REFERENCE STATE

0	to 933.45 K		crystal
933.45	to 2790.812 K		liquid
above	2790.812 K		ideal monatomic gas

Refer to the individual tables for details.

$A_r = 26.98154$ Aluminum (Al) $Al_1(ref)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	0.	0.	INFINITE	−4.539	0.	0.	0.
100	12.997	6.987	47.543	−4.056	0.	0.	0.
200	21.338	19.144	30.413	−2.254	0.	0.	0.
250	23.084	24.108	28.668	−1.140	0.	0.	0.
298.15	24.209	28.275	28.275	0.	0.	0.	0.
300	24.247	28.425	28.276	0.045	0.	0.	0.
400	25.784	35.630	29.248	2.553	0.	0.	0.
500	26.842	41.501	31.129	5.186	0.	0.	0.
600	27.886	46.485	33.283	7.921	0.	0.	0.
700	29.100	50.872	35.488	10.769	0.	0.	0.
800	30.562	54.850	37.663	13.749	0.	0.	0.
900	32.308	58.548	39.780	16.890	0.	0.	0.
933.450	32.959	59.738	40.474	17.982	____ CRYSTAL <−−> LIQUID ____		
933.450	31.751	71.213	40.474	28.693	TRANSITION		
1000	31.751	73.400	42.594	30.806	0.	0.	0.
1100	31.751	76.426	45.534	33.981	0.	0.	0.
1200	31.751	79.189	48.225	37.156	0.	0.	0.
1300	31.751	81.730	50.706	40.331	0.	0.	0.
1400	31.751	84.083	53.007	43.506	0.	0.	0.
1500	31.751	86.273	55.153	46.681	0.	0.	0.
1600	31.751	88.323	57.162	49.856	0.	0.	0.
1700	31.751	90.247	59.052	53.031	0.	0.	0.
1800	31.751	92.062	60.836	56.207	0.	0.	0.
1900	31.751	93.779	62.525	59.382	0.	0.	0.
2000	31.751	95.408	64.129	62.557	0.	0.	0.
2100	31.751	96.957	65.656	65.732	0.	0.	0.
2200	31.751	98.434	67.112	68.907	0.	0.	0.
2300	31.751	99.845	68.505	72.082	0.	0.	0.
2400	31.751	101.196	69.839	75.257	0.	0.	0.
2500	31.751	102.493	71.120	78.432	0.	0.	0.
2600	31.751	103.738	72.350	81.607	0.	0.	0.
2700	31.751	104.936	73.535	84.782	0.	0.	0.
2790.812	31.751	105.986	74.574	87.665	____ LIQUID <−−> IDEAL GAS ____		
2790.812	20.795	211.333	74.574	381.667	FUGACITY = 1 bar		
2800	20.795	211.401	75.023	381.858	0.	0.	0.
2900	20.796	212.131	79.738	383.938	0.	0.	0.
3000	20.798	212.836	84.163	386.017	0.	0.	0.
3100	20.800	213.518	88.325	388.097	0.	0.	0.
3200	20.804	214.178	92.248	390.178	0.	0.	0.
3300	20.808	214.818	95.952	392.258	0.	0.	0.
3400	20.815	215.440	99.458	394.339	0.	0.	0.
3500	20.823	216.043	102.780	396.421	0.	0.	0.
3600	20.833	216.630	105.934	398.504	0.	0.	0.
3700	20.846	217.201	108.934	400.588	0.	0.	0.
3800	20.862	217.757	111.790	402.673	0.	0.	0.
3900	20.881	218.299	114.515	404.760	0.	0.	0.
4000	20.904	218.828	117.116	406.849	0.	0.	0.
4100	20.932	219.345	119.603	408.941	0.	0.	0.
4200	20.964	219.849	121.984	411.036	0.	0.	0.
4300	21.002	220.343	124.265	413.134	0.	0.	0.
4400	21.046	220.826	126.455	415.236	0.	0.	0.
4500	21.088	221.299	128.557	417.341	0.	0.	0.
4600	21.143	221.763	130.578	419.452	0.	0.	0.
4700	21.206	222.219	132.523	421.570	0.	0.	0.
4800	21.276	222.666	134.396	423.694	0.	0.	0.
4900	21.352	223.105	136.202	425.824	0.	0.	0.
5000	21.439	223.537	137.945	427.964	0.	0.	0.
5100	21.535	223.963	139.627	430.112	0.	0.	0.
5200	21.641	224.382	141.253	432.271	0.	0.	0.
5300-	21.757	224.795	142.825	434.441	0.	0.	0.
5400	21.884	225.203	144.347	436.623	0.	0.	0.
5500	22.021	225.606	145.821	438.818	0.	0.	0.
5600	22.170	226.004	147.249	441.027	0.	0.	0.
5700	22.330	226.398	148.634	443.252	0.	0.	0.
5800	22.496	226.787	149.978	445.491	0.	0.	0.
5900	22.680	227.173	151.284	447.749	0.	0.	0.
6000	22.836	227.552	152.551	450.005	0.	0.	0.

