.061	101.873
250	76.150	345.361	360.354	−3.748	−356.447	−398.697	83.303
298.15	79.334	359.064	359.064	0.	−374.886	−404.700	70.902
300	79.433	359.555	359.066	0.147	−374.996	−404.885	70.497
350	81.623	371.976	360.042	4.177	−421.229	−407.328	60.790
400	83.104	382.978	362.234	8.297	−421.179	−405.345	52.933
450	84.118	392.829	365.096	12.480	−421.117	−403.370	46.822
500	84.816	401.730	368.322	16.704	−421.050	−401.401	41 934
600	85.616	417.274	375.222	25.231	−420.928	−397.483	34.604
700	85.968	430.502	382.198	33.813	−420.842	−393.583	29.370
800	86.103	441.992	388.970	42.417	−420.791	−389.693	25.444
900	86.137	452.136	395.436	51.030	−420.815	−385.806	22.392
1000	86.128	461.211	401.568	59.643	−420.984	−381.908	19.949
1100	86.102	469.419	407.369	68.255	−421.362	−377.984	17.949
1200	86.068	476.909	412.856	76.863	−425.936	−373.896	16.275
1300	86.033	483.797	418.052	85.469	−426.013	−369.557	14 849
1400	85.996	490.171	422.978	94.070	−426.184	−365.209	13.626
1500	85.958	496.103	427.658	102.668	−426.465	−360.844	12.566
1600	85.921	501.649	432.111	111.262	−426.870	−356.457	11.637
1700	85 884	506.857	436.356	119.852	−427.413	−352.040	10.817
1800	85.847	511.765	440.411	128.438	−428.111	−347.587	10.087
1900	85.812	516.406	444.289	137.021	−428.980	−343.091	9.432
2000	85.779	520.806	448.006	145.601	−444.720	−338.090	8.830
2100	85.748	524.991	451.573	154.177	−446.724	−332.710	8.276
2200	85.718	528.979	455.002	162.750	−448.760	−327.233	7.769
2300	85.691	532.789	458.302	171.321	−450.832	−321.663	7.305
2400	85.665	536.435	461.482	179.889	−452.939	−316.001	6.878
2500	85.641	539.932	464.550	188.454	−455.083	−310.252	6.482
2600	85.619	543.290	467.515	197.017	−457.263	−304 416	6.116
2700	85.598	546.521	470.381	205.578	−459.479	−298.495	5.775
2800	85.578	549.634	473.156	214.137	−461.730	−292.492	5.457
2900	85.560	552.637	475.846	222.693	−464.012	−286.407	5.159
3000	85.542	555.537	478.454	231.249	−466.323	−280.244	4.879
3100	85.525	558.342	480.986	239.802	−468.661	−274.002	4 617
3200	85.508	561.057	483.446	248.354	−471.022	−267.686	4.370
3300	85.492	563.688	485.838	256.904	−473.401	−261.294	4.136
3400	85.475	566.239	488.165	265.452	−475.796	−254.831	3.915
3500	85.459	568 717	490.432	273.999	−478.201	−248.297	3.706
3600	85.443	571.124	492.640	282.544	−480.614	−241.694	3.507
3700	85.426	573.465	494.793	291.087	−892.127	−227.236	3.208
3800	85.410	575 743	496.893	299.629	−893.307	−209.251	2.876
3900	85.393	577.961	498.944	308.169	−894.538	−191.233	2.561
4000	85.376	580.123	500.946	316.707	−895.815	−173.183	2.262
4100	85.358	582.231	502.903	325.244	−897.134	−155.101	1.976
4200	85.340	584.288	504.816	333.779	−898.489	−136.987	1 704
4300	85.322	586.296	506.688	342.312	−899.876	−118.839	1.444
4400	85.304	588.257	508.520	350.844	−901.291	−100.659	1.195
4500	85.285	590.174	510.313	359.373	−902.730	−82.447	0.957
4600	85.266	592.048	512.070	367.901	−904.190	−64.203	0.729
4700	85.247	593.882	513.791	376.426	−905.666	−45.926	0.510
4800	85.228	595.676	515.478	384.950	−907.155	−27.618	0.301
4900	85.208	597.433	517.133	393.472	−908.655	−9.279	0.099
5000	85.188	599.154	518.756	401.992	−910.161	9.091	−0.095
5100	85.168	600.841	520.349	410.509	−911.671	27.492	−0.282
5200	85.147	602.495	521.913	419.025	−913.184	45.921	−0.461
5300	85.127	604.116	523.449	427.539	−914.695	64.380	−0.635
5400	85.106	605.707	524.957	436.051	−916.204	82.867	−0.802
5500	85.086	607.269	526.440	444.560	−917.708	101.382	−0.963
5600	85.065	608.802	527.897	453.068	−919.205	119.925	−1.119
5700	85.044	610.307	529.330	461.573	−920.694	138.494	−1.269
5800	85.023	611.786	530.738	470.076	−922.173	157.088	−1.415
5900	85.002	613.239	532.125	478.578	−923.640	175.709	−1.556
6000	84.981	614.668	533.488	487.077	−925.095	194.354	−1.692

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

$S°(298.15\ K) = [172.05]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-616.1 \pm 67]\ kJ·mol^{-1}$

$\Delta\ H°(298.15\ K) = [-636.0 \pm 67]\ kJ·mol^{-1}$

Enthalpy of Formation

Larsen and Leddy[1] studied the reaction Zr(cr) + 3 $ZrBr_4$(g) = 4 $ZrBr_3$(cr) in the temperature range 473 to 973 K and pressure range 5 to 15 atm. They present a plot of the fractional reaction, for a series of temperatures, as a function of the reaction time; however, they express doubt concerning the attainment of thermodynamic equilibrium.

The Gibbs energy function change for this reaction was calculated at 100 K invervals from 500 to 1100 K. At each temperature, the equilibrium constant was assumed to be 1, and $\Delta_r H$(298.15 K) accordingly calculated. These values and the enthalpy of formation of $ZrBr_4$(g) [Refer to the $ZrBr_4$ table] were used to compute a series of values for the standard enthalpy of formation of $ZrBr_3$(cr). The following table gives representative values at four temperatures.

T/K	K_p	$\Delta_r H°$(298.15 K) kcal·mol^{-1}	$\Delta_f H°$($ZrBr_3$ cr, 298.15 K) kcal·mol^{-1}
500	1	−70.26	−132.8
700	1	−96.48	−139.3
900	1	−121.75	−145.6
1100	1	−146.28	−151.8

If one assumes an initial pressure of from 0 to 10 atm for $ZrBr_4$ and stoichiometric amounts of reactants, then, on the basis of zirconium, the reaction must proceed to the extent of 80 to 90% for the pressure of $ZrBr_4$ to attain a value of 1 atm and hence an equilibrium constant of 1. The data of Larsen and Leddy[1] indicate about 82% reaction at 973 K. It was assumed that around 1100 K the equilibrium constant attains a value of 1 giving −152 kcal·mol^{-1} (−635.968 kJ·mol^{-1}) for the enthaply of formation of $ZrBr_3$(cr) at 298.15 K. The limits of error were taken to be ±16 kcal·mol^{-1} which corresponds to a ±500 K temperature spread in the above table.

A 2nd law calculation of their data was carried out but the results are of doubtful value in view of the uncertainty in the attainment of equilibrium at the lower temperatures.

Heat Capacity and Entropy

The heat capacity was estimated in the same manner as for $ZrBr_4$(cr) [see $ZrBr_4$(cr) table]. The values for θ_D and θ_E were taken to be the same as those estimated for $ZrBr_4$(cr). The internal contribution was obtained from the estimated $ZrBr_3$ vibrational frequencies and the anharmonicity factor "a" was taken to be 2.5×10^{-3}. The specific heat above 300 K was obtained by graphical extrapolation.

It was assumed, in the above estimation, that the crystalline lattice is made up of $ZrBr_3$ molecules. However, Holze[2] concluded that crystalline ZrI_3 was composed of a chain lattice of $(Zr_2I_6)_n$ units. A chain lattice of $(Zr_2Br_6)_n$ units is probably a better representation of the solid state structure of $ZrBr_3$. Until more quantitative data becomes available, however, it is felt that the above analysis gives a fair approximation to the heat capacity of $ZrBr_3$.

Disproportionation Data

As detailed above, this was assumed to be 1100 ± 500 K.

Liquid Phase

It is assumed that the liquid phase is thermodynamically unstable under ordinary conditions.

Sublimation Data

The enthalpy of sublimation at 298.15 K was obtained from the difference in the enthalpy of formation of the gas and solid at 298.15 K. The sublimation point was obtained from the Gibbs energy crossover between gas and solid at one bar.

References

[1]E. M. Larsen and J. J. Leddy, J. Am. Chem. Soc. 78, 5983 (1956).
[2]E. Holze in R. F. Rolsten, "Iodide Metals and Metal Iodides," John Wiley and Sons, Inc., New York, p. 46 (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})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−22.372	−616.078	−616.078	INFINITE
100	74.421	74.693	255.609	−18.092	−616.874	−614.861	321.170
200	93.232	133.499	180.987	−9.498	−617.825	−612.489	159.966
298.15	99.483	172.054	172.054	0.	−635.968	−607.607	106.450
300	99.562	172.670	172.056	0.184	−636.040	−607.430	105.763
400	102.508	201.756	176.002	10.302	−680.202	−588.696	76.876
500	103.763	224.773	183.535	20.619	−678.047	−566.068	59.137
600	104.600	243 771	192.037	31.040	−675.896	−543.874	47.348
700	105.018	259.927	200.611	41.521	−673.790	−522.038	38.955
800	105.437	273.978	208.922	52.044	−671.745	−500.500	32.679
900	105.855	286.422	216.855	62.610	−669.773	−479.213	27.813
1000	106.064	297.587	224.380	73.207	−667.892	−458.142	23.931
1100	106.148	307.700	231.502	83.818	−666.128	−437.253	20.763
1200	106.232	316.940	238.242	94.437	−668.199	−416.298	18.121
1300	106.315	325.447	244.628	105.065	−666.140	−395.390	15.887
1400	106.357	333.327	250.685	115.698	−664.132	−374.639	13.978
1500	106.399	340.666	256.442	126.336	−662.185	−354.029	12.328
1600	106.441	347.534	261.923	136.978	−660.314	−333.547	10.889
1700	106.483	353.989	267.151	147.624	−658.530	−313.179	9.623
1800	106.525	360.076	272.146	158.275	−656.846	−292.913	8.500
1900	106.566	365.837	276.927	168.929	−655.276	−272.738	7.498
2000	106.608	371.304	281.510	179.588	−653.832	−252.642	6.598

PREVIOUS: March 1962 CURRENT: June 1964

$S°(298.15\ K) = [371.58]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-408]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-431]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[255](1)
[120](1)
[273](2)
[95](2)

Ground State Quantum Weight: [2] $\sigma = [3]$

Point Group: $[C_{3v}]$

Bond Distance: Zr–Br = [2.39] Å

Bond Angle: Br–Zr–Br = [98]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.77605 \times 10^{-111}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpies of formation, from the gaseous atoms, of the gaseous zirconium tetrahalides are computed from data issued in these JANAF tables. The zirconium–halide bond energy, taken as 1/4 of this enthaply of formation, is found to be linear with internuclear separation. From gaseous titanium tri– and tetrachloride, it is found that the bond energy of the trichloride is around 7 $kcal·mol^{-1}$ greater than that for titanium tetrachloride. This amount is added to the bond energy of zirconium tetrachloride to get that of zirconium trichloride which, when used with its estimated internuclear distance, is found to lie almost exactly on the bond energy versus internuclear distance curve for the tetrahalides. The bond energy for each of the gaseous trihalides of zirconium is determined from this curve and their estimated bond distances.

For zirconium tribromide, the enthaply of formation from the gaseous atoms is −329 kcal mol^{-1} and from the elements in their standard state, −103 kcal mol^{-1} (−430.952 $kJ·mol^{-1}$).

Heat Capacity and Entropy

The measured internuclear distances for the tribromides of P, As, and Sb are plotted as a function of the atomic weight of these atoms and a smooth curve is drawn through the points. The internuclear distance for $ZrBr_3$ is taken from this plot. The bond angle is assumed to be intermediate between the bond angles of $AsBr_3$ and $SbBr_3$; it is taken to be 98°. The principal moments of inertia are: $I_A = I_B = 101.4161 \times 10^{-39}$ gm cm^2, $I_C = 172.6792 \times 10^{-39}$ g·cm^2.

The measured vibrational frequencies for the tribromides of phosphorus, arsenic, and antimony are plotted as a function of internuclear distance. Smooth curves through these points are obtained for υ_1, υ_2, and υ_4; these curves and the estimated $ZrBr_3$ bond distance are used to obtain correlation values of υ_1, υ_2, and υ_4 for $ZrBr_3$. Force constants, assuming a valence force field and a Br–Zr–Br angle of 98°, are derived from the above values for υ_1 and υ_2. These force constants are then used to derive values for υ_3 and υ_4. By a process of successive approximation, a set of force constants are obtained which give frequencies in good agreement with the three correlation values. The three correlation frequencies and the derived frequency are used in this table.

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	−19.302	−407.993	−407.993	INFINITE
100	62.307	292.306	439.075	−14.677	−408.444	−428.192	223.664
200	75.575	340.557	378.756	−7.640	−410.951	−447.026	116.751
250	78.032	357.710	372.886	−3.794	−412.545	−455.867	95.248
298.15	79.443	371.585	371.585	0.	−430.952	−462.081	80.955
300	79.486	372.076	371.586	0.147	−431.062	−462.274	80.489
350	80.406	384.403	372.558	4.146	−477.309	−464.937	69.388
400	81.022	395.183	374.726	8.183	−477.306	−463.169	60.484
450	81.453	404.752	377.541	12.245	−477.310	−461.402	53.558
500	81.766	413.351	380.699	16.326	−477.324	−459.634	48.018
600	82.180	428.299	387.424	24.525	−477.396	−456.090	39.706
700	82.432	440.987	394.192	32.757	−477.538	−452.529	33.768
800	82.597	452.006	400.745	41.009	−477.765	−448.942	29.313
900	82.711	461 742	406.992	49.274	−478.093	−445.321	25.846
1000	82.793	470.460	412.911	57.550	−478.534	−441.657	23.070
1100	82.853	478.354	418.507	65.832	−479.098	−437.943	20.796
1200	82.900	485.566	423.799	74.120	−483.500	−433.950	18.889
1300	82.936	492.203	428.809	82.412	−483.777	−429.810	17.270
1400	82 964	498.350	433.559	90 707	−484.107	−425.647	15.881
1500	82.987	504.075	438.072	99.004	−484.501	−421.458	14.676
1600	83.006	509.431	442.366	107.304	−484.972	−417.240	13.621
1700	83.022	514.464	446.461	115.606	−485.533	−412.990	12.690
1800	83.035	519.210	450.372	123.909	−486.197	−408.704	11.860
1900	83.046	523.700	454.114	132.213	−486.977	−404.378	11.117
2000	83.056	527.960	457.701	140.518	−487.886	−400.008	10.447
2100	83.064	532.012	461.144	148.824	−488.940	−395.589	9.840
2200	83.071	535.876	464.453	157.130	−511.472	−390.370	9.269
2300	83.077	539.569	467.640	165.438	−513.267	−384.825	8.740
2400	83.083	543.105	470.711	173.746	−515.094	−379.202	8.253
2500	83.088	546.497	473.675	182.054	−516.955	−373.501	7.804
2600	83.092	549.756	476.539	190.363	−518.850	−367.726	7.388
2700	83.096	552.892	479.309	198.673	−520.778	−361.877	7.001
2800	83.099	555.914	481.991	206.983	−522.737	−355.956	6.640
2900	83.102	558.830	484.591	215.293	−524.727	−349.965	6.304
3000	83.105	561.647	487 113	223.603	−526.743	−343.904	5.988
3100	83.107	564.372	489.561	231 914	−528.784	−337.776	5.691
3200	83.110	567 011	491.941	240.224	−530.846	−331.582	5.413
3300	83.112	569.568	494.254	248.535	−532.924	−325.322	5.149
3400	83.114	572.049	496.506	256.847	−535.016	−319.000	4.901
3500	83.115	574.459	498.699	265.158	−537.117	−312.616	4.666
3600	83.117	576.800	500.836	273.470	−539.223	−306.172	4.442
3700	83.118	579.077	502.920	281.782	−541.330	−299.669	4.231
3800	83.120	581.294	504.954	290.093	−543.435	−293.110	4.029
3900	83.121	583.453	506.939	298.405	−545.533	−286.495	3.837
4000	83.122	585.557	508.878	306.718	−547.622	−279.826	3.654
4100	83.123	587.610	510.773	315.030	−549.697	−273.106	3.479
4200	83.124	589.613	512.627	323.342	−551.756	−266.335	3.312
4300	83.125	591.569	514.440	331.655	−553.796	−259.515	3.152
4400	83.126	593.480	516.215	339.967	−555.815	−252.648	2.999
4500	83.127	595.348	517.953	348.280	−557.811	−245.735	2.852
4600	83.127	597.175	519.655	356.593	−559.781	−238.778	2.711
4700	83.128	598.963	521.324	364.905	−561.723	−231.779	2.576
4800	83.129	600.713	522.959	373.218	−1124.574	−213.121	2.319
4900	83.129	602.427	524.564	381.531	−1126.110	−194.117	2.069
5000	83.130	604.107	526.138	389.844	−1127.632	−175.081	1.829
5100	83.131	605.753	527.683	398.157	−1129.139	−156.015	1.598
5200	83.131	607.367	529.200	406.470	−1130.628	−136.920	1.375
5300	83.132	608.951	530.690	414.783	−1132.097	−117.796	1.161
5400	83.132	610.504	532.153	423.096	−1133.545	−98.644	0.954
5500	83.132	612.030	533.592	431.410	−1134.971	−79.466	0.755
5600	83.133	613.528	535.006	439.723	−1136.372	−60.263	0.562
5700	83.133	614.999	536.396	448.036	−1137.749	−41.034	0.376
5800	83.134	616.445	537.764	456.350	−1139.100	−21.782	0.196
5900	83.134	617.866	539.110	464.663	−1140.424	−2.506	0.022
6000	83.134	619.263	540.434	472.976	−1141.720	16.791	−0.146

PREVIOUS. June 1964 (1 atm) CURRENT June 1964 (1 bar)

$S°(298.15\ K)$ = [516.0] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -228.3 \pm 8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -253.1 \pm 8\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[5]
[4450]	[5]
[6900]	[5]

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[110](1)	[75](1)	[95](2)
[70](1)	[100](1)	[24](2)
[110](1)	[115](1)	[190](2)

Point Group: $[D_{2h}]$ σ = [4]
Bond Distance: Fe–Br = [2.24] Å
Bond Angles: $Fe–Br_{bridge}–Fe$ = [90]°; $Br_{bridge}–Fe–Br_{bridge}$ = [90]°; $Br–Fe–Br_{bridge}$ = [135]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.44991 × 10^{-110}] $g^3·cm^6$

Enthaply of Formation

The chemical equilibria, 622–665 K, for the reaction $Fe_2Br_4(g) = 2\ FeBr_2(g)$ were studied by Porter and Schoonmaker,[1] using a mass spectrometer. Based on the reported partial pressures for the two species, the enthalpy change $\Delta_r H°(298.15\ K)$ for the reaction is evaluated by both the 2nd and 3rd law method to be 40.36 ± 2.0 and 40.75 ± 0.2 $kcal·mol^{-1}$, respectively. Using the 3rd law $\Delta_r H°$ value and $\Delta_f H°(FeBr_2, g, 298.15\ K) = -9.9 \pm 0.5\ kcal·mol^{-1}$, the enthaply of formation $\Delta_f H°(Fe_2Br_4, g, 298.15\ K)$ is calculated as −60.5 ± 2.0 $kcal·mol^{-1}$ (−253.132 $kJ·mol^{-1}$) and is adopted.

Heat Capacity and Entropy

The molecular structure is assumed to be planar. The two Fe atoms are at the two opposite corners of a square. The other two corners of the square are occupied by two Br atoms. The two remaining Br atoms are situated outside the square on a straight line joining the two Fe atoms. The Fe–Br bond distance was estimated to be the same as that in the $FeBr_2(g)$ molecule. The first six vibrational frequencies were estimated by comparison with those for $K_2Br_2(g)$ calculated by Berkowitz[2]. The last three degenerate frequencies were assigned arbitrarily in order to give good second and third law agreement for the heats of dissociation of dimer to monomer. The order of the frequencies listed above is arbitrary and not related to their species types.

The electronic levels and quantum weights were estimated by comparison with those for $FeBr_2(g)$. The principal moments of inertia are: $I_A = 66.5764 \times 10^{-39}$, $I_B = 434.5679 \times 10^{-39}$, and $I_C = 501.1443 \times 10^{-39}\ g·cm^2$.

References

[1]R. F. Porter and R. C. Schoonmaker, J. Phys. Chem. 63, 626 (1959).
[2]J. Berkowitz, J. Chem. Phys. 32, 1519 (1960).

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	−33.210	−228.310	−228.310	INFINITE
100	115.643	379.131	629.897	−25.077	−226.608	−252.539	131.913
200	127.972	464.315	527.906	−12.718	−227.590	−278.305	72.686
250	129.727	493.080	518.165	−6.271	−229.050	−290.829	60.765
298.15	130.683	516.018	516.018	0.	−253.132	−299.931	52.547
300	130.711	516.827	516.021	0.242	−253.263	−300.221	52.273
350	131.315	537.025	517.614	6.794	−314.584	−304.690	45.473
400	131.711	554.587	521.162	13.370	−314.351	−303.294	39.606
450	131.986	570.117	525.755	19.963	−314.236	−301.920	35.046
500	132.185	584.034	530.900	26.567	−314.242	−300.553	31.399
600	132.461	608.160	541.826	39.801	−314.620	−297.787	25.925
700	132.671	628.595	552.799	53.057	−315.491	−294.920	22.007
800	132.880	646.325	563.406	66.335	−316.948	−291.890	19.058
900	133.125	661.989	573.506	79.635	−319.234	−288.631	16.752
1000	133.420	676.030	583.069	92.961	−322.950	−285.051	14.890
1100	133.765	688.762	592.108	106.320	−328.442	−280.967	13.342
1200	134.155	700.418	600.655	119.716	−332.810	−276.496	12.036
1300	134.577	711.172	608.748	133.152	−333.862	−271.761	10.920
1400	135.018	721.162	616.425	146.632	−335.056	−266.941	9.960
1500	135.466	730.492	623.722	160.156	−336.391	−262.030	9.125
1600	135.908	739.249	630.671	173.725	−337.869	−257.025	8.391
1700	136.335	747.501	637.303	187.337	−341.395	−251.885	7.739
1800	136.737	755.306	643.644	200.991	−343.842	−246.550	7.155
1900	137.110	762.709	649.717	214.684	−374.643	−239.671	6.589
2000	137.448	769.750	655.544	228.412	−377.891	−232.483	6.072
2100	137.749	776.464	661.144	242.172	−381.144	−225.132	5.600
2200	138.012	782.878	666.533	255.960	−384.408	−217.627	5.167
2300	138.238	789.018	671.726	269.773	−387.691	−209.973	4.769
2400	138.426	794.906	676.736	283.607	−390.997	−202.175	4.400
2500	138.579	800.560	681.577	297.457	−394.332	−194.239	4.058
2600	138.699	805.997	686.258	311.321	−397.699	−186.169	3.740
2700	138.789	811.234	690.791	325.196	−401.100	−177.968	3.443
2800	138.850	816.282	695.183	339.078	−404.536	−169.642	3.165
2900	138.886	821.155	699.443	352.965	−408.008	−161.191	2.903
3000	138.899	825.864	703.579	366.855	−411.514	−152.621	2.657
3100	138.892	830.418	707.598	380.744	−415.052	−143.933	2.425
3200	138.867	834.828	711.505	394.632	−1115.220	−120.283	1.963
3300	138.828	839.100	715.307	408.517	−1115.013	−89.194	1.412
3400	138.774	843.244	719.009	422.397	−1114.894	−58.111	0.893
3500	138.710	847.266	722.617	436.272	−1114.860	−27.030	0.403
3600	138.636	851.172	726.134	450.139	−1114.908	4.052	−0.059
3700	138.555	854.970	729.565	463.999	−1115.036	35.136	−0.496
3800	138.467	858.664	732.914	477.850	−1115.239	66.224	−0.910
3900	138.373	862.259	736.184	491.692	−1115.517	97.318	−1.303
4000	138.276	865.761	739.380	505.524	−1115.865	128.421	−1.677
4100	138.175	869.174	742.504	519.347	−1116.284	159.533	−2.032
4200	138.072	872.503	745.560	533.159	−1116.769	190.656	−2.371
4300	137.968	875.751	748.550	546.961	−1117.321	221.792	−2.694
4400	137.863	878.921	751.477	560.753	−1117.938	252.941	−3.003
4500	137.757	882.018	754.344	574.534	−1118.620	284.105	−3.298
4600	137.652	885.045	757.153	588.304	−1119.365	315.285	−3.580
4700	137.547	888.004	759.905	602.064	−1120.173	346.481	−3.851
4800	137.443	890.899	762.604	615.814	−1121.046	377.696	−4.110
4900	137.341	893.732	765.252	629.553	−1121.984	408.930	−4.359
5000	137.240	896.505	767.849	643.282	−1122.987	440.183	−4.599
5100	137.140	899.222	770.398	657.001	−1124.057	471.457	−4.829
5200	137.042	901.884	772.901	670.710	−1125.196	502.752	−5.050
5300	136.946	904.494	775.360	684.410	−1126.407	534.071	−5.264
5400	136.852	907.053	777.775	698.099	−1127.691	565.412	−5.469
5500	136.760	909.563	780.148	711.780	−1129.052	596.779	−5.668
5600	136.671	912.026	782.481	725.452	−1130.495	628.170	−5.859
5700	136.583	914.444	784.775	739.114	−1132.021	659.589	−6.044
5800	136.497	916.819	787.032	752.768	−1133.637	691.033	−6.223
5900	136.414	919.152	789.251	766.414	−1135.348	722.508	−6.397
6000	136.333	921.444	791.435	780.051	−1137.158	754.012	−6.564

PREVIOUS. September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$S°(298.15\ K) = [461.3 \pm 20.9]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -739.7 \pm 2.09\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -767.8 \pm 20.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[182](1)	[188](1)	[100](1)
[120](1)	[228](1)	[100](1)
[207](1)	[125](1)	[75](1)
[134](1)	[125](1)	[75](1)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: [D_{2h}]
Bond Distances: Mg–Br = [2.34] Å; Mg–Br'(bridge) = [2.60] Å
Bond Angles: Mg–Br'_{bridge}–Mg = [90]°; Br'_{bridge}–Mg–Br'_{bridge} = [90]°
Br–Mg–Br'(bridge) = [135]°
Product of Moments of Inertia: $I_A I_B I_C$ = [2.55371 × 10^{-110}] $g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°$ of the dimer is based on an analysis of mass spectrometric data reported by Berkowitz and Marquart[1] These studies have revealed the presence of approximately 2% dimer in the equilibrium vapor over $MgBr_2$(cr) at around 800 K. The existence of the dimer was inferred from the observed ion intensities for $Mg_2Br_3^+$. Berkowitz and Marquart[1] reported a 2nd law $\Delta_r H$(803 K) of 12.9 kcal·mol^{-1} for the process $MgBr_2$(cr) + $MgBr_2$(g) = Mg_2Br_4(g). When corrected to 298.15 K this value gives $\Delta_r H°$ = 14.0 kcal·mol^{-1} which leads to $\Delta_f H°(Mg_2Br_4, g, 298.15\ K) = -183.7$ kcal·mol^{-1}. The absolute pressure of Mg_2Br_4(g) was also measured at 798 K by integrating the ion current during complete volatilization of a previously weighed sample. A 3rd law analysis of the reported pressure gives $\Delta_{sub} H°(298.15\ K) = 67.4$ kcal·mol^{-1} for 2 $MgBr_2$(cr) = Mg_2Br_4(g). This value for the enthalpy of sublimation leads to $\Delta_f H°(Mg_2Br_4, g, 298.15\ K) = -183.2$ kcal·mol^{-1} which is in excellent agreement with the 2nd law result. We adopt an average value (−183.5 kcal·mol^{-1}, −767.764 kJ·mol^{-1}) of these two results. The uncertainty in $\Delta_f H°$ is estimated as ±5.0 kcal·mol^{-1}, and the adopted $\Delta_f H°$ value value corresponds to a dimerization energy for $MgBr_2$(g) of 38.7 kcal·mol^{-1}.

Heat Capacity and Entropy

The dimer molecule is assumed to have a bridge–bond structure of D_{2h} symmetry similar to that suggested by Thompson and Carlson[2] for the dimers of several transition metal dichlorides. The two outer Mg–Br bond lengths are assumed to be the same as that for $MgBr_2$[3](2.34 Å). The four ring Mg–Br'(bridge) bond lengths are taken to be somewhat longer (2.6 Å). The four atoms which lie in the ring form a square. The Br'(bridge)–Mg–Br bond angle is estimated as 135°. The principal moments of inertia are: $I_A = 89.6957 \times 10^{-39}$, $I_B = 490.6138 \times 10^{-39}$, and $I_C = 580.3094 \times 10^{-39}$ g·cm^2.

The vibratonal frequencies of the ring (first six listed) are taken equal to those for Na_2Br_2.[3] These frequencies were obtained by Berkowitz[4] from ionic model calculations. The remaining six frequencies are estimated by analogy with those for $MgBr_2$ and Mg_2Cl_4.[3] Following the observations made by Thompson and Carlson,[2] all of the dimer frequencies are assumed to lie above the bending frequency (ν_2 = 70 cm^{-1}) of the monomer.[3] Our adopted functions for the monomer and dimer reproduce the pressures measured by Berkowitz and Marquart[1] and show that the dimer becomes an increasingly important vapor species with rising temperatures.

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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	−30.967	−739.716	−739.716	INFINITE
100	105.171	329.984	572.231	−24.225	−739.844	−760.172	397.073
200	124.475	410.634	473.038	−12.481	−741.917	−779.818	203.668
250	127.401	438.757	463.463	−6.176	−743.586	−789.111	164.876
298.15	129.013	461.347	461.347	0.	−767.764	−795.072	139.293
300	129.061	462.145	461.349	0.239	−767.897	−795.241	138.464
350	130.087	482.123	462.925	6.719	−829.242	−796.439	118.862
400	130.763	499.540	466.436	13.242	−828.965	−791.773	103.395
450	131.231	514.971	470.988	19.792	−828.738	−787.138	91.369
500	131.569	528.816	476.090	26.363	−828.560	−782.526	81.750
600	132.011	552.846	486.940	39.544	−828.353	−773.342	67.325
700	132.280	573.218	497.847	52.759	−828.359	−764.175	57.023
800	132.455	590.893	508.398	65.996	−828.602	−754.993	49.296
900	132.575	606.502	518.448	79.248	−829.116	−745.764	43.283
1000	132.661	620.474	527.964	92.510	−847.114	−735.037	38.394
1100	132.725	633.122	536.958	105.780	−848.273	−723.773	34.369
1200	132.774	644.672	545.460	119.055	−849.443	−712.403	31.010
1300	132.812	655.302	553.506	132.334	−850.626	−700.935	28.164
1400	132.842	665.145	561.133	145.617	−1106.643	−683.042	25.485
1500	132.866	674.311	568.376	158.903	−1105.152	−652.837	22.734
1600	132.886	682.887	575.268	172.190	−1103.681	−622.731	20.330
1700	132.903	690.943	581.838	185.480	−1102.230	−592.716	18.212
1800	132.916	698.540	588.112	198.771	−1100.804	−562.786	16.332
1900	132.928	705.727	594.115	212.063	−1099.407	−532.934	14.651
2000	132.938	712.546	599.868	225.356	−1098.042	−503.155	13.141
2100	132.947	719.032	605.389	238.650	−1096.714	−473.443	11.776
2200	132.954	725.217	610.696	251.945	−1095.426	−443.794	10.537
2300	132.961	731.127	615.805	265.241	−1094.180	−414.203	9.407
2400	132.966	736.786	620.729	278.538	−1092.980	−384.664	8.372
2500	132.971	742.214	625.480	291.834	−1091.828	−355.175	7.421
2600	132.976	747.429	630.071	305.132	−1090.724	−325.731	6.544
2700	132.980	752.448	634.511	318.430	−1089.669	−296.328	5.733
2800	132.983	757.284	638.810	331.728	−1088.663	−266.964	4.980
2900	132.987	761.951	642.976	345.026	−1087.704	−237.634	4.280
3000	132.989	766.459	647.018	358.325	−1086.793	−208.337	3.627
3100	132.992	770.820	650.941	371.624	−1085.927	−179.070	3.017
3200	132.994	775.042	654.754	384.923	−1085.104	−149.830	2.446
3300	132.997	779.135	658.461	398.223	−1084.323	−120.614	1.909
3400	132.999	783.105	662.069	411.523	−1083.582	−91.422	1.405
3500	133.000	786.961	665.583	424.823	−1082.880	−62.252	0.929
3600	133.002	790.707	669.006	438.123	−1082.214	−33.100	0.480
3700	133.004	794.351	672.345	451.423	−1081.585	−3.966	0.056
3800	133.005	797.898	675.603	464.724	−1080.990	25.150	−0.346
3900	133.006	801.353	678.783	478.024	−1080.430	54.251	−0.727
4000	133.007	804.721	681.890	491.325	−1079.905	83.339	−1.088
4100	133.009	808.005	684.926	504.626	−1079.414	112.414	−1.432
4200	133.010	811.210	687.894	517.926	−1078.959	141.477	−1.760
4300	133.011	814.340	690.799	531.227	−1078.540	170.530	−2.072
4400	133.011	817.398	693.641	544.529	−1078.158	199.574	−2.369
4500	133.012	820.387	696.425	557.830	−1077.815	228.610	−2.654
4600	133.013	823.311	699.152	571.131	−1077.514	257.638	−2.926
4700	133.014	826.171	701.824	584.432	−1077.255	286.660	−3.186
4800	133.014	828.972	704.444	597.734	−1077.043	315.677	−3.435
4900	133.015	831.714	707.013	611.035	−1076.878	344.690	−3.674
5000	133.016	834.401	709.534	624.337	−1076.764	373.701	−3.904
5100	133.016	837.036	712.008	637.638	−1076.703	402.710	−4.125
5200	133.017	839.618	714.438	650.940	−1076.698	431.717	−4.337
5300	133.017	842.152	716.824	664.242	−1076.751	460.726	−4.541
5400	133.018	844.639	719.168	677.544	−1076.866	489.736	−4.737
5500	133.018	847.079	721.471	690.845	−1077.046	518.749	−4.927
5600	133.019	849.476	723.736	704.147	−1077.293	547.765	−5.109
5700	133.019	851.831	725.962	717.449	−1077.611	576.787	−5.286
5800	133.020	854.144	728.152	730.751	−1078.003	605.814	−5.456
5900	133.020	856.418	730.307	744.053	−1078.471	634.849	−5.621
6000	133.020	858.654	732.428	757.355	−1079.019	663.893	−5.780