PREVIOUS: June 1979 (1 atm) CURRENT: June 1983 (1 bar)

Aluminum (Al) CRYSTAL $A_r = 26.98154$ Aluminum (Al) $Al_1(cr)$

$S°(298.15\ K) = 28.275 \pm 0.08\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 933.45 \pm 0.01\ K$

$\Delta_f H°(0\ K) = 0\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ{\cdot}mol^{-1}$
$\Delta_{fus} H° = 10.711 \pm 0.21\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted thermal functions for Al(cr) are derived from the studies of Giauque and Meads,[1] Berg,[2] Downie and Martin,[3] Takahashi,[4,5] McDonald,[6] Brooks,[7] Pochapsky[8] and Ditmars *et al.*[9] The mathematical and graphical treatment of these eight studies yields a continuous and smooth heat capacity curve. In contrast, CODATA[9] has recommended an $S°(298.15\ K)$ value which is 0.075 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ greater than ours. Their result was based on an analysis of the low temperature heat capacity data of Giauque and Meads[1] and Berg[2] At the time of their analysis, the studies of Downie and Martin[3] and Takahashi[4,5] had not been published. The three more recent studies[3,4,5,8] suggest a lower heat capacity in the vicinity of 298.15 K, thus the lower entropy in comparison with CODATA.[10]

Roberts[11] surveyed the superconductive properties of the elements and recommended a critical temperature of 1.175 ± 0.002 K for Al(cr). Since this temperature is so low, the effects of superconductivity on the thermodynamic functions are not considered. The entropy contribution due to superconductivity will be less than 0.002 $J{\cdot}K^{-1}{\cdot}mol^{-1}$. The data of Giauque and Meads[1] and Downie and Martin[3] agree at temperatures up to 150 K but drift apart by 0.2 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ at 200 K and 0.17 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ at 300 K, with the Downie and Martin study being lower. The Takahashi[4,5] study is even lower at ~298 K. The high temperature heat capacity values are derived from the enthalpy study of Ditmars *et al.*[9] Their curve is intermediate between those derived from previous studies[4,5,6,7,8] and implies a flatter C_p curve near the melting point (in comparison to previous interpretations). Numerous other heat capacity and enthalpy studies are available but were omitted in this analysis. A detailed discussion of the Group IIIA metals (B, Al, and Ga) is in preparation by the JANAF staff.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

There are no sublimation studies for Al(cr). The adopted value of $\Delta_{sub}H°(298.15\ K)$ is the value recommended by CODATA.[10] Refer to the ideal gas table for details.