PREVIOUS. June 1974 (1 atm) CURRENT. June 1974 (1 bar)

$S°(298.15\ K)$ = [209.2 ± 17] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K)$ = −304.2 ± 8 $kJ·mol^{-1}$

Enthalpy of Formation

Shchukarev *et al.*[1] have measured the enthalpy of solution of $MoBr_4$(cr) from which Dellien *et al.*[2] have obtained $\Delta_f H°(MoBr_4, cr, 298.15\ K)$ = −70.35 $kcal·mol^{-1}$. Brewer[3] has reviewed the equilibrium data of Oppermann[4] (see the discussion on the $MoBr_4$(g) table[5] as well as the above measurements and obtained $\Delta_f H°(298.15\ K)$ = −72.7 ± 2 $kcal·mol^{-1}$ (−304.177 $kJ·mol^{-1}$) which is the value adopted here. This differs from the value $\Delta_f H°(298.15\ K)$ = −76.8 $kcal·mol^{-1}$ adopted by NBS.[6]

Heat Capacity and Entropy

Brewer[3] estimated $C_p°(298.15\ K)$ = 31.8 ± 2 $cal·K^{-1}·mol^{-1}$ and $S°(298.15\ K)$ = 50.0 $cal·K^{-1}·mol^{-1}$ (209.200 $kJ·mol^{-1}$). Other estimates are $C_p°(298.15\ K)$ = 29.5 $cal·K^{-1}·mol^{-1}$ from the ionic contributions of Kubaschewski and Unal[7] and $S°(298.15\ K)$ = 51.4 $cal·K^{-1}·mol^{-1}$ from the additive entropy constants of Stull and Prophet.[8] We adopt Brewer's values[3] of $C_p°$ and $S°$ at 298.15 K and estimate $C_p°$ at higher temperatures by comparison with $MoBr_2$(cr) and $MoBr_3$(cr).[5]

Decomposition Data

T_{dcm} is the calculated temperature at which $\Delta_r G° = 0$ for the reaction $MoBr_4$(cr) = $MoBr_3$(cr) + 0.5 Br_2(g). Carnell *et al.*[9] have given conditions for the formation of $MoBr_4$(cr) and its dissociation to $MoBr_3$(cr).

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[3] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, September 29, 1978; preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[4] H. Oppermann, Z. anorg. allg. Chem. 395, 249 (1973).
[5] JANAF Thermochemical Tables: $MoBr_4$(g), $MoBr_3$(cr) and $MoBr_2$(cr), 9–30–78.
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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	133.051	209.200	209.200	0.	−304.177	−267.261	46.823
300	133.093	210.023	209.203	0.246	−304.255	−267.031	46.494
400	135.143	248.601	214.449	13.661	−362.256	−242.498	31.667
500	136.817	278.930	224.418	27.256	−358.593	−212.982	22.250
600	138.909	304.061	235.656	41.043	−354.861	−184.208	16.037
700	140.844	325.621	247.004	55.032	−351.022	−156.068	11.646
800	142.674	344.549	258.038	69.208	−347.071	−128.486	8.389
900	144.400	361.454	268.606	83.563	−343.011	−101.405	5.885
1000	146.022	376.753	278.668	98.085	−338.850	−74.782	3.906

PREVIOUS: CURRENT: September 1978

$S°(298.15\ K) = 418.89 \pm 8\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -142.4 \pm 8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -171.1 \pm 8\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ, cm^{-1}	g_i
0	[3]
[15000]	[11]
[20000]	[9]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[230](1)	[80](3)
[70](2)	[390](3)

Point Group: T_d
Bond Distance: Mo–Br = 2.39 ± 0.02
Bond Angle: Br–Mo–Br = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = 8.25596 \times 10^{-111}\ g^3·cm^6$

Enthalpy of Formation

Oppermann[1] made careful pressure measurements on the systems $MoBr_3(cr) + Br_2(g)$, $MoBr_{2+x}(cr) + MoBr_{3-y}(cr)$ and $MoBr_2(cr) + Mo(cr)$. Brewer,[2] by comparison with the tungsten–bromide system, indicated the possibility of intermediate phases between $MoBr_2$ and $MoBr_3$ and thus modified the treatment of the data. Brewer used a 3rd law treatment combined with independent data on the enthalpies of formation of $MoBr_2(cr)$, $MoBr_3(cr)$ and $MoBr_4(cr)$ and removed the restriction that $x = 0$ and $y = 0$. For this reason we adopt the value of $\Delta_f H°(298.15\ K)$ obtained by Brewer, $-40.9 \pm 2\ kcal·mol^{-1}$ ($-171.126\ kJ·mol^{-1}$), rather than the value of $-36.7\ kcal·mol^{-1}$ reported by Dellien *et al.*[7]

Heat Capacity and Entropy

Brewer[2] used a slight modification of the vibrational frequencies and internuclear distance estimated by Lofgren.[3] He assumed an Mo–Br distance of 2.42 Å in all the molybdenum bromides. The electron diffraction study of Spiridonov and Romanov[4] established the structure of $MoBr_4(g)$ to be a regular tetrahedron with an Mo–Br distance of 2.39 ± 0.02 Å.[5] This is the value adopted here. Our value for the product of the moments of inertia $I_A I_B I_C = 8.256 \times 10^{-111}\ g^3·cm^6$ is 8% lower than Brewer's value ($8.898 \times 10^{-111}\ g^3·cm^6$). This reduces $S°$ by 0.1 $cal·K^{-1}·mol^{-1}$ at all temperatures. Electronic levels are assumed to be the same as the MoF_4 levels,[6] which Brewer[2] estimated from crystal field theory.

References

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[6] JANAF Thermochemical Tables: $MoCl_6(g)$, $MoCl_5(g)$ and $MoCl_4(g)$, 12-31-68; $MoF_4(g)$, 12-30-78.
[7] I. Dellien, F. M. Hall, and L. G. Hepler, Chem. Rev. 76, 283 (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	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0	0.	INFINITE	−24.839	−142.361	−142.361	INFINITE
100	80.869	316.427	506.136	−18.971	−142.571	−162.741	85.007
200	97.616	378.758	428.168	−9.882	−145.126	−182.014	47.537
250	100.942	400.931	420.574	−4.911	−146.904	−191.039	39.915
298.15	102.884	418.889	418.889	0.	−171.126	−196.728	34.466
300	102.942	419.526	418.891	0.190	−171.259	−196.887	34.281
350	104.222	435.498	420.150	5.372	−232.592	−197.799	29.520
400	105.084	449.474	422.960	10.606	−232.260	−192.851	25.184
450	105.690	461.888	426.609	15.876	−231.937	−187.944	21.816
500	106.131	473.048	430.704	21.172	−231.625	−183.073	19.126
600	106.716	492.454	439.426	31.817	−231.036	−173.419	15.097
700	107.074	508.934	448.208	42.508	−230.495	−163.859	12.227
800	107.308	523.248	456.713	53.228	−230.001	−154.374	10.080
900	107.470	535.897	464.822	63.967	−229.556	−144.948	8.413
1000	107.587	547.226	472.506	74.720	−229.164	−135.569	7.081
1100	107.673	557.485	479.772	85.483	−228.829	−126.226	5.994
1200	107.739	566.856	486.645	96.254	−228.561	−116.911	5.089
1300	107.791	575.482	493.151	107.031	−228.366	−107.615	4.324
1400	107.832	583.472	499.321	117.812	−228.254	−98.331	3.669
1500	107.867	590.913	505.181	128.597	−228.232	−89.053	3.101
1600	107.899	597.875	510.760	139.385	−228.309	−79.772	2.604
1700	107.929	604.418	516.078	150.177	−228.495	−70.483	2.166
1800	107.960	610.587	521.159	160.971	−228.800	−61.180	1.775
1900	107.995	616.426	526.021	171.769	−229.234	−51.857	1.426
2000	108.037	621.966	530.681	182.570	−229.810	−42.507	1.110
2100	108.089	627.238	535.154	193.377	−230.538	−33.125	0.824
2200	108.153	632.268	539.455	204.189	−231.430	−23.704	0.563
2300	108.232	637.077	543.596	215.008	−232.496	−14.238	0.323
2400	108.328	641.686	547.587	225.836	−233.747	−4.723	0.103
2500	108.444	646.110	551.440	236.674	−235.192	4.849	−0.101
2600	108.581	650.366	555.164	247.525	−236.853	14.482	−0.291
2700	108.741	654.467	558.766	258.391	−238.765	24.185	−0.468
2800	108.924	658.425	562.255	269.274	−240.987	33.963	−0.634
2900	109.132	662.250	565.638	280.177	−279.479	43.877	−0.790
3000	109.365	665.954	568.920	291.101	−280.510	55.045	−0.958
3100	109.623	669.544	572.109	302.050	−281.550	66.247	−1.116
3200	109.904	673.029	575.208	313.027	−282.591	77.483	−1.265
3300	110.209	676.416	578.224	324.032	−283.625	88.751	−1.405
3400	110.536	679.710	581.161	335.069	−284.646	100.051	−1.537
3500	110.884	682.920	584.022	346.140	−285.645	111.380	−1.662
3600	111.251	686.048	586.813	357.247	−286.616	122.737	−1.781
3700	111.635	689.102	589.537	368.391	−287.550	134.121	−1.893
3800	112.035	692.084	592.196	379.574	−288.443	145.529	−2.000
3900	112.447	695.000	594.795	390.798	−289.286	156.961	−2.102
4000	112.870	697.852	597.336	402.064	−290.075	168.413	−2.199
4100	113.301	700.644	599.822	413.372	−290.803	179.885	−2.292
4200	113.738	703.380	602.255	424.724	−291.467	191.373	−2.380
4300	114.178	706.061	604.638	436.120	−292.062	202.876	−2.464
4400	114.620	708.691	606.973	447.560	−292.584	214.393	−2.545
4500	115.061	711.272	609.262	459.044	−293.031	225.920	−2.622
4600	115.498	713.806	611.507	470.572	−293.400	237.457	−2.696
4700	115.931	716.294	613.710	482.144	−293.689	249.000	−2.767
4800	116.356	718.739	615.873	493.758	−293.898	260.549	−2.835
4900	116.772	721.143	617.997	505.414	−294.025	272.102	−2.901
5000	117.177	723.506	620.084	517.112	−885.455	289.387	−3.023
5100	117.570	725.830	622.134	528.849	−887.097	312.901	−3.205
5200	117.949	728.117	624.151	540.625	−888.805	336.446	−3.380
5300	118.313	730.367	626.134	552.439	−890.575	360.026	−3.548
5400	118.662	732.582	628.084	564.288	−892.410	383.639	−3.711
5500	118.993	734.762	630.004	576.170	−894.306	407.287	−3.868
5600	119.307	736.909	631.894	588.086	−896.265	430.970	−4.020
5700	119.603	739.024	633.755	600.031	−898.283	454.689	−4.167
5800	119.880	741.106	635.588	612.006	−900.362	478.442	−4.309
5900	120.139	743.158	637.394	624.007	−902.498	502.232	−4.446
6000	120.378	745.179	639.174	636.033	−904.696	526.060	−4.580

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

$S°(298.15\ K)$ = [426.20 ± 12.6] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−426.4 ± 84] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−456.4 ± 84] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[207](1)
[59](2)
[231](3)
[73](3)

Ground State Quantum Weight: [1] σ = 12
Point Group: [T_d]
Bond Distance: Pb–Br = [2.58] Å
Bond Angle: Br–Pb–Br = [109.4712]°
Product of Moments of Inertia: $I_A I_B I_C$ = [1.30647 × 10^{-110}] $g^3·cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(0\ K)$ = −101.9 ± 20 kcal mol^{-1} (−426.350 ± 84 $kJ·mol^{-1}$) is derived from the dissociation energy for the process $PbBr_4(g) = Pb(g) + 4\ Br(g)$. $D_0°$ = 11.34 eV is estimated from an intercomparison of the lead mono–, di–, and tetra– halides.[1] This adopted $D_0°$ value for $PbBr_4$(g) is greater than the $D_0°$ value for $PbBr_2$(g) by a factor of 2.09. The auxiliary values $\Delta_f H°$(Pb, g, 0 K) = 46.91 $kcal·mol^{-1}$ and $\Delta_f H°$(Br, g, 0 K) = 28.188 $kcal·mol^{-1}$ are used[1] $\Delta_f H°(PbBr_4, g, 298.15\ K) = -109.1 \pm 20$ $kcal·mol^{-1}$ (−456.361 ± 84 $kJ·mol^{-1}$) is calculated from $\Delta_f H°(0\ K)$.

Heat Capacity and Entropy

The molecular constants and vibrational frequencies are those calculated by Aleksandrovskaya *et al.*[2] Later works[3–5] mistakenly cite this work as observed data and use a bond distance of 2.54 Å rather than the 2.58 Å originally published.[2]

The principal moments of inertia are $I_A = I_B = I_C$ = 23.5227 × 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 PbI2(g), 12–31–73, PbCl(g) and $PbCl_2$(g), 6–30–73, Pb(g), 3–31–62;Br(g), 9–30–61.
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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	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−25.895	−426.359	−426.359	INFINITE
100	86.541	319.504	516.117	−19.661	−427.478	−444.976	232.432
200	100.868	385.092	435.680	−10.118	−430.262	−461.457	120.520
250	103.277	407.885	427.917	−5.008	−432.089	−469.054	98.003
298.15	104.631	426.201	426.201	0.	−456.361	−473.357	82.930
300	104.671	426.849	426.203	0.194	−456.497	−473.462	82.437
350	105.543	443.054	427.481	5.451	−517.895	−472.925	70.580
400	106.122	457.188	430.330	10.743	−517.637	−466.519	60.921
450	106.525	469.711	434.023	16.060	−517.400	−460.144	53.412
500	106.816	480.951	438.163	21.394	−517.183	−453.794	47.408
600	107.199	500.463	446.969	32.096	−516.809	−441.152	38.406
700	107.433	517.006	455.823	42.829	−521.375	−427.769	31.921
800	107.585	531.363	464.388	53.580	−521.146	−414.412	27.058
900	107.690	544.041	472.547	64.344	−520.895	−401.085	23.278
1000	107.765	555.391	480.274	75.117	−520.625	−387.788	20.256
1100	107.821	565.665	487.577	85.896	−520.337	−374.518	17.784
1200	107.863	575.048	494.481	96.681	−520.030	−361.275	15.726
1300	107.896	583.683	501.015	107.469	−519.714	−348.058	13.985
1400	107.922	591.680	507.209	118.260	−519.404	−334.865	12.494
1500	107.944	599.127	513.092	129.053	−519.113	−321.694	11.202
1600	107.961	606.094	518.689	139.848	−518.849	−308.542	10.073
1700	107.975	612.640	524.025	150.645	−518.619	−295.405	9.077
1800	107.987	618.812	529.121	161.443	−518.430	−282.280	8.192
1900	107.998	624.651	533.997	172.243	−518.289	−269.165	7.400
2000	108.006	630.190	538.669	183.043	−518.200	−256.055	6.687
2100	108.014	635.460	543.154	193.844	−695.388	−235.834	5.866
2200	108.020	640.485	547.464	204.645	−695.027	−213.960	5.080
2300	108.026	645.287	551.614	215.448	−694.797	−192.099	4.363
2400	108.031	649.885	555.613	226.251	−694.701	−170.245	3.705
2500	108.036	654.295	559.473	237.054	−694.741	−148.392	3.100
2600	108.039	658.532	563.202	247.858	−694.917	−126.535	2.542
2700	108.043	662.610	566.809	258.662	−695.225	−104.669	2.025
2800	108.046	666.539	570.301	269.466	−695.660	−82.789	1.544
2900	108.049	670.330	573.685	280.271	−696.216	−60.891	1 097
3000	108.051	673.993	576.968	291.076	−696.882	−38.972	0.679
3100	108.054	677.537	580.155	301.881	−697.649	−17.030	0.287
3200	108.056	680.967	583.252	312.687	−698.506	4.939	−0.081
3300	108.058	684.292	586.264	323.493	−699.441	26.936	−0.426
3400	108.059	687.518	589.195	334.298	−700.441	48.963	−0.752
3500	108.061	690.650	592.049	345.104	−701.495	71.019	−1.060
3600	108.062	693.695	594.831	355.911	−702.590	93.107	−1.351
3700	108.064	696.655	597.543	366.717	−703.715	115.225	−1.627
3800	108.065	699.537	600.189	377.523	−704.858	137.373	−1.888
3900	108.066	702.344	602.773	388.330	−706.009	159.552	−2.137
4000	108.067	705.080	605.296	399.136	−707.158	181.761	−2.374
4100	108.068	707.749	607.763	409.943	−708.294	203.998	−2.599
4200	108.069	710.353	610.174	420.750	−709.411	226.262	−2.814
4300	108.070	712.896	612.534	431.557	−710.501	248.553	−3.019
4400	108.071	715.380	614.843	442.364	−711.556	270.869	−3.216
4500	108.071	717.809	617.104	453.171	−712.571	293.208	−3.403
4600	108.072	720.184	619.320	463.978	−713.541	315.570	−3.583
4700	108.073	722.509	621.490	474.786	−714.462	337.952	−3.756
4800	108.073	724.784	623.619	485.593	−715.329	360.353	−3.921
4900	108.074	727.012	625.706	496.400	−716.141	382.771	−4.080
5000	108.074	729.196	627.754	507.208	−716.893	405.206	−4.233
5100	108.075	731.336	629.764	518.015	−717.586	427.656	−4.380
5200	108.075	733.435	631.738	528.823	−718.217	450.117	−4.521
5300	108.076	735.493	633.676	539.630	−718.785	472.591	−4.658
5400	108.076	737.513	635.580	550.438	−719.291	495.075	−4.789
5500	108.077	739.496	637.452	561.245	−719.734	517.567	−4.915
5600	108.077	741.444	639.292	572.053	−720.114	540.067	−5.038
5700	108.077	743.357	641.100	582.861	−720.433	562.573	−5.155
5800	108.078	745.236	642.880	593.669	−720.691	585.083	−5.269
5900	108.078	747.084	644.630	604.476	−720.888	607.599	−5.379
6000	108.078	748 900	646.353	615.284	−721.028	630.116	−5.486

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

$S°(298.15\ K) = [278.24 \pm 1.3]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 278.4 \pm 1.0\ K$

$\Delta_f H°(298.15\ K) = -457.31 \pm 8.4\ kJ·mol^{-1}$
$\Delta_{fus} H° =$ Unknown

Enthalpy of Formation

Schafer and Heine[1] measured the enthalpy of solution of Si(cr) in an HF solution containing AgF. For the overall reaction $SiBr_4(l) + 4\ Ag(cr) = Si(cr) + 4\ AgBr(cr)$, they reported $\Delta_r H°(298.15\ K) = +13.3\ kcal·mol^{-1}$.Using auxiliary data for AgBr,[2] we calculate $\Delta_f H°(298.15\ K) = -109.3\ kcal·mol^{-1}$ ($-457.311\ kJ·mol^{-1}$) for $SiBr_4(l)$. We adopt this value and assign an uncertainty of $\pm 2.0\ kcal·mol^{-1}$. Wolf *et al.*[3] studied the enthalpies of solution of $SiBr_4(l)$ and $Na_2SiO_3(cr)$ in caustic solution. The net reaction of interest, $SiBr_4(l) + 6\ NaOH(cr) = Na_2SiO_3(cr) + 4\ NaBr(cr) + 3\ H_2O(l)$, yielded $\Delta_r H°(298.15\ K) = -199.32\ kcal·mol^{-1}$ based on the appropriate combination of results from five solution studies. Using current auxiliary data,[4,5] we update this value to $\Delta_r H°(298.15\ K) = -198.06\ kcal·mol^{-1}$ and calculate $\Delta_f H°(298.15\ K) = -114.8\ kcal·mol^{-1}$ for $SiBr_4(l)$. This data is suspect due to uncertainties in the conversion of data from Na_2SiO_3 (calorimetric solution) to $Na_2SiO_3(cr)$. The final state of the calorimetric solution is not well defined or well known and thus large uncertainties result.

Heat Capacity and Entropy

The heat capacity from 25–100°C was determined calorimetrically within 2% by Sladkov.[6] The constant value of 35.0 $cal·K^{-1}·mol^{-1}$ is extrapolated to 800 K. The entropy at 298.15 K is chosen so as to bring the 2nd and 3rd law analysis of the vapor pressure data into agreement.

Fusion Data

Pohland[7] reported the melting point of $SiBr_4$ to be 5.2°C (±1°C). No data are available on the enthalpy of fusion.

Vaporization Data

T_{vap} is calculated as that temperature for which $\Delta_r G° = 0$ for the process $SiBr_4(l) = SiBr_4(g)$ [$f = 1$ bar]. $\Delta_{vap} H°$ is calculated as the difference between the $\Delta_f H°$ values for the ideal gas and the liquid at T_{vap}. Normal boiling points (p = 1 atm) reported in the literature are 426.0 K[7] and 426.6 K,[8] and 427.8 K (766 mm Hg).[9] A normal boiling point ($p = 1$ bar) should be slightly lower than our calculated T_{vap} which corresponds to $f = 1$ bar. Refer to the $SiBr_4(g)$ table for a possible explanation of this discrepancy.

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
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	146.440	278.236	278.236	0.	−457.311	−443.896	77.769
300	146.440	279.142	278.239	0.271	−457.357	−443.812	77.275
400	146.440	321.270	283.983	14.915	−513.795	−427.415	55.815
500	146.440	353.947	294.829	29.559	−508.812	−406.401	42.456
600	146.440	380.646	306.975	44.203	−503.983	−386.374	33.637
700	146.440	403.220	319.153	58.847	−499.264	−367.147	27.397
800	146.440	422.774	330.911	73.491	−494.634	−348.591	22.761

PREVIOUS: CURRENT: December 1976

$S°(298.15\ K) = 379.36 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -385.55 \pm 16.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -415.47 \pm 16.7\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
246.7(1)	494 (3)
84.8(2)	133.6(3)

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distance: Si–Br = 2.15 ± 0.02 Å
Bond Angle: Br–Si–Br = 109.47122°
Product of the Moments of Inertia: $I_A I_B I_C = 4.37533 \times 10^{-111}\ g^3 \cdot cm^6$

Enthalpy of Formation

Pohland[1] has studied the vaporization of $SiBr_4$ from 260–426 K (0.8–755.5 mm Hg). This vapor pressure data (20 points) is 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 = 656 K and P_c = 41.3 atm as suggested in the review article by Lapidus *et al.*[2] are used to calculate B. The recent study on orthobaric densities by Nisel'son *et al.*[3] reported T_c = 663 K. The use of this latter value does not signficantly affect the results.

A 2nd and 3rd law analysis of this corrected data[1] yields $\Delta_{vap}H°(298.15\ K) = 10.0\ kcal \cdot mol^{-1}$. The entropy of the liquid at 298.15 K is adjusted so as to bring the 2nd and 3rd law results into agreement. This treatment suggests that the five lowest pressure data points (260–345 K, 0.8–60.3 mm Hg) are biased. These five points are not included in the above analysis. Any vapor pressure equation used to represent this data will be significantly altered in neglecting these five data points.

We adopt $\Delta_{vap}H°(298.15\ K) = 10.0\ kcal \cdot mol^{-1}$ which leads to $\Delta_f H°(298.15\ K) = -99.3\ kcal \cdot mol^{-1}$ ($-415.471\ kJ \cdot mol^{-1}$).[4] Using auxiliary data,[4] we calculate $\Delta_a H°(SiBr_4, g) = 311.54\ kcal \cdot mol^{-1}$ (1303.48 $kJ \cdot mol^{-1}$). This value is 4.03 times the dissociation energy of SiBr(g).[4]

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark and Rippon,[5] who recorded the Raman spectra in the vapor phase (210°C). The spectral data were interpreted in terms of a tetrahedral structure. This structure is consistent with the electron diffraction data of Lister and Sutton,[6] Yamasaki *et al.*,[7] and Spitzer *et al.*,[8] which suggested a tetrahedral structure with a Si–Br bond distance of 2.15 ± 0.02 Å. We adopt this bond distance. The principal moments of inertia are: $I_A = I_B = I_C = 163.5574 \times 10^{-39}\ g \cdot cm^2$. Shimanouchi, in a recent compilation of molecular vibrational frequencies,[9] suggested somewhat different values (249, 90, 487, 137 cm^{-1}) based on earlier infrared and Raman studies by Trumpy,[10] Delwaulle,[11] and Radhakrishnan,[12] and Long *et al.*[13] These frequencies would lead to a $S°(298.15\ K)$ value of 90.3 $cal \cdot K^{-1} \cdot mol^{-1}$ (377.9 $J \cdot K^{-1} \cdot mol^{-1}$). Much literature has been published on the inter–relationships between force constants and vibrational frequencies. Since the majority of this work was published prior to the Clark and Rippon study,[5] it will not be further discussed or referenced. The same situation exists for temperature dependent thermochemical tabulations of $SiBr_4$(g).

References

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

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
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	−22.313	−385.548	−385.548	INFINITE
100	70.691	287.079	459.223	−17.214	−386.301	−403.857	210.953
200	88.479	342.240	388.009	−9.154	−389.222	−420.368	109.789
250	93.599	362.569	380.944	−4.594	−391.143	−427.942	89.414
298.15	97.009	379.365	379.365	0.	−415.471	−432.207	75.721
300	97.117	379.965	379.367	0.180	−415.609	−432.311	75.272
350	99.568	395.131	380.559	5.100	−477.023	−431.728	64.432
400	101.316	408.547	383.235	10.125	−476.745	−425.276	55.535
450	102.594	420.558	386.726	15.224	−476.453	−418.860	48.620
500	103.552	431.419	390.661	20.379	−476.152	−412.477	43.091
600	104.857	450.424	399.083	30.805	−475.541	−399.799	34.806
700	105.676	466.654	407.605	41.334	−474.936	−387.224	28.895
800	106.222	480.803	415.889	51.931	−474.354	−374.733	24.468
900	106.603	493.337	423.811	62.573	−473.801	−362.314	21.028
1000	106.879	504.584	431.336	73.248	−473.285	−349.955	18.280
1100	107.085	514.781	438.466	83.947	−472.809	−337.645	16.033
1200	107.243	524.106	445.219	94.664	−472.375	−325.377	14.163
1300	107.366	532.695	451.622	105.394	−471.986	−313.143	12.582
1400	107.464	540.655	457.701	116.136	−471.645	−300.938	11.228
1500	107.544	548.072	463.481	126.886	−471.357	−288.755	10.055
1600	107.609	555.015	468.987	137.644	−471.123	−276.590	9.030
1700	107.663	561.540	474.242	148.408	−521.126	−263.990	8.111
1800	107.709	567.696	479.264	159.177	−520.785	−248.874	7.222
1900	107.747	573.520	484.073	169.949	−520.470	−233.777	6.427
2000	107.780	579.048	488.685	180.726	−520.184	−218.695	5.712
2100	107.809	584.307	493.114	191.505	−519.932	−203.627	5 065
2200	107.833	589.323	497.374	202.287	−519.717	−188.570	4 477
2300	107.855	594.117	501.477	213.072	−519.543	−173.522	3.941
2400	107.874	598.707	505.433	223.858	−519.412	−158.480	3.449
2500	107.890	603.111	509.253	234.647	−519.324	−143.443	2.997
2600	107.905	607.343	512.945	245.436	−519.280	−128.410	2.580
2700	107.918	611.416	516.517	256.228	−519.279	−113.376	2.193
2800	107.930	615.341	519.977	267.020	−519.320	−98.342	1.835
2900	107.941	619.128	523.331	277.814	−519.400	−83.306	1.500
3000	107.950	622.788	526.585	288.608	−519.515	−68.267	1.189
3100	107.959	626.328	529.746	299.404	−519.663	−53.222	0.897
3200	107.967	629.756	532.818	310.200	−519.837	−38.173	0.623
3300	107.974	633.078	535.806	320.997	−520.034	−23.118	0.366
3400	107.981	636.301	538.715	331.795	−520.248	−8.057	0.124
3500	107.987	639.432	541.548	342.593	−520.474	7.010	−0.105
3600	107.992	642.474	544.309	353.392	−904.858	32.546	−0.472
3700	107.997	645.433	547.003	364.192	−904.677	58.583	−0.827
3800	108.002	648.313	549.631	374.992	−904.495	84.614	−1.163
3900	108.006	651.118	552.197	385.792	−904.305	110.640	−1.482
4000	108.010	653.853	554.705	396.593	−904.103	136.662	−1.785
4100	108.014	656.520	557.156	407.394	−903.883	162.679	−2.073
4200	108.017	659.123	559.552	418.196	−903.643	188.689	−2.347
4300	108.021	661.665	561.898	428.998	−903.377	214.694	−2.608
4400	108.024	664.148	564.193	439.800	−903.083	240.693	−2.857
4500	108.026	666.576	566.442	450.602	−902.756	266.684	−3.096
4600	108.029	668.950	568.644	461.405	−902.396	292.667	−3.323
4700	108.031	671.273	570.803	472.208	−901.999	318.643	−3.541
4800	108.034	673.548	572.920	483.011	−901.563	344.610	−3.750
4900	108.036	675.775	574.997	493.815	−901.087	370.567	−3.950
5000	108.038	677.958	577.034	504.618	−900.570	396.514	−4.142
5100	108.040	680.097	579.034	515.422	−900.010	422.450	−4.327
5200	108.042	682.195	580.998	526.226	−899.407	448.374	−4.504
5300	108.043	684.253	582.927	537.031	−898.760	474.288	−4.674
5400	108.045	686.273	584.822	547.835	−898.070	500.188	−4.838
5500	108.047	688.255	586.685	558.640	−897.335	526.075	−4.996
5600	108.048	690.202	588.516	569.444	−896.557	551.948	−5.148
5700	108.049	692.115	590.317	580.249	−895.735	577.807	−5.295
5800	108.051	693.994	592.088	591.054	−894.871	603.650	−5.436
5900	108.052	695.841	593.831	601.859	−893.966	629.479	−5.573
6000	108.053	697.657	595.546	612.665	−893.018	655.292	−5.705

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

$S°(298.15\ K) = 243.6 \pm 6.7\ J·K^{-1}·mol^{-1}$
$T_{fus} = 311.4\ K$

$\Delta_f H°(0\ K) = -592.68 \pm 4.6\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -617.98 \pm 4.2\ kJ·mol^{-1}$
$\Delta_{fus} H° = 12.887\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(TiBr_4, cr, 298.15\ K)$ has been determined calorimetrically by several investigators as follows.

Source	Reaction	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Nelson *et al.*[1]	$Ti(cr) + 2\ Br_2(g) = TiBr_4(cr)$	−147.3 ± 1.1
Johnson *et al.*[2]	$TiCl_4(l) + 2\ Br_2(l) = TiBr_4(cr) + 2\ Cl_2(g)$	−147.6 ± 1.3
Schlafer and Schmidtke[3]	$Ti(cr) + 2\ Br_2(l) = TiBr_4(cr)$	−147.7 ± 0.3
Gross, *et al.*[4]	$Ti(cr) + 2\ Br_2(l) = TiBr_4(cr)$	−148.1 ± 0.3

The chosen value of $\Delta_f H°(298.15\ K) = -147.7 \pm 1.0$ kcal·mol^{-1} (617.977 ± 4.2 kJ·mol^{-1}) is the average of these determinations. The value from the work of Nelson *et al.*[1] is obtained from their enthalpy of reaction and the JANAF value for the enthalpy of vaporization of bromine. The value obtained from Johnson *et al.*[2] is a combination of their enthalpy of reaction and the JANAF value for the enthalpy of formation of $TiCl_4(l)$.

Heat Capacity and Entropy

The heat capacity of $TiBr_4(cr)$ has been measured over the temperature range 51 to 298.15 K by King *et al.*[5] They reported a value of 42.74 cal·K^{-1}·mol^{-1} for $S°(298.15\ K)–S°(51\ K)$ based on their measurements. The value of $S°(51\ K)$ is estimated as 15.46 cal·K^{-1}·mol^{-1}. King *et al.*[5] reported an estimate of 14.75 ± 1.60 cal·K^{-1}·mol^{-1} for the same quantity. The former estimate is used so that the values of $\Delta_{sub} H°(298.15\ K)$ obtained by both 2nd and 3rd law methods are in agreement. See $TiBr_4(g)$ table for details The value of $H°(51\ K)–H°(0\ K)$ is estimated as 0.372 kcal·mol^{-1}. This estimate is based on a Debye–Einstein extrapolation of the measured heat capacity with vibrational contributions removed.

Fusion Data

The melting temperature and heat of melting were reported by King *et al.*[5]

References

[1]R. A. Nelson, W. H. Johnson and E. J. Prosen, J. Res. Nat. Bur Stand. **62**, 67 (1959).
[2]W. H. Johnson, A. A. Gilliland and E. J. Prosen, J. Res. Nat. Bur. Stand. **63**, 161 (1959).
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[4]P. Gross, C. Hayman and D. L. Levi, Trans. Faraday Soc. **53**, 1601 (1957).
[5]E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, 20 pp. (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})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0	0.	INFINITE	−28.556	−592.684	−592.684	INFINITE
100	94 098	120.922	349.954	−22.903	−593.178	−593.675	310.104
200	117 273	194.146	255.191	−12.209	−594.203	−593.819	155.090
298.15	131.503	243.622	243.622	0.	−617.977	−590.681	103.485
300	131.815	244.436	243.624	0.244	−618.060	−590.512	102.817
311.400	133.779	249.388	243.745	1 757	--- CRYSTAL <--> LIQUID ---		
400	133.779	282.886	248.860	13.611	−676.266	−569.177	74.327
500	133.779	312.738	258.761	26.989	−673.012	−542.785	56.704
600	133.779	337.129	269.852	40.366	−669.899	−517.034	45.012
700	133.779	357.751	280.974	53.744	−666.885	−491.796	36 698
800	133 779	375.615	291.712	67.122	−663.937	−466.985	30 491
900	133.779	391.372	301 927	80.500	−661.078	−442.539	25.684
1000	133.779	405.467	311.589	93.878	−658.370	−418.404	21 855
1100	133 779	418.218	320.712	107.256	−655.873	−394.530	18.735
1200	133 779	429.858	329.329	120.634	−657.574	−370.753	16.138
1300	133 779	440.566	337 480	134.012	−654.777	−346.966	13.941
1400	133 779	450.480	345.202	147.390	−652.077	−323.390	12.066
1500	133 779	459.710	352.531	160.768	−649.487	−300.004	10.447

PREVIOUS. June 1964 CURRENT: June 1968

$S°(298.15\ K)$ = [284.168] $J·K^{-1}·mol^{-1}$
T_{fus} = 311.4 K

$\Delta_f H°(298.15\ K)$ = [−605.345] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 12.887 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(311.4\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

King *et al.*[1] reported the heat capacity of $TiBr_4(l)$ between the melting point and normal boiling point. $S°(TiBr_4, l, 298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

The melting temperature and heat of melting were reported by King *et al.*[1]

Vaporization Data

The boiling temperature, T_{vap}, is taken as the point at which K_p = 1 for the reaction $TiBr_4(l) = TiBr_4(g)$ at one bar. The enthalpy of vaporization is calculated as the difference between $\Delta_f H°$ of the liquid and gas at the boiling temperature. The vapor pressure data are discussed in the table for $TiBr_4(g)$.