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.539	0.	0.	0.
100	12.997	6.987	47.543	−4.056	0.	0.	0.
200	21.338	19.144	30.413	−2.254	0.	0.	0.
250	23.084	24.108	28.668	−1.140	0.	0.	0.
298.15	24.209	28.275	28.275	0.	0.	0.	0.
300	24.247	28.425	28.276	0.045	0.	0.	0.
350	25.113	32.231	28.574	1.280	0.	0.	0.
400	25.784	35.630	29.248	2.553	0.	0.	0.
450	26.335	38.699	30.130	3.856	0.	0.	0.
500	26.842	41.501	31.129	5.186	0.	0.	0.
600	27.886	46.485	33.283	7.921	0.	0.	0.
700	29.100	50.872	35.488	10.769	0.	0.	0.
800	30.562	54.850	37.663	13.749	0.	0.	0.
900	32.308	58.548	39.780	16.890	0.	0.	0.
933.450	32.959	59.738	40.474	17.982	--- CRYSTAL <--> LIQUID ---		
1000	34.358	62.055	41.834	20.221	−10.585	0.760	−0.040
1100	36 722	65.438	43.827	23.772	−10.209	1.878	−0.089
1200	39.408	68.746	45 766	27.576	−9.580	2.951	−0.128

PREVIOUS. June 1979   CURRENT. June 1983

$S°(298.15\ K) = [39.549]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(298.15\ K) = [10.562]\ kJ·mol^{-1}$

$T_{fus} = 933.45 \pm 0.01\ K$

$\Delta_{fus}H° = 10.711 \pm 0.21\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of liquid aluminum is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(933.45\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The adopted heat capacity values are derived from the enthalpy study of McDonald.[1] The enthalpy data, ten experimental points in the liquid region (941–1647 K), were measured in crucibles of BN and TiB_2 sealed in a platinum-rhodium capsule. This containment procedure reduced the problem with the reactivity of liquid aluminum. This data suggests a constant liquid heat capacity of 7.589 $cal·K^{-1}·mol^{-1}$ for this 700 K range.

The liquid enthalpy data of Awbery and Griffiths,[2] four points in the liquid region (937–1036 K), agree within 1% with our adopted enthalpy values. The enthalpy studies of Wust *et al.*[3] and Umino[4] are lower by as much as 4% and 12%, respectively. The heat capacity values of Schmidt *et al.*,[5] 17 values in the range 933–1300 K, are not constant but lie 6–11% lower than our adopted values.

Fusion Data

There are numerous enthalpy of fusion studies reported in the literature Twelve studies [1-3, 5-13] reported values in the range 2.46 to 2.66 $kcal·mol^{-1}$, with a rather isolated value at 2.15 $kcal·mol^{-1}$.[4] We adopt a value 2.560 ± 0.05 $kcal·mol^{-1}$ based on the enthalpy data of McDonald.[1] The chosen value has eliminated uncertainty due to reaction of liquid aluminum and its vessel by use of BN and TiB_2 containers.

The adopted melting temperature, $T_{fus} = 933.45$ K, is a secondary standard on IPTS–68.[14,15]

Vaporization Data

The vaporization studies are summarized on the Al(g) table. The boiling point (fugacity of one bar), $T_{vap} = 2790.812$ K, is calculated as the temperature for which $\Delta_f G° = 0$ for Al(l) = Al(g). The difference in the enthalpy of formation of Al(l) and Al(g) at T_{vap} is the enthalpy of vaporization, $\Delta_{vap}H° = 294.001\ kJ·mol^{-1}$.