Reference

[1]E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, 20 pp. (1961).

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	151.879	284.168	284.168	0.	−605.345	−590.138	103.390
300	151.879	285.107	284.171	0.281	−605.391	−590.044	102.736
400	151.879	328.800	290.128	15.469	−661.776	−573.053	74.833
500	151.879	362.691	301.377	30.657	−656.712	−551.461	57.611
600	151.879	390.382	313.974	45.845	−651.789	−530.876	46.217
700	151.879	413.794	326.605	61.033	−646.966	−511.106	38.139
800	151.879	434.075	338.799	76.221	−642.207	−492.023	32.126
900	151.879	451.964	350.399	91.408	−637.539	−473.531	27.483
1000	151.879	467.966	361.369	106.596	−633.020	−455.552	23.796

PREVIOUS June 1964 CURRENT: June 1968

CRYSTAL–LIQUID

0 to 311.4 K crystal
above 311.4 K liquid

Refer to the individual tables for details.

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
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	−28.556	−592.684	−592.684	INFINITE
100	94.098	120.922	349.954	−22.903	−593.178	−593.675	310.104
200	117.273	194.146	255.191	−12.209	−594.203	−593.819	155.090
298.15	131.503	243.622	243.622	0.	−617.977	−590.681	103.485
300	131.815	244.436	243.624	0.244	−618.060	−590.512	102.817
311.400	133.779	249.388	243.745	1.757	CRYSTAL <--> LIQUID		
311.400	151.879	290.772	243.745	14.644	TRANSITION		
400	151.879	328.800	258.549	28.101	−661.776	−573.053	74.833
500	151.879	362.691	276.114	43.289	−656.712	−551.461	57.611
600	151.879	390.382	292.921	58.476	−651.789	−530.876	46.217
700	151.879	413.794	308.559	73.664	−646.966	−511.106	38.139
800	151.879	434.075	323.009	88.852	−642.207	−492.023	32.126
900	151.879	451.964	336.363	104.040	−637.539	−473.531	27.483
1000	151.879	467.966	348.738	119.228	−633.020	−455.552	23.796

PREVIOUS: CURRENT: June 1968

$S°(298.15\ K) = 398.60 \pm 4.2\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -520.3 \pm 5.0\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -550.2 \pm 5.0\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
229.5(1)	382 (3)
74 (2)	90.5(3)

Ground State Quantum Weight: 1 $\sigma = 12$
Point Group: T_d
Bond Distance: Ti–Br = 2.31 Å
Bond Angle: Br–Ti–Br = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = 6.73056 \times 10^{-111}\ g^3\cdot cm^6$

Enthalpy of Formation

The enthalpy of formation of $TiBr_4$ (g) is calculated from those of $TiBr_4$ (cr) and $TiBr_4$ (l) and the enthalpies of reaction for the processes (A) $TiBr_4(cr) = TiBr_4(g)$ and (B) $TiBr_4(l) = TiBr_4(g)$. 2nd and 3rd law analyses of the vapor pressure data for these processes yield the following results. The first four investigations employed the spoon gauge method, the last investigation being a manometric determination.

Source	Reaction	Points	T/K	2nd law	3rd law	$cal\cdot K^{-1}\cdot mol^{-1}$	$kcal\cdot mol^{-1}$
Boni, 1966[1]	A	13	275–311	16.4 ± 0.2	16.19	−0.6 ± 0.5	−131.5
Funaki *et al.*, 1961[2]	B	14	385–493	12.2 ± 0.3	12.92	1.6 ± 0.3	−131.8
Seki, 1941[3]	A	12	286–306	15.4 ± 0.5	15.90	1.6 ± 1.6	−131.8
Hall *et al.*, 1958[4]	B	89*	341–499	13.2 ± 0.1	13.14	−0.1 ± 0.1	−131.5
Keavney & Smith, 1960[5]	A	14	287–310	16.1 ± 0.3	16.14	0.2 ± 0.8	−131.6

* Four points rejected due to failure of a statistical test.

The adopted value of $-131.5\ kcal\cdot mol^{-1}$ ($-550.196\ kJ\cdot mol^{-1}$) is that obtained from the data of Hall *et al.*,[4] whose 3rd law drift was adjusted to zero by changing the entropy of the crystal within its uncertainty.

Heat Capacity and Entropy

The interatomic distance was reported by Lister and Sutton.[6] The tetrahedral configuration is confirmed by spectroscopic studies.[7,8] The principal moments of inertia are: $I_A = I_B = I_C = 188.8066 \times 10^{-39}\ g\cdot cm^2$.

The vibrational frequencies have been reported by Delwaulle and Francois[7] and by Miller and Carlson.[8] These values are based primarily on the Raman and infrared spectra of $TiBr_4$(l), the value of υ_3 being the only frequency measured for $TiBr_4$(g).

The electronic spectra of $TiBr_4$ in solution have been measured by Dijkgraaf.[9] Di Sipio *et al.*[10] have reported the near ultraviolet spectra of $TiBr_4$(g). Both of these studies indicate that $TiBr_4$ has no low lying electronic levels which would contribute significantly to the entropy.

References

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[3] S. Seki, J. Chem. Soc. Japan **62**, 789 (1941).
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[5] J. J. Keavney and N. O. Smith, J Phys. Chem. **64**, 737 (1960).
[6] M. W. Lister and L. E. Sutton, Trans. Faraday Soc. **37**, 393 (1941).
[7] M. L. Delwaulle and F. Francois, Compt. Rend. **220**, 173 (1945).
[8] F. A. Miller and G. L. Carlson, Spectrochim. Acta **16**, 6 (1960).
[9] C. Dijkgraaf, Spectrochim. Acta **21**, 769 (1965).
[10] L. Di Sipio, G. DeMichelis, E. Tondello and L. Oleari, Gazz. Chim. Ital. **96**, 1785 (1966).

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
	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−23.904	−520.252	−520.252	INFINITE
100	76.813	300.230	482.949	−18.272	−520.766	−539.194	281.646
200	94.011	359.619	407.640	−9.604	−523.818	−556.528	145.350
250	98.156	381.078	400.246	−4.792	−525.801	−564.484	117.943
298.15	100.711	398.601	398.601	0.	−550.196	−569.107	99.705
300	100.790	399.224	398.603	0.186	−550.336	−569.224	99.111
350	102.533	414.900	399.837	5.272	−611.838	−569.000	84.919
400	103.734	428.675	402.598	10.431	−611.665	−562.892	73.506
450	104.591	440.945	406.189	15.640	−611.496	−556.805	64.632
500	105.222	451.999	410.227	20.886	−611.333	−550.737	57.535
600	106.066	471.264	418.841	31.454	−611.030	−538.647	46.893
700	106.588	487.657	427.530	42.089	−610.760	−526.605	39.296
800	106.932	501.914	435.956	52.766	−610.513	−514.599	33.600
900	107.171	514.523	443.999	63.472	−610.326	−502.623	29.171
1000	107.343	525.824	451.626	74.198	−610.269	−490.660	25.629
1100	107.471	536.061	458.844	84.939	−610.410	−478.694	22.731
1200	107.568	545.417	465.674	95.691	−614.736	−466.586	20.310
1300	107.644	554.030	472.144	106.452	−614.557	−454.248	18.252
1400	107.705	562.009	478.281	117.219	−614.467	−441.921	16.488
1500	107.754	569.442	484.114	127.992	−614.482	−429.597	14.960
1600	107.794	576.398	489.667	138.770	−614.618	−417.267	13.622
1700	107.827	582.934	494.963	149.551	−614.891	−404.925	12.442
1800	107.855	589.098	500.023	160.335	−615.318	−392.563	11.392
1900	107.879	594.930	504.866	171.122	−615.917	−380.172	10.452
2000	107.899	600.464	509.508	181.911	−631.391	−367.291	9.593
2100	107.917	605.729	513.966	192.702	−633.132	−354.043	8.806
2200	107.932	610.749	518.252	203.494	−634.911	−340.712	8.090
2300	107.945	615.547	522.379	214.288	−636.732	−327.299	7.433
2400	107.957	620.142	526.357	225.083	−638.596	−313.805	6.830
2500	107.967	624.549	530.197	235.879	−640.504	−300.233	6.273
2600	107.976	628.784	533.908	246.676	−642.457	−286.584	5.758
2700	107.984	632.859	537.498	257.474	−644.453	−272.859	5.279
2800	107.991	636.786	540.974	268.273	−646.492	−259.059	4.833
2900	107.998	640.576	544.344	279.073	−648.570	−245.185	4.416
3000	108.004	644.237	547.613	289.873	−650.684	−231.240	4.026
3100	108.009	647.779	550.787	300.673	−652.831	−217.223	3.660
3200	108.014	651.208	553.872	311.475	−655.005	−203.136	3.316
3300	108.018	654.532	556.872	322.276	−657.201	−188.981	2.991
3400	108.022	657.756	559.792	333.078	−659.415	−174.760	2.685
3500	108.026	660.888	562.636	343.881	−661.641	−160.473	2.395
3600	108.029	663.931	565.408	354.683	−663.873	−146.122	2.120
3700	108.032	666.891	568.111	365.486	−1075.206	−123.921	1.749
3800	108.035	669.772	570.748	376.290	−1076.202	−98.198	1.350
3900	108.038	672.578	573.324	387.093	−1077.245	−72.447	0.970
4000	108.040	675.314	575.839	397.897	−1078.329	−46.669	0.609
4100	108.042	677.982	578.298	408.701	−1079.447	−20.864	0.266
4200	108.045	680.585	580.703	419.506	−1080.595	4.969	−0.062
4300	108.047	683.127	583.055	430.310	−1081.767	30.829	−0.375
4400	108.048	685.611	585.358	441.115	−1082.958	56.718	−0.673
4500	108.050	688.040	587.613	451.920	−1084.163	82.633	−0.959
4600	108.052	690.414	589.822	462.725	−1085.378	108.575	−1.233
4700	108.053	692.738	591.987	473.530	−1086.599	134.544	−1.495
4800	108.055	695.013	594.110	484.336	−1087.821	160.538	−1.747
4900	108.056	697.241	596.192	495.141	−1089.041	186.558	−1.989
5000	108.057	699.424	598.235	505.947	−1090.255	212.604	−2.221
5100	108.058	701.564	600.240	516.753	−1091.462	238.673	−2.445
5200	108.059	703.662	602.209	527.559	−1092.657	264.765	−2.660
5300	108.060	705.721	604.142	538.365	−1093.838	290.881	−2.867
5400	108.061	707.741	606.042	549.171	−1095.004	317.019	−3.067
5500	108.062	709.723	607.909	559.977	−1096.151	343.178	−3.259
5600	108.063	711.671	609.745	570.783	−1097.279	369.358	−3.445
5700	108.064	713.583	611.550	581.590	−1098.386	395.558	−3.625
5800	108.065	715.463	613.325	592.396	−1099.469	421.776	−3.799
5900	108.066	717.310	615.072	603.202	−1100.528	448.014	−3.966
6000	108.066	719.126	616.791	614.009	−1101.562	474.269	−4.129

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

$S°(298.15\ K) = [224.7 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 723 \pm 1\ K$

$\Delta_f H°(0\ K) = [-734.3 \pm 8.4]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -760.7 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° =$ Unknown

Enthalpy of Formation

Turnbull[1] measured the enthalpies of reaction for the dissolution of the zirconium tetrahalides in caustic and in water. The reported enthalpies of reaction and the corresponding reactions may be combined to yield the following:

$$ZrBr_4(cr) + 4NaCl(aq) = ZrCl_4(cr) + 4NaBr(aq),\ \Delta_r H°(298.15\ K) = -8.10 \pm 0.9\ kcal \cdot mol^{-1}$$

$$ZrBr_4(cr) + 4Cl^-(aq) = ZrCl_4(cr) + 4Br^-(aq),\ \Delta_r H°(298.15\ K) = -9.83 \pm 0.6\ kcal \cdot mol^{-1}$$

Using auxiliary data,[2,4] we calculate $\Delta_f H°(298.15\ K) = -182.67$ and $-181.02\ kcal \cdot mol^{-1}$ for $ZrBr_4(cr)$ from these two reactions. We adopt a mean of these two values, $\Delta_f H°(298.15\ K) = -181.8\ kcal \cdot mol^{-1}$ ($-760.651\ kJ \cdot mol^{-1}$), and assign an uncertainty of $\pm 1.5\ kcal \cdot mol^{-1}$. This same value was suggested by NBS.[3]

Heat Capacity and Entropy

There are no heat capacity and enthalpy data reported in the literature for $ZrBr_4(cr)$. The adopted heat capacity values are estimated so as to give reasonable trends in comparison with $ZrCl_4$ and ZrI_4 and to be consistent with the existing sublimation data.

The crystal data compilation of Donnay and Ondik[5] tabulated both $ZrCl_4$ and $ZrBr_4$ as cubic structures. Thus, the adopted heat capacity values are estimated so as to parallel those for $ZrCl_4$. The heat capacity values below 300 K are calculated by summing contributions due to hindered translations, librations, and internal vibrations of the crystal. The parameters used in the calculations are determined by a correlation with corresponding parameters for $ZrCl_4$[6] and a consideration of the sublimation data for $ZrBr_4$.[6] The high temperature heat capacities are obtained graphically.

Fusion Data

The melting point was observed by Rahlfs and Fischer[7] to be 723 ± 1 K and by Nisel'son[8] to be 723 ± 0.5 K.

Sublimation Data

The sublimation data is treated in the $ZrBr_4(g)$ table.[6] The enthalpy of sublimation is adopted as $\Delta H°(298.15\ K) = 27.7 \pm 0.3\ kcal \cdot mol^{-1}$ ($115.897 \pm 1.3\ kJ \cdot mol^{-1}$). The sublimation temperture, T_{sub}, is calculated as that temperature for which $\Delta_r G° = 0$ for the process $ZrBr_4(cr) = ZrBr_4(g)$ at one bar. Since T_{sub} is less than T_{fus}, the liquid phase is thermodynamically unstable at a pressure of one atmosphere.

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[6] JANAF Thermochemical Tables: $ZrCl_4(cr)$ and $ZrBr_4(g)$, 6–30–75.
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[8] L. A. Nisel'son, Russ. J. Inorg. Chem. 7, 354 (1962).

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
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−28.162	−734.298	−734.298	INFINITE
100	93.625	103.324	328.883	−22.556	−735.164	−733.321	383.048
200	116.077	176.515	235.865	−11.870	−736.473	−730.998	190.917
298.15	124.805	224.689	224.689	0.	−760.651	−725.293	127.068
300	124.917	225.462	224.692	0.231	−760.747	−725.073	126.246
400	129.286	262.045	229.650	12.958	−819.539	−700.929	91.532
500	131.629	291.157	239.139	26.009	−816.496	−671.627	70.164
600	133.344	315.313	249.879	39.260	−813.375	−642.945	55.973
700	134.725	335.974	260.738	52.666	−810.213	−614.789	45.876
800	135.896	354.041	271.295	66.197	−807.037	−587.089	38.333
900	137.068	370.115	281.398	79.845	−803.864	−559.786	32.489
1000	138.239	384.617	291.007	93.610	−800.703	−532.835	27.832

PREVIOUS: March 1964 CURRENT: June 1975

$S°(298.15\ K) = 414.49 \pm 0.4\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -615.2 \pm 8.4\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -644.8 \pm 8.4\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
223 (1)
60 (2)
315 (3)
72 (3)

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distance: Zr–Br = 2.44 ± 0.02 Å
Bond Angle: Br–Zr–Br = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = 9.34800 \times 10^{-111}\ g^3\cdot cm^6$

Enthaply of Formation

The enthaply of formation for $ZrBr_4$(g) is calculated from the enthaplies of formation and sublimation of $ZrBr_4$(cr) at 298.15 K. The adopted value for the enthaply of sublimation, $\Delta_{sub}H°(298.15\ K) = 27.7 \pm 0.3\ kcal\cdot mol^{-1}$, is based on the mean of the 3rd law results from the following sublimation data.

In analyzing the vapor pressure data for the four sublimation studies,[1–4] corrections were made for non–ideality by means of the equation $\Delta G°/T = -R\ln p - Bp/T$. The Berthelot equation of state and the critical constants $T_c = 805.15$ K and $P_c = 42.9$ atm, as reported by Nisel'son and Sokolova,[5] are used to calculate B.

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}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Rahlfs and Fischer[1]	static	15	538–633	27.85 ± 0.24	27.78 ± 0.09	−0.1 ± 0.4	−154.02
Schlafer and Skoludek[2]	static	eqn	494–620	28.59	27.66	−1.7	−154.14
Berdonosova *et al.*[3]		17	489–606	28.87 ± 0.12	28.03 ± 0.12	−1.5 ± 0.2	−153.77
Normanton and Shelton[4]	effusion	eqn	400–500	26.32	27.30	2.2	−154.50

For the enthalpy of sublimation, we adopt the mean of the 3rd law results and assign an uncertainty of ±0.3 kcal·mol^{-1}. Combining the adopted $\Delta_{sub}H°(298.15\ K)$ value with the enthalpy of formation of $ZrBr_4$(cr), $\Delta_f H°(298.15\ K) = -181.8 \pm 1.5$ kcal·mol^{-1},[6] we calculate $\Delta_f H°(298.15\ K) = -154.1$ kcal·mol^{-1} (−644.754 kJ·mol^{-1}) for $ZrBr_4$(g) and assign an uncertainty of ±2.0 kcal·mol^{-1} (±8.4 kJ·mol^{-1}).

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark *et al.*,[7–9] who recorded the Raman spectra of $ZrBr_4$in the vapor phase (380–420°C). These studies by Clark *et al.*[7–9] indicated that $ZrBr_4$ is a tetrahedral monomer in the vapor phase. Shimanouchi, in his compilation of molecular vibrational frequencies,[10] also adopted the values of Clark *et al.*[7–9] for $ZrBr_4$(g). Rahlfs and Fischer,[1] through vapor density measurements, had earlier concluded that $ZrBr_4$ was monomeric in the vapor phase.

Berdonosov *et al.*[11] referenced an electron diffraction study by Cherkasov[12] which showed that, in the vapor phase, the Zr–Br internuclear distance was 2.44 ± 0.02 Å. We adopt this value. The principal moments of inertia are. $I_A = I_B = I_C = 210.6556 \times 10^{-39}\ g\cdot cm^2$.

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 $ZrBr_4$(g). One exception is that Clark *et al.*[7] calculated thermodynamic properties based on their experimental vibrational frequencies. Their tabulation is very similar to ours in the range 100–1000 K; the difference in entropy being less than 0.02 cal·K^{-1}·mol^{-1} in this range.

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[12] I. A. Cherkasov, Diploma Thesis, Moscow State University, 1961 [as referenced in[11]].

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	−24.954	−615.192	−615.192	INFINITE
100	81.107	312.254	501.497	−18.924	−615.635	−634.686	331.526
200	97.300	374.463	423.743	−9.856	−618.562	−652.677	170.462
250	100.676	396.571	416.167	−4.899	−620.453	−660.995	138.107
298.15	102.669	414.487	414.487	0.	−644.754	−665.984	116.678
300	102.730	415.122	414.489	0.190	−644.891	−666.115	115.981
350	104.052	431.064	415.745	5.362	−706.291	−666.288	99.438
400	104.947	445.021	418.550	10.588	−706.012	−660.593	86.265
450	105.577	457.420	422.193	15.852	−705.736	−654.932	76.022
500	106.038	468.569	426.283	21.143	−705.465	−649.301	67.832
600	106.649	487.960	434.994	31.780	−704.959	−638.117	55.553
700	107.023	504.431	443.766	42.465	−704.517	−627.013	46.788
800	107.269	518.739	452.263	53.180	−704.156	−615.966	40.218
900	107.439	531.384	460.366	63.916	−703.896	−604.959	35.111
1000	107.561	542.710	468.044	74.667	−703.750	−593.976	31.026
1100	107.652	552.966	475.305	85.428	−703.727	−583.000	27.684
1200	107.721	562.336	482.173	96.196	−707.543	−571.800	24.890
1300	107.775	570.961	488.675	106.971	−707.238	−560.500	22.521
1400	107.818	578.949	494.842	117.751	−706.988	−549.223	20.492
1500	107.852	586.389	500.700	128.534	−706.806	−537.961	18.733
1600	107.881	593.351	506.275	139.321	−706.704	−526.708	17.195
1700	107.904	599.892	511.592	150.110	−706.698	−515.459	15.838
1800	107.924	606.060	516.670	160.902	−706.800	−504.208	14.632
1900	107.941	611.896	521.530	171.695	−707.025	−492.947	13.552
2000	107.955	617.433	526.188	182.490	−707.388	−481.671	12.580
2100	107.967	622.700	530.659	193.286	−707.903	−470.373	11.700
2200	107.978	627.723	534.958	204.083	−729.907	−458.301	10.881
2300	107.987	632.523	539.096	214.882	−731.183	−445.927	10.127
2400	107.995	637.119	543.085	225.681	−732.503	−433.496	9.435
2500	108.003	641.528	546.936	236.481	−733.868	−421.009	8.797
2600	108.009	645.764	550.656	247.281	−735.278	−408.468	8.206
2700	108.015	649.840	554.254	258.082	−736.732	−395.870	7.659
2800	108.020	653.769	557.739	268.884	−738.228	−383.219	7.149
2900	108.024	657.559	561.116	279.686	−739.763	−370.513	6.674
3000	108.028	661.221	564.392	290.489	−741.335	−357.754	6.229
3100	108.032	664.764	567.573	301.292	−742.939	−344.941	5.812
3200	108.036	668.194	570.664	312.095	−744.571	−332.077	5.421
3300	108.039	671.518	573.670	322.899	−746.226	−319.160	5.052
3400	108.041	674.743	576.596	333.703	−747.898	−306.194	4.704
3500	108.044	677.875	579.445	344.507	−749.582	−293.179	4.375
3600	108.046	680.919	582.221	355.312	−751.273	−280.114	4.064
3700	108.049	683.880	584.929	366.117	−752.966	−267.003	3.769
3800	108.051	686.761	587.571	376.922	−754.655	−253.847	3.489
3900	108.052	689.568	590.151	387.727	−756.336	−240.646	3.223
4000	108.054	692.303	592.670	398.532	−758.003	−227.401	2.970
4100	108.056	694.972	595.133	409.338	−759.653	−214.116	2.728
4200	108.057	697.575	597.541	420.143	−761.281	−200.791	2.497
4300	108.059	700.118	599.897	430.949	−762.884	−187.426	2.277
4400	108.060	702.602	602.203	441.755	−764.459	−174.025	2.066
4500	108.061	705.031	604.462	452.561	−766.002	−160.589	1.864
4600	108.062	707.406	606.674	463.367	−767.512	−147.119	1.671
4700	108.063	709.730	608.842	474.173	−768.985	−133.616	1.485
4800	108.064	712.005	610.967	484.980	−1331.356	−108.465	1.180
4900	108.065	714.233	613.052	495.786	−1332.403	−82.977	0.885
5000	108.066	716.416	615.098	506.593	−1333.426	−57.468	0.600
5100	108.067	718.556	617.106	517.399	−1334.423	−31.938	0.327
5200	108.068	720.655	619.077	528.206	−1335.391	−6.391	0.064
5300	108.068	722.713	621.013	539.013	−1336.329	19.177	−0.189
5400	108.069	724.733	622.915	549.820	−1337.234	44.761	−0.433
5500	108.070	726.716	624.784	560.627	−1338.107	70.361	−0.668
5600	108.070	728.664	626.622	571.434	−1338.944	95.977	−0.895
5700	108.071	730.576	628.429	582.241	−1339.746	121.608	−1.114
5800	108.072	732.456	630.206	593.048	−1340.510	147.252	−1.326
5900	108.072	734.303	631.955	603.855	−1341.237	172.909	−1.531
6000	108.073	736.120	633.676	614.662	−1341.926	198.579	−1.729

PREVIOUS. June 1975 (1 atm) CURRENT: June 1975 (1 bar)

$S°(298.15\ K) = [258.78 \pm 6.3]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 527 \pm 3\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -556.05 \pm 12.6\ kJ·mol^{-1}$
$\Delta_{fus} H° = 24.016 \pm 6.3\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted value for the enthalpy of formation of $NbBr_5$(cr), $\Delta_f H°(298.15\ K) = -132.9 \pm 3.0\ kcal·mol^{-1}$ ($-556.054 \pm 12.6\ kJ·mol^{-1}$) is based on the study of the direct bromination of Nb(cr) by Gross *et al.*[1]

Shchukarev *et al.*[2] studied the hydrolysis of $NbBr_5$(cr). Using the experimental results reported by Shchukarev *et al.*[2] and auxiliary data,[4,5] we calculate, $\Delta_f H°(298.15\ K) = -135.5 \pm 1.2\ kcal·mol^{-1}$. Schafer and Heine[3] also determined the enthaply of formation of $NbBr_5$(cr) via calorimetric measurements of the heats of solution of Nb(cr) and $NbBr_5$(cr) in hydrofluoric acid. Using their data and auxiliary results,[4,5] we calculate $\Delta_f H°(298.15\ K) = -131.86 \pm 1.0\ kcal·mol^{-1}$. These two solution results[2,3] are in reasonable agreement with the adopted value. The direct bromination[1] is thought to be the more reliable.

Heat Capacity and Entropy

The heat capacity and entropy are estimated in comparison with $NbCl_5$(cr).[4] As there is no low temperature heat capacity data reported in the literature, the entropy at 298.15 K is calculated from the equation $\Delta_{sub}S°(298.15\ K) = S°(g, 298.15\ K) - S°(cr, 298.15\ K)$; $S°(g, 298.15\ K) = 107.35\ cal·K^{-1}·mol^{-1}$ as given in the $NbBr_5$(g) table[4] and $\Delta_{sub}S°(298.15\ K) = 45.5\ cal·K^{-1}·mol^{-1}$ as suggested by comparison with $NbCl_5$ and $TaCl_5$.[4]

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 $\Delta_f H°(298.15\ K)$ values for $NbBr_5$(g) and $NbBr_5$(cr). Two sublimation studies are summarized in the $NbBr_5$(g) table.[4]

References

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[4] JANAF Thermochemical Tables: $NbCl_5$(cr), $TaCl_5$(l), $NaBr_5$(l) and $NbBr_5$(g), 12-31-74, Nb_2O_5, 12-31-72.
[5] U. S. Nat. Bur. Stand. Tech. Note 270-3, 264 pp. (1968).

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							
250							
298.15	147.904	258.780	258.780	0.	−556.054	−508.887	89.155
300	147.904	259.695	258.783	0.274	−556.176	−508.593	88.554
400	147.904	302.245	264.585	15.064	−630.093	−477.367	62.338
500	147.904	335.249	275.540	29.854	−627.096	−439.535	45.918
527.000	147.904	343.027	278.800	33.848	--- CRYSTAL <---> LIQUID ---		
600	147.904	362.215	287.807	44.645	−624.217	−402.295	35.023
700	147.904	385.014	300.107	59.435	−621.429	−365.530	27.276
800	147.904	404.764	311.982	74.226	−618.717	−329.159	21.492

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = [274.005]\ J·K^{-1}·mol^{-1}$
$T_{fus}H° = 527 \pm 3\ K$

$\Delta_fH°(298.15\ K) = [-545.074]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 24.016 \pm 6.3\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(298.15)$ is calculated from that of $NbBr_5$(cr) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(527\ K)-H(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be identical with that of $NbCl_5$(l)[3] including the assumed glass transition at 350 K. The entropy at 298.15 K is calcualted in a manner analogous to that used for $\Delta_fH°(298.15\ K)$.

Fusion Data

The adopted melting point, $T_{fus} = 527 \pm 3$ K (254°C), is based on the studies by Nisel'son *et al.*[1] and Berdonosov *et al.*[2] The melting point was determined by Nisel'son *et al.*[1] from cooling curves, $T_{fus} = 255$°C. Berdonosov *et al.*[2] determined the melting point by three methods: $T_{fus} = 252.0 \pm 1.5$ based on an analysis of their vapor pressure data, $T_{fus} = 255 \pm 2$ based on visual observation, and $T_{fus} = 254 \pm 1$ based on cooling curves.

The heat of melting is chosen to be $\Delta_{fus}H° = 5.74 \pm 1.5\ kcal·mol^{-1}$ ($24.016 \pm 6.3\ kJ·mol^{-1}$). This value is consistent with the vaporization data and the thermodynamic functions we have adopted. The entropy of melting, $\Delta_{fus}S° = 10.89\ cal·K^{-1}·mol^{-1}$ is somewhat lower than anticipated, based on the expected similarity with $NbCl_5$ and $TaCl_5$ as far as condensed phase dimerization is concerned.[3]

Vaporization Data

T_{vap}, the normal boiling point, is calculated as that temperature for which the Gibbs energy approaches zero for the process $NbBr_5(l) = NbBr_5(g)$. $\Delta_{vap}H°$ is calculated as the difference between the $\Delta_fH°$ values for $NbBr_5$(g) and $NbBr_5$(l) at T_{vap}. Two vaporization studies are summarized in the $NbBr_5$(g) table.

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[3]JANAF Thermochemical Tables: $NbCl_5$(l), 12-31-74.

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							
250							
298.15	147.904	274.005	274.005	0.	−545.074	−502.446	88.026
300	147.904	274.920	274.008	0.274	−545.196	−502.181	87.438
350	147.904	297.720	275.809	7.669	−620.672	−490.908	73.264
350.000	147.904	297.720	275.809	7.669	GLASS <--> LIQUID		
350.000	228.280	297.720	275.809	7.669	TRANSITION		
400	224.848	327.984	280.486	18.999	−615.178	−472.748	61.735
500	216.564	377.299	295.131	41.084	−604.887	−438.351	45.794
527.000	215.228	388.599	299.634	46.884	--- CRYSTAL <--> LIQUID ---		
600	206.397	415.912	312.167	62.247	−595.635	−405.932	35.339
700	194.430	446.854	329.276	82.304	−587.580	−374.969	27.981
800	180.611	471.921	345.594	101.061	−580.902	−345.069	22.531
900	166.218	492.368	360.805	118.407	−575.705	−315.918	18.335

PREVIOUS: CURRENT: December 1974

298.15	to	527 K	crystal
above		527 K	liquid

Refer to the individual tables for details.

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

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
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							
100							
200							
250							
298.15	147.904	258.780	258.780	0.	−556.054	−508.887	89.155
300	147.904	259.695	258.783	0.274	−556.176	−508.593	88.554
400	147.904	302.245	264.585	15.064	−630.093	−477.367	62.338
500	147.904	335.249	275.540	29.854	−627.096	−439.535	45.918
527.000	147.904	343.027	278.800	33.848	____ CRYSTAL <--> LIQUID ____		
527.000	215.228	388.599	278.800	57.864	TRANSITION		
600	206.397	415.912	293.867	73.227	−595.635	−405.932	35.339
700	194.430	446.854	313.591	93.284	−587.580	−374.969	27.981
800	180.611	471.921	331.870	112.041	−580.902	−345.069	22.531
900	166.218	492.368	348 605	129.387	−575.705	−315.918	18.335

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = 449.26 \pm 3.1\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -406.5 \pm 12.6\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -443.6 \pm 12.6\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
234.0 (1)	[375.6](2)
178.0 (1)	119.0 (2)
[288.9](1)	67.0 (2)
[106.2](1)	101.0 (2)

Ground State Quantum Weight: [1] $\sigma = 6$

Point group: D_{3h}

Bond Distance: Nb–Br = 2.45 ± 0.02 Å

Bond Angles: Br*–Nb–Br* = 120°; Br*–Nb–Br** = 90°; Br**–Nb–Br** = 180°

(* – equatorial ** – axial)

Product of the Moments of Inertia: $I_A I_B I_C = 1.85664 \times 10^{-110}\ g^3·cm^6$

Enthalpy of Formation

The vapor pressures over $NbBr_5$(cr, l) have been measured by Alexander and Fairbrother[1] and Berdonosov *et al* [2] A 2nd and 3rd law analysis of their data is given below. The enthalpy of formation for $NbBr_5$(g) is derived from the sublimation data of Berdonosov *et al*.[2] Our 3rd law analysis of their data gives $\Delta_{sub}H°(298.15\ K) = 26.88\ kcal·mol^{-1}$ which leads to the adopted value, $\Delta_f H°(298.15\ K) = -106.02\ kcal·mol^{-1}$ ($-443.588\ kJ·mol^{-1}$) for $NbBr_5$(g). The sublimation data of Alexander and Fairbrother[1] is not acceptable as it leads to a large entropy drift, $-45 \pm 6\ cal·K^{-1}·mol^{-1}$.

The enthalpy of melting is chosen as 5.74 $kcal·mol^{-1}$ so as to give reasonable entropy drifts for the vaporization data.

Source	Reaction[a]	Method	Data Points	T/K	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$
Alexander and Fairbrother[1]	A	static	4	480–517	50.82 ± 2.94	27.77 ± 1.57	−45 ± 6
Berdonosov *et al*.[2]	A	static	12[b]	478–524	27.28 ± 0.16	26.88 ± 0.04	−0.8 ± 0.3
Alexander and Fairbrother[1]	B	static	26	528–635	24.07 ± 0.13	24.26 ± 0.06	+0.3 ± 0.2
Berdonosov *et al*.[2]	B	static	14	529–606	24.80 ± 0.27	24.23 ± 0.09	−1.0 ± 0.5

[a]Reaction: (A) $NbBr_5(l) = NbBr_5(g)$, (B) $NbBr_5(cr) = NbBr_5(g)$

[b]One point rejected due to a statistical test.