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

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	24.209	39.549	39.549	0.	10.562	7.201	−1.262
300	24.247	39.699	39.550	0.045	10.562	7.180	−1.250
350	25.113	43.505	39.848	1.280	10.562	6.617	−0.987
400	25.784	46.904	40.522	2.553	10.562	6.053	−0.790
450	26.335	49.973	41.404	3.856	10.562	5.489	−0.637
500	26.842	52.774	42.403	5.186	10.562	4.926	−0.515
600	27.886	57.759	44.557	7.921	10.562	3.798	−0.331
700	29.100	62.146	46.762	10.769	10.562	2.671	−0.199
720.000	29.371	62.969	47.201	11.353	GLASS <--> LIQUID		
720.000	31.751	62.969	47.201	11.353	TRANSITION		
800	31.751	66.315	48.948	13.893	10.706	1.535	−0.100
900	31.751	70.054	51.089	17.068	10.740	0.384	−0.022
933 450	31.751	71.213	51.790	18.131	--- CRYSTAL <--> LIQUID ---		
1000	31.751	73.400	53.156	20.244	0.	0.	0.
1100	31.751	76.426	55.136	23.419	0.	0.	0.
1200	31.751	79.189	57.027	26.594	0.	0.	0.
1300	31.751	81.730	58.831	29.769	0.	0.	0.
1400	31.751	84.083	60.552	32.944	0.	0.	0.
1500	31.751	86.273	62.194	36.119	0.	0.	0.
1600	31.751	88.323	63.764	39.294	0.	0.	0.
1700	31.751	90.247	65.266	42.469	0.	0.	0.
1800	31.751	92.062	66.704	45.644	0.	0.	0.
1900	31.751	93.779	68.085	48.819	0.	0.	0.
2000	31.751	95.408	69.410	51.994	0.	0.	0.
2100	31.751	96.957	70.686	55.169	0.	0.	0.
2200	31.751	98.434	71.914	58.344	0.	0.	0.
2300	31.751	99.845	73.098	61.519	0.	0.	0.
2400	31 751	101.196	74.240	64.694	0.	0.	0.
2500	31.751	102.493	75.345	67.870	0.	0.	0.
2600	31.751	103.738	76.413	71.045	0.	0.	0.
2700	31.751	104.936	77.447	74.220	0.	0.	0.
2790.812	31.751	105.986	78.359	77.103	---- FUGACITY = 1 bar ----		
2800	31.751	106.091	78.450	77.395	−293.901	0.968	−0.018
2900	31.751	107.205	79.422	80.570	−292.806	11.499	−0.207
3000	31.751	108.281	80.366	83.745	−291.710	21.953	−0.382

PREVIOUS June 1979 CURRENT· June 1983

Aluminum (Al) CRYSTAL-LIQUID $A_r = 26.98154$ Aluminum (Al) $Al_1(cr,l)$

0	to 933.45 K	crystal
above	933.45 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°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−4.539	0.	0.	0.
100	12.997	6.987	47.543	−4.056	0.	0.	0.
200	21.338	19.144	30.413	−2.254	0.	0.	0.
250	23.084	24.108	28.668	−1.140	0.	0.	0.
298.15	24.209	28.275	28.275	0.	0.	0.	0.
300	24.247	28.425	28.276	0.045	0.	0.	0.
350	25.113	32.231	28.574	1.280	0.	0.	0.
400	25 784	35.630	29.248	2.553	0.	0.	0.
450	26.335	38.699	30.130	3.856	0.	0.	0.
500	26.842	41.501	31.129	5.186	0.	0.	0.
600	27.886	46.485	33.283	7.921	0.	0.	0.
700	29.100	50.872	35.488	10.769	0.	0.	0.
800	30.562	54.850	37.663	13.749	0.	0.	0.
900	32.308	58.548	39.780	16.890	0.	0.	0.
933.450	32.959	59.738	40.474	17.982	CRYSTAL <--> LIQUID		
933.450	31.751	71.213	40.474	28.693	TRANSITION		
1000	31.751	73.400	42.594	30.806	0.	0.	0.
1100	31.751	76.426	45.534	33.981	0.	0.	0.
1200	31.751	79.189	48.225	37.156	0.	0.	0.
1300	31.751	81.730	50.706	40.331	0.	0.	0.
1400	31.751	84 083	53.007	43.506	0.	0.	0.
1500	31.751	86.273	55.153	46.681	0.	0.	0.
1600	31.751	88.323	57.162	49.856	0.	0.	0.
1700	31.751	90.247	59.052	53.031	0.	0.	0.
1800	31.751	92.062	60.836	56.207	0.	0.	0.
1900	31.751	93.779	62.525	59.382	0.	0.	0.
2000	31.751	95.408	64.129	62.557	0.	0.	0.
2100	31.751	96.957	65.656	65.732	0.	0.	0.
2200	31.751	98.434	67.112	68.907	0.	0.	0.
2300	31.751	99.845	68.505	72.082	0.	0.	0.
2400	31.751	101.196	69.839	75.257	0.	0.	0.
2500	31.751	102.493	71.120	78.432	0.	0.	0.
2600	31.751	103.738	72.350	81.607	0.	0.	0.
2700	31.751	104.936	73.535	84.782	0.	0.	0.
2790.812	31.751	105.986	74.574	87.665	---- FUGACITY = 1 bar ----		
2800	31.751	106.091	74.677	87.957	−293.901	0.968	−0.018
2900	31.751	107.205	75.780	91.132	−292.805	11.479	−0.207
3000	31.751	108.281	76.846	94.307	−291.710	21.953	−0.382

PREVIOUS: CURRENT: June 1983

Aluminum (Al) $Al_1(cr,l)$

Aluminum (Al) IDEAL GAS $A_r = 26.98154$ Aluminum (Al) $Al_1(g)$

IP(Al, g) = 48278.37 ± 0.02 cm^{-1}
$S°(298.15\ K) = 164.553 \pm 0.03\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 327.3 \pm 4.2\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 329.7 \pm 4.2\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2P°_{1/2}$	0	2
$^2P°_{3/2}$	112.061	4
$^2S_{1/2}$	25347.756	2
.	.	.
.	.	.
$^2D_{5/2}$	48182.	6
IP	48278.37	

Enthalpy of Formation

The enthalpy of formation is derived from the vaporization measurements of Brewer and Searcy (1383–1468 K),[1] Porter *et al.* (932 K),[2] Potter and Hildenbrand (1400–1611 K),[3] Rao and Motzfeld (1556 K),[4] and Johnson *et al.* (1327 K).[5] The adopted value $\Delta_f H°$(Al, g, 298.15 K) = 78.8 ± 1.0 $kcal{\cdot}mol^{-1}$ is that adopted by CODATA.[6] The difference in $S°$(Al, cr, 298.15 K) between our adopted value and that of CODATA[6] would create a change of only 0.02 $kcal^{-1}{\cdot}mol^{-1}$in $\Delta_f H°$(Al, g, 298.15 K). Other vaporization studies have been omitted in this analysis: Farkas (1476 K)[7] Baur and Brunner (1734-2237 K),[8] and Priselkov *et al.* (1273–1473 K).[9]

Heat Capacity and Entropy

The electronic energy levels are given in the compilation by Martin and Zalubas.[10] Although we list only the ground state, the two lowest excited states, the highest observed excited state (below the ionization limit), and the ionization potential for Al(g), all levels below the ionization limit listed by Martin and Zalubas[10] are used in the calculation. The 105 observed levels below the ionization limit are too numerous to list completely. However, they include contributions from observed levels to n = 35. The contributions are from excitations of the 3p electron in the ground state configuration, $1s^2 2s^2 2p^6 3s^2 3p$. There is a contribution at ~29000 cm^{-1} due to the excitation of a 3s electron, giving rise to a $1s^2 2s^2 2p^6 3s 3p^2$ configuration. Other contributions of this latter type lie above the ionization limit.

The electronic level at 112.061 cm^{-1} has a significant effect on the thermodynamic values at low temperatures. The higher electronic states have an effect on the values above 3000 K. The Gibbs energy function values up to 4000 K are essentially independent of the estimated missing levels (for $n < 35$), the cut-off procedure, and the inclusion of levels for $n > 3$.

The thermal functions at 298.15 K agree with recent CODATA recommendations[6] except for two minor differences. First, the entropy differs by 0.1094 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ because this table uses a standard state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, an entropy difference of 0.004 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ arises due to the use of slightly different values for the fundamental constants.