Heat Capacity and Entropy

Monomeric $NbBr_5$(g) was shown by Spiridonov and Romanov,[4,5] using electron diffraction techniques, to have a trigonal bipyramidal structure of D_{3h} symmetry: all the Nb–Br bond lengths being equal within expeirmental uncertainty, Nb–Br = 2.45 ± 0.02 Å. Skinner and Sutton[3] 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.[4,5] The principal moments of inertia are: $I_A = 238.9340 \times 10^{-39}$, $I_B = I_C = 278.7563 \times 10^{-39}\ g·cm^2$. A normal coordinate treatment of $NbBr_5$(g) in the Urey–Bradley force fields was performed by So[7] using the reported vibrational frequencies of Beattie and Ozin.[6] This work by So[7] was intended to check the correctness of the reported fundamental frequencies and predict those unobserved frequencies (ν_3, ν_4, ν_5). Beattie and Ozin[6] had recorded the gas phase Raman spectra of niobium and tantalum chloride and bromide. We adopt the results of So[7] which support the work of Beattie and Ozin.[6]

References

[1]K. A. Alexander and F. Fairbrother, J. Chem. Soc. (London) **1949**, S223 (1949).

[2]S. S. Berdonosov, A. V. Lapitskii, and E. K. Bakov, Russ. J. Inorg. Chem. **10**, 173 (1965).

[3]H. Skinner and L. Sutton, Trans. Faraday Soc. **36**, 668 (1940).

[4]V P. Spiridonov and G. V Romanov, Vestn. Mosk. Univ., Khim. **21**, 109 (1966).

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[6]I. R. Beattie and G. A. Ozin, J. Chem. Soc. (London) **A1969**, 1691.

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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	−29.426	−406.500	−406.500	INFINITE
100	95.964	325.261	555.381	−23.012	−407.850	−425.658	222.341
200	118 641	400.321	460.586	−12.053	−411.242	−442.220	115.496
250	123.151	427.323	451.317	−5.998	−413.411	−449.724	93.965
298.15	125.806	449.259	449.259	0.	−443.588	−453.212	79.401
300	125.886	450.037	449.261	0.233	−443.750	−453.271	78.922
350	127.648	469.585	450.801	6.574	−520.280	−450.669	67.259
400	128.840	486.712	454.242	12.988	−519.703	−440.764	57.558
450	129.681	501.939	458.711	19.452	−519.118	−430.932	50.021
500	130.295	515.635	463.730	25.953	−518.532	−421.165	43.999
600	131.109	539.469	474.425	39.026	−517.370	−401.801	34.980
700	131.610	559.720	485.200	52.164	−516.234	−382.629	28.552
800	131.938	577.317	495.639	65.343	−515.135	−363.618	23.742
900	132.165	592.871	505.595	78.548	−514.078	−344.743	20.008
1000	132.328	606.805	515.032	91.773	−513.067	−325.983	17.028
1100	132.449	619.423	523.957	105.012	−512.107	−307.321	14.593
1200	132.541	630.952	532.400	118.262	−511.197	−288.745	12.569
1300	132.613	641.564	540.394	131.520	−510.339	−270.242	10.858
1400	132.670	651.394	547.976	144.784	−509.536	−251.804	9.395
1500	132.717	660.548	555.179	158.054	−508.796	−233.421	8.128
1600	132.754	669.115	562.035	171.327	−508.128	−215.084	7.022
1700	132.786	677.164	568.573	184.604	−507.544	−196.787	6.047
1800	132.812	684.755	574.819	197.884	−507.055	−178.522	5.181
1900	132.835	691.936	580.796	211.167	−506.671	−160.281	4.406
2000	132.854	698.750	586.525	224.451	−506.404	−142.058	3.710
2100	132.870	705.233	592.024	237.737	−506.262	−123.844	3.080
2200	132.884	711.414	597.312	251.025	−506.257	−105.635	2.508
2300	132.897	717.321	602.402	264.314	−506.399	−87.422	1.985
2400	132.908	722.978	607.309	277.604	−506.702	−69.200	1.506
2500	132.917	728.403	612.045	290.896	−507.181	−50.961	1.065
2600	132.926	733.617	616.621	304.188	−507.862	−32.700	0.657
2700	132.933	738.633	621.048	317.481	−508.781	−14.408	0.279
2800	132.940	743.468	625.334	330.774	−536.348	4.407	−0.082
2900	132.946	748.133	629.489	344.069	−536.593	23.725	−0.427
3000	132.952	752.640	633.519	357.364	−536.884	43.051	−0.750
3100	132.957	757.000	637.432	370.659	−537.215	62.387	−1.051
3200	132.961	761.221	641.235	383.955	−537.580	81.735	−1.334
3300	132.965	765.313	644.933	397.251	−537.974	101.095	−1.600
3400	132.969	769.282	648.533	410.548	−538.389	120.467	−1.851
3500	132.973	773.137	652.038	423.845	−538.820	139.851	−2.087
3600	132 976	776.883	655.454	437.143	−539.260	159.248	−2.311
3700	132.979	780.526	658.785	450.440	−539 701	178.657	−2.522
3800	132.981	784.072	662.036	463.738	−540.138	198.077	−2.723
3900	132.984	787.527	665.210	477.037	−540.564	217.510	−2.913
4000	132.986	790.894	668.310	490.335	−540.973	236.953	−3.094
4100	132.988	794.177	671.340	503.634	−541.361	256.406	−3.267
4200	132.990	797.382	674.303	516.933	−541.722	275.868	−3.431
4300	132.992	800.511	677.202	530.232	−542.051	295.338	−3.588
4400	132.994	803.569	680.039	543.531	−542.344	314.816	−3.737
4500	132.996	806.558	682.818	556.831	−542.599	334.300	−3.880
4600	132.997	809.481	685.539	570.130	−542.811	353.789	−4.017
4700	132.998	812.341	688.207	583.430	−542.977	373.282	−4.149
4800	133.000	815.141	690.822	596.730	−543.096	392.779	−4.274
4900	133.001	817.884	693.388	610.030	−543.166	412.277	−4.395
5000	133.002	820.571	695.904	623.330	−543.184	431.776	−4.511
5100	133.003	823.204	698.375	636.631	−543.149	451.275	−4.622
5200	133.004	825.787	700.800	649.931	−1233.733	480.082	−4.822
5300	133.005	828.321	703.183	663.231	−1233.923	513.042	−5.056
5400	133.006	830.807	705.523	676.532	−1234.031	546.001	−5.282
5500	133.007	833.247	707.823	689.833	−1234.158	578.966	−5.499
5600	133.008	835.644	710.084	703.133	−1234.259	611.932	−5.708
5700	133.009	837.998	712.308	716.434	−1234.333	644.901	−5.910
5800	133.009	840.311	714.495	729.735	−1234.381	677.870	−6.105
5900	133.010	842.585	716.647	743.036	−1234.405	710.840	−6.293
6000	133.011	844.821	718.764	756.337	−1234.405	743.810	−6.475

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = [272 \pm 21]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 559 \pm 10\ K$

$\Delta_f H°(0\ K) =$ Unknown
$\Delta_f H°(298.15\ K) = -311.7 \pm 13\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 17.154\ kJ\ mol^{-1}$

Enthalpy of Formation

Shchukarev and Kokovin[1] have measured calorimetrically the enthalpy of reaction $\Delta_r H°(298.15\ K) = -187.475 \pm 0.9\ kcal \cdot mol^{-1}$ for $WBr_5(cr) + 1/2Br_2(l) + 8NaOH(77.4H_2O) \rightarrow Na_2WO_4(cr) + 6NaBr(cr) + 4H_2O(l)$. This leads to $\Delta_f H°(WBr_5, cr, 298.15\ K) = -74.5 \pm 3\ kcal \cdot mol^{-1}(-311.708 \pm 13\ kJ \cdot mol^{-1})$, using $\Delta_f H°(NaOH \cdot 77.4H_2O, 298.15\ K) = -112.348\ kcal \cdot mol^{-1}$,[2] $\Delta_f H°(NaWO_4, cr, 298.15\ K) = -369.2\ kcal \cdot mol^{-1}$,[3] $\Delta_f H°(NaBr, cr, 298.15\ K) = -86.38\ kcal \cdot mol^{-1}$ [3] and $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315\ kcal \cdot mol^{-1}$.[4]

Heat Capacity and Entropy

$C_p°(300\ K) = 6.2\ cal \cdot K^{-1} \cdot g\text{-}atom^{-1}$ and $C_p°(559\ K) = 7.25\ cal \cdot K^{-1} \cdot g\text{-}atom^{-1}$ are estimated using the method described by Kubaschewski and Evans.[5] Between 300 K and 559 K, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, $S°(298.15\ K) = 65\ cal \cdot K^{-1} \cdot mol^{-1}$ (271 960 $J \cdot K^{-1} \cdot mol^{-1}$), is estimated from that of $WCl_5(cr)$[3] and the entropy difference between bromides and chlorides. The latter is estimated to be 13 $cal \cdot K^{-1} \cdot mol^{-1}$ based on an extrapolation to pentavalent compounds of the entropy values of bromides and chlorides given by Latimer.[7] Both WBr_5 and WCl_5 are paramagnetic with an effective moment of about 1.1 Bohr magnetons as indicated by Figgis and Lewis.[8]

Fusion Data

Shchukarev *et al.*[6] have found the melting point, 559 K, by the thermographic method and 568 K by the tensimetric method. The value of 559 K is adopted in the tabulation.

The heat of melting is calculated from the difference between the enthalpies of sublimation and vaporization at the melting point. The enthalpies are both calculated from a 2nd law analysis of the vapor pressure data reported by Shchukarev *et al.*,[6] who gave the uncorrected enthalpy of fusion, 5 $kcal \cdot mol^{-1}$. This value, when corrected for $\Delta C_p°$ of vaporization and sublimation, is in good agreement with the value adopted in the tabulation.

References

[1] S. A. Shchukarev and G. A. Kokovin, Zh. Neorg. Khim. 9, 1309 (1964).
[2] The value $\Delta_f H°(NaOH \cdot 77.4H_2O, 298.15\ K) = -112.348\ kcal \cdot mol^{-1}$ is calculated from $\Delta_f H°(NaOH \cdot \infty H_2O, 298.15\ K) = -112.448\ kcal \cdot mol^{-1}$ and $\phi_L = 100\ cal\ mol^{-1}$ for $NaOH(\infty H_2O) \rightarrow NaOH(77.4H_2O)$. The former is obtained from JANAF NaOH(cr) table (March 31, 1966) and the latter is obtained from V. B. Parker, U. S. Nat. Bur. Stand. NSRDS–NBS 2, (1965).
[3] JANAF Thermochemcial Tables: Na_2WO4(cr), 6–30–67; NaBr(cr), 9–30–64, WCl_5(cr), 12–31–66.
[4] U. S. Nat. Bur. Stand. Tech. Note 270–1, 124 pp. (1965).
[5] O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).
[6] S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. 4, 2185 (1959).
[7] W. M. Latimer, J. Amer. Chem. Soc. 73, 1480 (1951).
[8] B. N. Figgis and J. L. Lewis, "Progress in Inorg. Chem.," Vol. 6, p. 121, Interscience Publishers, New York, (1964).

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
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	155.461	271.960	271.960	0.	−311.708	−269.605	47.234
300	155.645	272.922	271.963	0.288	−311.815	−269.343	46.897
400	165.686	319.074	278.188	16.354	−384.412	−239.991	31.340
500	175.728	357.110	290.273	33.419	−379.091	−204.484	21.362
559.000	182.004	377.052	298.393	43.971	--- CRYSTAL <--> LIQUID ---		
600	185.770	390.077	304.218	51.516	−372.851	−170.133	14.811
700	195.811	419.468	318.618	70.595	−365.719	−136.898	10.215
800	205.853	446.270	332.923	90.678	−357.662	−104.748	6.839
900	215.894	471.096	346.912	111.765	−348.673	−73.664	4.275
1000	225.936	494.362	360.506	133.857	−338.750	−43.631	2.279

PREVIOUS: December 1962 CURRENT: June 1967

$S°(298.15\ K)$ = [293.341] $J·K^{-1}·mol^{-1}$
T_{fus} = 559 ± 10 K

$\Delta_f H°(298.15\ K)$ = [−298.059] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 17.154 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(WBr_5, l, 298.15\ K)$ is calculated from that of WBr_5(cr) by adding the $\Delta_{fus}H°$ and the difference in enthalpy, $H°(559\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be a constant, 7.25 $cal·K^{-1}·g$-atom.

$S°(298.15\ K)$ is calcualted 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 of reaction $WBr_5(l) \rightarrow WBr_5(g)$ approaches zero. The difference between the enthalpies of formation for liquid and gas at the normal boiling point is $\Delta_{vap}H°$.

Shchukarev *et al.*[1] derived the boiling point 665 K and the enthalpy of vaporization 14.5 ± 0.5 $kcal·mol^{-1}$ from vapor pressure data. Our 2nd law values, corrected for $\Delta C_p°$, are T_{vap} = 666 K and $\Delta_{vap}H°$ = 13.8 $kcal·mol^{-1}$. The adopted values are significantly different because the 2nd law value of $\Delta_{vap}S$ is not adopted in the table.

Reference

[1] S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. 4, 2185 (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							
100							
200							
298.15	182.004	293.341	293.341	0.	−298.059	−262.330	45.959
300	182.004	294.467	293.344	0.337	−298.117	−262.108	45.637
400	182.004	346.826	300.483	18.537	−368.580	−235.260	30.722
500	182.004	387.439	313.964	36.738	−362.123	−202.680	21.174
600	182.004	420.622	329.059	54.938	−355.779	−171.389	14.921
700	182.004	448.678	344.195	73.138	−349.526	−141.153	10.533
800	182.004	472.982	358.808	91.339	−343.351	−111.808	7.300
900	182.004	494.419	372.708	109.539	−337.250	−83.232	4.831
1000	182.004	513.595	385.855	127.740	−331.218	−55.332	2.890

PREVIOUS December 1962 CURRENT: June 1967

298.15	to	559 K	crystal
above		559 K	liquid

Refer to the individual tables for details.

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

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
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							
100							
200							
298.15	155.461	271.960	271.960	0.	−311.708	−269.605	47.234
300	155.645	272.922	271.963	0.288	−311.815	−269.343	46.897
400	165.686	319.074	278.188	16.354	−384.412	−239.991	31.340
500	175.728	357.110	290.273	33.419	−379.091	−204.484	21.362
559.000	182.004	377.052	298.393	43.971	___ CRYSTAL <---> LIQUID ___		
559.000	182.004	407.740	298.393	61.125	TRANSITION		
600	182.004	420.622	306.310	68.587	−355.779	−171.389	14.921
700	182.004	448.678	324.696	86.788	−349.526	−141.153	10.533
800	182.004	472.982	341.747	104.988	−343.351	−111.808	7.300
900	182.004	494.419	357.543	123.188	−337.250	−83.232	4.831
1000	182.004	513.595	372.206	141.389	−331.218	−55.332	2.890

PREVIOUS: CURRENT: June 1967

$S°(298.15\ K)$ = [461.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -162.9 \pm 21\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -199.2 \pm 21\ kJ·mol^{-1}$

Eletronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[7000]	[2]
[14000]	[2]

Vibrational Frequencies and Degeneracies	
ν_i, cm^{-1}	ν_i, cm^{-1}
[300](1)	[240](2)
[250](1)	[100](2)
[235](1)	[70](2)
[90](1)	[110](2)

Ground State Quantum Weight: [2] σ = [6]
Point Group: [D_{3h}]
Bond Distance: W–Br = [2.40] Å
Bond Angles: Br*–W–Br* = [120°]; Br*–W–Br** = [90°]
Br**–W–Br** = [180°]
*Equatorial **Axial
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.6458] × 10^{-110} $g^3·cm^6$

Enthalpy of Formation

Shchukarev *et al.*[5] measured the vapor pressure of WBr_5(cr, l) using a null manometer. Their results are given as below. The adopted enthalpy of formation is −47.6 $kcal·mol^{-1}$ (−199.158 $kJ·mol^{-1}$).

Reaction	Data Points	T/K	$\Delta_f H°$(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}
WBr_5(l) → WBr_5(g)	13	573.3–657.5	18.37	24.11	9.4 ± 0.1	−47.13
WBr_5(cr) → WBr_5(g)	6	443.5–496.5	21.61	26.46	9.4 ± 0.4	−48.04

Heat Capacity and Entropy

The molecular configuration is assumed to be a trigonal bipyramid similar to that of $MoCl_5$ determined by electron diffraction.[1] The bond distance is estimated to be the same as that in WBr_6(g). The principal moments of inertia are: I_A = 229.2811 × 10^{-39} and $I_B = I_C$ = 267.4946 × 10^{-39} $g·cm^2$.

All vibrational frequencies are estimated from those of WCl_5(g),[2] using the average value of $\nu(WBr_5)/\nu(WCl_5)$ = 0.62 for modes which are independent of the central atom and 0.68 for modes involving the central atom. These average values of 0.62 and 0.68 are obtained from the ratios of corresponding vibrational frequencies of ReX_6^{2-}, SnX_6^{2-} and PtX_6^{2-} summarized by Siebert[3] and Nakamoto.[4]

The electronic levels and quantum weights are estimated to be the same as those in WCl_5(g).[2]

References

[1] R. V. G. Ewens and M. W. Lister, Trans. Faraday Soc. 34, 1358 (1938).
[2] JANAF Thermochemical Table: WCl_5(g), 12–31–66.
[3] H. Siebert, "Anwendungen der Schwingunsspektroskopie in der Anorganischen Chemie," Springer–Verlag, Berlin, (1966).
[4] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, (1963).
[5] S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. 4, 2185 (1959).