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.919	327.320	327.320	INFINITE
100	25.192	139.619	184.197	−4.458	329.297	316.034	−165.079
200	22.133	155.883	166.528	−2.129	329.824	302.476	−78.999
250	21.650	160.764	164.907	−1.036	329.804	295.639	−61.770
298.15	21.390	164.553	164.553	0.	329.699	289.068	−50.643
300	21.383	164.686	164.554	0.040	329.694	288.816	−50.287
350	21.221	167.969	164.813	1.104	329.524	282.016	−42.089
400	21.117	170.795	165.388	2.163	329.309	275.243	−35.943
450	21.046	173.278	166.130	3.217	329.060	268.499	−31.167
500	20.995	175.492	166.957	4.268	328.781	261.785	−27.348
600	20.930	179.314	168.708	6.363	328.141	248.444	−21.629
700	20.891	182.537	170.460	8.454	327.385	235.219	−17.552
800	20.866	185.325	172.147	10.542	326.492	222.112	−14.502
900	20.849	187.781	173.751	12.628	325.436	209.126	−12.137
1000	20.836	189.977	175.266	14.712	313.605	197.027	−10.292
1100	20.827	191.963	176.695	16.795	312.513	185.422	−8.805
1200	20.821	193.775	178.044	18.877	311.420	173.917	−7.570
1300	20.816	195.441	179.319	20.959	310.327	162.503	−6.529
1400	20.811	196.984	180.526	23.041	309.233	151.172	−5.640
1500	20.808	198.419	181.672	25.122	308.139	139.921	−4.872
1600	20.805	199.762	182.761	27.202	307.045	128.742	−4.203
1700	20.803	201.023	183.798	29.283	305.950	117.631	−3.614
1800	20.801	202.212	184.789	31.363	304.856	106.585	−3.093
1900	20.800	203.337	185.736	33.443	303.760	95.600	−2.628
2000	20.798	204.404	186.643	35.523	302.665	84.673	−2.211
2100	20.797	205.419	187.513	37.603	301.570	73.800	−1.836
2200	20.796	206.386	188.349	39.682	300.475	62.979	−1.495
2300	20.795	207.311	189.153	41.762	299.379	52.209	−1.186
2400	20.795	208.196	189.928	43.841	298.284	41.486	−0.903
2500	20.794	209.044	190.676	45.921	297.188	30.808	−0.644
2600	20.794	209.860	191.398	48.000	296.092	20.175	−0.405
2700	20.794	210.645	192.097	50.080	294.997	9.583	−0.185
2790.812	20.795	211.333	192.712	51.968	---- FUGACITY = 1 bar ----		
2800	20.795	211.401	192.773	52.159	0.	0.	0.
2900	20.796	212.131	193.428	54.239	0.	0.	0.
3000	20.798	212.836	194.063	56.318	0.	0.	0.
3100	20.800	213.518	194.680	58.398	0.	0.	0.
3200	20.804	214.178	195.279	60.478	0.	0.	0.
3300	20.808	214.818	195.861	62.559	0.	0.	0.
3400	20.815	215.440	196.428	64.640	0.	0.	0.
3500	20.823	216.043	196.980	66.722	0.	0.	0.
3600	20.833	216.630	197.518	68.805	0.	0.	0.
3700	20.846	217.201	198.042	70.889	0.	0.	0.
3800	20.862	217.757	198.553	72.974	0.	0.	0.
3900	20.881	218.299	199.053	75.061	0.	0.	0.
4000	20.904	218.828	199.541	77.150	0.	0.	0.
4100	20.932	219.345	200.017	79.242	0.	0.	0.
4200	20.964	219.849	200.484	81.337	0.	0.	0.
4300	21.002	220.343	200.940	83.435	0.	0.	0.
4400	21.046	220.826	201.386	85.537	0.	0.	0.
4500	21.088	221.299	201.823	87.642	0.	0.	0.
4600	21.143	221.763	202.252	89.753	0.	0.	0.
4700	21.206	222.219	202.672	91.870	0.	0.	0.
4800	21.276	222.666	203.084	93.995	0.	0.	0.
4900	21.352	223.105	203.488	96.125	0.	0.	0.
5000	21.439	223.537	203.885	98.264	0.	0.	0.
5100	21.535	223.963	204.274	100.413	0.	0.	0.
5200	21.641	224.382	204.657	102.572	0.	0.	0.
5300	21.757	224.795	205.033	104.742	0.	0.	0.
5400	21.884	225.203	205.403	106.924	0.	0.	0.
5500	22.021	225.606	205.766	109.119	0.	0.	0.
5600	22.170	226.004	206.124	111.328	0.	0.	0.
5700	22.330	226.398	206.476	113.553	0.	0.	0.
5800	22.496	226.787	206.823	115.792	0.	0.	0.
5900	22.680	227 173	207.165	118.050	0.	0.	0.
6000	22.836	227.552	207.501	120.306	0.	0.	0.