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	−30.021	−162.933	−162.933	INFINITE
100	98.777	334.646	569.460	−23.481	−164.028	−183.070	95.626
200	121.036	411.719	472.895	−12.235	−167.043	−201.022	52.501
250	124.972	439.192	463.494	−6.076	−169.080	−209.292	43.729
298.15	127.212	461.411	461.411	0.	−199.158	−213.540	37.411
300	127.279	462.198	461.413	0.235	−199.318	−213.629	37.196
350	128.733	481.935	462.969	6.638	−275.765	−211.832	31.614
400	129.704	499.193	466.441	13.101	−275.116	−202.743	26.476
450	130.382	514.511	470.947	19.604	−274.468	−193.735	22.488
500	130.873	528.275	476.003	26.136	−273.824	−184.799	19.306
600	131.522	552.199	486.768	39.258	−272.558	−167.114	14.549
700	131.918	572.505	497.602	52.432	−271.332	−149.637	11.166
800	132.180	590.138	508.091	65.638	−270.152	−132.334	8.640
900	132.368	605.718	518.090	78.866	−269.023	−115.175	6.685
1000	132.517	619.673	527.562	92.110	−267.947	−98.139	5.126
1100	132.650	632.309	536.520	105.368	−266.926	−81.208	3.856
1200	132.781	643.857	544.990	118.640	−265.959	−64.367	2.802
1300	132.921	654.490	553.010	131.925	−265.045	−47.605	1.913
1400	133.073	664.346	560.614	145.225	−264.185	−30.912	1.153
1500	133.242	673.533	567.840	158.540	−263.379	−14.278	0.497
1600	133.426	682.138	574.717	171.873	−262.629	2.304	−0.075
1700	133.624	690.233	581.276	185.226	−261.936	18.841	−0.579
1800	133.835	697.877	587.544	198.599	−261.302	35.338	−1.025
1900	134.055	705.118	593.543	211.993	−260.733	51.803	−1.424
2000	134.281	712.000	599.295	225.410	−260.231	68.239	−1.782
2100	134.511	718.557	604.820	238.849	−259.801	84.652	−2.106
2200	134.743	724.820	610.133	252.312	−259.447	101.045	−2.399
2300	134.974	730.815	615.251	265.798	−259.173	117.425	−2.667
2400	135.202	736.564	620.186	279.307	−258.982	133.795	−2.912
2500	135.425	742.088	624.953	292.838	−258.875	150.158	−3.137
2600	135.643	747.404	629.561	306.392	−258.849	166.518	−3.345
2700	135.854	752.527	634.021	319.966	−258.933	182.880	−3.538
2800	136.057	757.471	638.342	333.562	−259.158	199.246	−3.717
2900	136.252	762.249	642.533	347.178	−259.561	215.625	−3.884
3000	136.438	766.871	646.601	360.812	−260.166	232.020	−4.040
3100	136.614	771.348	650.553	374.465	−261.013	248.439	−4.186
3200	136.781	775.688	654.396	388.135	−262.127	264.890	−4.324
3300	136.939	779.899	658.136	401.821	−263.529	281.381	−4.454
3400	137.087	783.990	661.777	415.522	−265.249	297.918	−4.577
3500	137.225	787.966	665.326	429.238	−267.344	314.511	−4.694
3600	137.353	791.833	668.787	442.967	−269.906	331.171	−4.805
3700	137.473	795.598	672.163	456.708	−307.794	348.100	−4.914
3800	137.583	799.266	675.460	470.461	−307.985	365.829	−5.029
3900	137.683	802.841	678.681	484.224	−308.156	383.563	−5.137
4000	137.775	806.328	681.828	497.997	−308.300	401.301	−5.240
4100	137.859	809.731	684.907	511.779	−308.414	419.043	−5.339
4200	137.934	813.054	687.918	525.569	−308.493	436.786	−5.432
4300	138.002	816.300	690.866	539.366	−308.533	454.532	−5.521
4400	138.061	819.474	693.753	553.169	−308.532	472.278	−5.607
4500	138.114	822.577	696.582	566.978	−308.487	490.023	−5.688
4600	138.159	825.613	699.354	580.791	−308.394	507.767	−5.766
4700	138.198	828.585	702.072	594.609	−308.251	525.508	−5.840
4800	138.230	831.495	704.738	608.431	−308.058	543.246	−5.912
4900	138.257	834.345	707.354	622.255	−307.812	560.979	−5.980
5000	138.277	837.138	709.922	636.082	−307.513	578.706	−6.046
5100	138.293	839.877	712.443	649.910	−307.159	596.428	−6.109
5200	138.303	842.562	714.920	663.740	−306.751	614.140	−6.169
5300	138.308	845.197	717.353	677.571	−306.288	631.846	−6.227
5400	138.309	847.782	719.745	691.402	−305.770	649.542	−6.283
5500	138.306	850.320	722.096	705.233	−305.198	667.228	−6.337
5600	138.299	852.812	724.408	719.063	−304.571	684.902	−6.389
5700	138.288	855.260	726.682	732.892	−303.891	702.566	−6.438
5800	138.274	857.665	728.920	746.720	−303.158	720.216	−6.486
5900	138.256	860.028	731.122	760.547	−302.373	737.854	−6.532
6000	138.236	862.352	733.290	774.371	−301.537	755.478	−6.577

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

$S°(298.15\ K)$ = [313.8 ± 21] $J·K^{-1}·mol^{-1}$
T_{fus} = 582 K

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K)$ = −343.088 $kJ·mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

Shchukarev and Kokovin[1] have measured calorimetrically the enthalpy of reaction $\Delta_r H°(298.15\ K)$ = −180.0 ± 0.8 $kcal·mol^{-1}$ for WBr_6(cr) + 8NaOH(77.4H_2O) → Na_2WO_4(cr) + 6NaBr(cr) + 4H_2O(l). This leads to $\Delta_f H°(WBr_6, cr, 298.15\ K)$ = −82.0 ± 3 $kcal·mol^{-1}$ (−343.088 ± 13 $kJ·mol^{-1}$), using $\Delta_f H°$(NaOH·77.4H_2O, 298.15 K) = −112.348 $kcal·mol^{-1}$,[2] $\Delta_f H°(Na_2WO_4, cr, 298.15\ K)$ = −369.2 $kcal·mol^{-1}$,[3] $\Delta_f H°$(NaBr, cr, 298.15 K) = −86.38 $kcal·mol^{-1}$[3] and $\Delta_f H°(H_2O, l, 298\ 15\ K)$ = −68.315 $kcal·mol^{-1}$.[4]

Heat Capacity and Entropy

$C_p°(300\ K)$ = 6.2 $cal·K^{-1}$ $g\text{-}atom^{-1}$ and $C_p°(582\ K)$ = 7.25 $cal·K^{-1}$ $g\text{-}atom^{-1}$ are estimated using the method described by Kubaschewski and Evans.[5] Between 300 and 582 K, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, $S°(WBr_6, cr, 298.15\ K)$ = 75 $cal·K^{-1}·mol^{-1}$ (313.800 $J·K^{-1}·mol^{-1}$), is estimated by assuming $S°(WBr_6, 298.15\ K) = S°(WCl_6, 298.15\ K) + 6[S°(Br^-, 298.15\ K) - S°(Cl^-, 298.15\ K)]$ The value, $S°(WCl_6, cr, 298.15\ K)$ = 57 $cal·K^{-1}$ mol^{-1}, is obtained from WCl_6(cr, α)[3]; and the value, $S°(Br^-, 298.15\ K) - S°(Cl^-, 298.15\ K)$ = 3 $cal·K^{-1}·mol^{-1}$, is obtained from the average entropy values for Br^- and Cl^- ions given by Latimer[6] and Kelley.[7]

Fusion Data

Shchukarev *et al.*[8] have found the melting point, 582 K, under 50 atm pressure of Br_2(g) by the thermographic method. The heat of fusion is unknown.

References

1S. A. Shchukarev and G. A. Kokovin, Zh. Neorg. Khim. 9, 1309 (1964).
[2]This value, $\Delta_f H°$(NaOH·77.4H_2O, 298.15 K) = −112.348 $kcal·mol^{-1}$ is calculated from $\Delta_f H°$(NaOH·∞H_2O, 298.15 K) = 112.448 $kcal·mol^{-1}$ and ϕ_L = 100 $kcal·mol^{-1}$ for NaOH(∞H_2O) → NaOH(77.4H_2O). The former is obtained from JANAF NaOH(cr) table (March 31, 1966) and the latter is obtained from V. B. Parker, U. S. Nat. Bur. Stand. NSRDS−NBS 2, (1965).
[3]JANAF Thermochemical Tables: Na_2WO_4(cr), 6–30–67; NaBr(cr), 6–30–64, WCl_6(cr, α), 12–31–66.
[4]U. S. Nat. Bur. Stand. Tech. Note 270–1, 124 pp. (1965).
[5]O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).
[6]W. M. Latimer, J. Amer. Chem. Soc. 73, 1480 (1951).
[7]K. K. Kelley, personal communication, (June, 1960).
[8]S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. 4, 2185 (1959).

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	181.385	313.800	313.800	0.	−343.088	−290.769	50.942
300	181.586	314.923	313.803	0.336	−343.217	−290.444	50.571
400	192.464	368.651	321.056	19.038	−430.418	−254.610	33.249
500	203.342	412.767	335.110	38.829	−424.217	−211.356	22.080
600	214.221	450.802	351.291	59.707	−417.055	−169.440	14.751
700	225.099	484.642	367.966	81.673	−408.905	−128.801	9.611
800	235.978	515.410	384.501	104.727	−399.754	−89.399	5.837
900	246.856	543.832	400.645	128.868	−389.593	−51.204	2.972
1000	257.734	570.404	416.306	154.098	−378.419	−14.195	0.741

PREVIOUS: December 1962 CURRENT: June 1967

$S°(298.15\ K)$ = [482.7 ± 42] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−199.8 ± 42] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−243.1 ± 42] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[250](1)	[110](3)
[200](2)	[130](3)
[250](3)	[70](3)

Ground State Quantum Weight: [1] σ = [24]
Point Group: [O_h]
Bond Distance: W–Br = [2.40] Å
Bond Angle: Br–W–Br = [90]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [2.85707 × 10^{-110}] $g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(WBr_6, g, 298.15\ K)$ = −58.1 $kcal·mol^{-1}$ (−243.090 $kJ·mol^{-1}$) is calculated from that of the crystal plus the estimated enthalpy of sublimation $\Delta_{sub}H°(298.15\ K)$ = 23.9 $kcal·mol^{-1}$ for $WBr_6(cr) \rightarrow WBr_6(g)$. The value of $\Delta_{sub}H°(298.15\ K)$ is assumed to be the same as that for $WCl_6(cr) \rightarrow WCl_6(g)$. Refer to the WCl_6 table (December 31, 1966) for details.

Heat Capacity and Entropy

The molecular configuration is assumed to be an octahedron similar to those of WF_6(g) and WCl_6(g) as determined by electron diffraction. The bond distance is estimated to be 2.40 Å by assuming $r_{W-Br} = r_{W-Cl} + (r_{Na-Br} - r_{Na-Cl})$. The bond distances, W–Cl, Na–Br and Na–Cl, are given in JANAF WCl(g), NaBr(g) and NaCl(g) tables, as 2.26 Å, 2.50 Å, and 2.36 Å respectively. The principal moments of inertia are: $I_A = I_B = I_C = 305.7081 \times 10^{-39}\ g·cm^2$.

All vibrational frequencies are estimated from those of WCl_6(g)[1], using the average value of $\upsilon(WBr_6)/\upsilon(WCl_6)$ = 0.62 for modes which are independent of the central atom and 0.68 for modes involving the central atom. These average values of 0.62 and 0.68 are obtained from the ratios of corresponding vibrational frequencies of ReX_6^-, SnX_6^- and PtX_6^- summarized by Siebert,[2] and Nakamoto.[3]

References

[1]J. C. Evans and G. Y-S Lo, The Dow Chemical Company, personal communication, (June 6, 1967), have obtained the six fundamental vibrational frequencies of 408, 312, 367, 165, 206 and 97 cm^{-1} for WCl_6(g) by infrared spectrometry.
[2]H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie," Springer–Verlag, Berlin, (1966).
[3]K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, (1963).

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	−35.204	−199.793	−199.793	INFINITE
100	116.477	331.931	611.326	−27.940	−201.561	−217.638	113.683
200	144.174	423.537	496.369	−14.566	−204.899	−232.499	60.722
250	148.782	456.254	485.179	−7.231	−207.167	−239.149	49.968
298.15	151.369	482.699	482.699	0.	−243.090	−241.129	42.245
300	151.446	483.636	482.702	0.280	−243.275	−241.116	41.982
350	153.112	507.116	484.553	7.897	−334.833	−235.752	35.184
400	154.218	527.638	488.683	15.582	−333.877	−221.663	28.946
450	154.988	545.849	494.042	23.313	−332.922	−207.694	24.108
500	155.544	562.209	500.055	31.077	−331.971	−193.830	20.249
600	156.277	590.639	512.853	46.672	−330.092	−166.379	14.485
700	156.723	614.765	525.732	62.323	−328.257	−139.240	10.390
800	157.014	635.713	538.199	78.011	−326.472	−112.360	7.336
900	157.214	654.219	550.082	93.723	−324.741	−85.700	4.974
1000	157.358	670.791	561.339	109.452	−323.068	−59.230	3.094
1100	157.464	685.794	571.981	125.193	−321.455	−32.925	1.563
1200	157.545	699.498	582.045	140.944	−319.904	−6.764	0.294
1300	157.608	712.111	591.571	156.702	−318.418	19.270	−0.774
1400	157.659	723.793	600.604	172.465	−316.999	45.192	−1.686
1500	157.699	734.672	609.183	188.233	−315.651	71.016	−2.473
1600	157.732	744.851	617.348	204.005	−314.376	96.752	−3.159
1700	157.760	754.414	625.132	219.779	−313.181	122.410	−3.761
1800	157.783	763.432	632.567	235.557	−312.071	148.001	−4.295
1900	157.802	771.963	639.681	251.336	−311.050	173.532	−4.771
2000	157.819	780.058	646.500	267.117	−310.127	199.012	−5.198
2100	157.834	787.758	653.044	282.900	−309.306	224.448	−5.583
2200	157.846	795.101	659.336	298.684	−308.593	249.848	−5.932
2300	157.857	802.118	665.392	314.469	−307.992	275.218	−6.250
2400	157.866	808.836	671.230	330.255	−307.507	300.564	−6.542
2500	157.875	815.281	676.864	346.042	−307.140	325.893	−6.809
2600	157.882	821.473	682.308	361.830	−306.887	351.208	−7.056
2700	157.889	827.432	687.573	377.618	−306.774	376.517	−7.284
2800	157.895	833.174	692.671	393.408	−306.833	401.824	−7.496
2900	157.900	838.715	697.612	409.197	−307.101	427.138	−7.694
3000	157.905	844.068	702.405	424.988	−307.598	452.464	−7.878
3100	157.909	849.246	707.059	440.778	−308.363	477.811	−8.051
3200	157.913	854.259	711.581	456.570	−309.418	503.188	−8.214
3300	157.917	859.119	715.979	472.361	−310.784	528.602	−8.367
3400	157.920	863.833	720.258	488.153	−312.486	554.063	−8.512
3500	157.923	868.411	724.426	503.945	−314.581	579.578	−8.650
3600	157.926	872.860	728.488	519.738	−317.157	605.162	−8.781
3700	157.929	877.187	732.449	535.530	−355.072	631.014	−8.908
3800	157.931	881.398	736.313	551.323	−355.301	657.668	−9.040
3900	157.933	885.501	740.086	567.116	−355.517	684.327	−9.166
4000	157.935	889.499	743.772	582.910	−355.713	710.993	−9.285
4100	157.937	893.399	747.374	598.703	−355.883	737.663	−9.398
4200	157.939	897.205	750.896	614.497	−356.020	764.336	−9.506
4300	157.940	900.921	754.342	630.291	−356.120	791.013	−9.609
4400	157.942	904.552	757.715	646.085	−356.177	817.691	−9.707
4500	157.943	908.102	761.017	661.880	−356.187	844.370	−9.801
4600	157.945	911.573	764.253	677.674	−356.146	871.049	−9.891
4700	157.946	914.970	767.423	693.468	−356.051	897.726	−9.977
4800	157.947	918.295	770.532	709.263	−355.899	924.401	−10.060
4900	157.948	921.552	773.581	725.058	−355.687	951.071	−10.139
5000	157.949	924.743	776.573	740.853	−355.414	977.738	−10.214
5100	157.950	927.871	779.509	756.648	−355.078	1004.398	−10.287
5200	157.951	930.938	782.391	772.443	−354.678	1031.050	−10.357
5300	157.952	933.947	785.223	788.238	−354.212	1057.695	−10.424
5400	157.953	936.899	788.004	804.033	−353.682	1084.330	−10.489
5500	157.953	939.797	790.738	819.828	−353.085	1110.954	−10.551
5600	157.954	942.643	793.425	835.624	−352.423	1137.567	−10.611
5700	157.955	945.439	796.067	851.419	−351.695	1164.168	−10.668
5800	157.955	948.186	798.667	867.215	−350.903	1190.754	−10.724
5900	157.956	950.886	801.224	883.010	−350.046	1217.327	−10.777
6000	157.957	953.541	803.740	898.806	−349.125	1243.885	−10.829

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

Continued from page 460

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