PREVIOUS. June 1979 (1 atm) CURRENT: June 1983 (1 bar)

Aluminum, Ion (Al^+) **IDEAL GAS** **M_r = 26.98099** **Aluminum, Ion (Al^+)** **$Al_1^+(g)$**

$IP(Al^+, g) = 151862.7 \pm 0.4\ cm^{-1}$
$S°(298.15\ K) = 149.950 \pm 0.04\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 904.86 \pm 4.2\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [912.713]\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.00	1
$^3P_0$	37393.03	1
$^3P_1$	37453.91	3
$^3P_2$	37577.79	5
$^1P_1$	59852.02	3

Enthalpy of Formation

$\Delta_f H°(Al^+, g, 0\ K)$ is calculated from $\Delta_f H°(Al, g, 0\ K)$[1] using the spectroscopic value of $IP(Al) = 48278.37 \pm 0.02\ cm^{-1}(577.538 \pm 0.0002\ kJ{\cdot}mol^{-1})$ from Martin and Zalubas.[2] The ionization limit is converted from cm^{-1} to $kJ{\cdot}mol^{-1}$ using the factor $1\ cm^{-1} = 0.01196266\ kJ{\cdot}mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Al^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Al, g, 0\ K)$ by using IP(Al) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for Al(g), $Al^+(g)$, and e^-(ref). $\Delta_f H°(Al \rightarrow Al^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298\ 15\ K)$ should be changed by $-6.197\ kJ{\cdot}mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Martin and Zalubas,[2] 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[6] 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 first four excited states; the next excited state is $85481.35\ cm^{-1}$ above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first four excited states. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[6]

References

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	904.858		
100	20.786	127.243	168.431	−4.119			
200	20.786	141.651	151.852	−2.040			
250	20.786	146.289	150.292	−1.001			
298.15	20.786	149.950	149.950	0.	912.713	870.181	−152.452
300	20.786	150.079	149.951	0.038	912.745	869.917	−151.466
350	20.786	153.283	150.204	1.078	913.589	862.712	−128.753
400	20.786	156.059	150.766	2.117	914.394	855.388	−111.702
450	20.786	158.507	151.493	3.156	915.169	847.965	−98.429
500	20.786	160.697	152.306	4.196	915.919	840.458	−87.802
600	20.786	164.487	154.029	6.274	917.340	825.230	−71.843
700	20.786	167.691	155.758	8.353	918.650	809.774	−60.426
800	20.786	170.466	157.427	10.431	919.826	794.138	−51.852
900	20.786	172.915	159.014	12.510	920.843	778.364	−45.175
1000	20.786	175.105	160.516	14.589	911.084	763.246	−39.868
1100	20.786	177.086	161.934	16.667	912.066	748.415	−35.539
1200	20.786	178.894	163.273	18.746	913.049	733.494	−31.928
1300	20.786	180.558	164.539	20.824	914.031	718.492	−28.869
1400	20.786	182.099	165.739	22.903	915.013	703.413	−26.245
1500	20.786	183.533	166.878	24.982	915.995	688.265	−23.968
1600	20.786	184.874	167.961	27.060	916.977	673.051	−21.973
1700	20.786	186.134	168.994	29.139	917.959	657.775	−20.211
1800	20.786	187.322	169.979	31.217	918.941	642.442	−18.643
1900	20.786	188.446	170.922	33.296	919.924	627.054	−17.239
2000	20.786	189.512	171.825	35.375	920.906	611.615	−15.974
2100	20.786	190.527	172.692	37.453	921.888	596.126	−14.828
2200	20.786	191.493	173.524	39.532	922.870	580.590	−13.785
2300	20.786	192.417	174.326	41.610	923.852	565.010	−12.832
2400	20.786	193.302	175.098	43.689	924.834	549.387	−11.957
2500	20.786	194.151	175.844	45.768	925.816	533.723	−11.152
2600	20.786	194.966	176.563	47.846	926.799	518.020	−10.407
2700	20.786	195.750	177.260	49.925	927.781	502.280	−9.717
2800	20.786	196.506	177.934	52.004	634.862	487.470	−9.094
2900	20.786	197.236	178.587	54.082	636.939	482.169	−8.685
3000	20.786	197.940	179.220	56.161	639.017	476.797	−8.302
3100	20.787	198.622	179.835	58.239	641.094	471.355	−7.942
3200	20.787	199.282	180.433	60.318	643.172	465.847	−7.604
3300	20.788	199.922	181.013	62.397	645.248	460.273	−7.286
3400	20.788	200.542	181.579	64.476	647.325	454.637	−6.985
3500	20.790	201.145	182.129	66.555	649.400	448.939	−6.700
3600	20.791	201.730	182.666	68.634	651.475	443.183	−6.430
3700	20.793	202.300	183.189	70.713	653.549	437.368	−6.175
3800	20.796	202.855	183.699	72.792	655.622	431.498	−5.931
3900	20.800	203.395	184.197	74.872	657.693	425.573	−5.700
4000	20.805	203.922	184.684	76.952	659.763	419.594	−5.479
4100	20.811	204.435	185.159	79.033	661.830	413.565	−5.269
4200	20.818	204.937	185.624	81.115	663.896	407.484	−5.068
4300	20.828	205.427	186.079	83.197	665.958	401.355	−4.875
4400	20.839	205.906	186.524	85.280	668.018	395.178	−4.691
4500	20.853	206.374	186.960	87.365	670.077	388.953	−4.515
4600	20.869	206.833	187.387	89.451	672.130	382.684	−4.346
4700	20.888	207.282	187.806	91.539	674.179	376.369	−4.183
4800	20.910	207.722	188.216	93.628	676.223	370.011	−4.027
4900	20.935	208.153	188.618	95.721	678.264	363.610	−3.876
5000	20.965	208.577	189.013	97.816	680.298	357.168	−3.731
5100	20.999	208.992	189.401	99.914	682.326	350.686	−3.592
5200	21.037	209.400	189.782	102.015	684.347	344.163	−3.457
5300	21.079	209.801	190.156	104.121	686.362	337.602	−3.327
5400	21.127	210.196	190.523	106.232	688.369	331.003	−3.202
5500	21.181	210.584	190.884	108.347	690.368	324.366	−3.081
5600	21.240	210.966	191.240	110.468	692.358	317.694	−2.963
5700	21.305	211.342	191.589	112.595	694.339	310.986	−2.850
5800	21.376	211.714	191.933	114.729	696.313	304.243	−2.740
5900	21.453	212.080	192.271	116.870	698.274	297.466	−2.634
6000	21.538	212.441	192.604	119.020	700.247	290.654	−2.530

PREVIOUS June 1979 (1 atm)   CURRENT: June 1983 (1 bar)

Aluminum, Ion (Al^+) **$Al_1^+(g)$**

Aluminum, Ion (Al^-) IDEAL GAS $M_r = 26.98209$ Aluminum, Ion (Al^-) $Al_1^-(g)$

$EA(Al, g) = 0.441 \pm 0.010$ eV
$S°(298.15\ K) = 168.135 \pm 0.08\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 284.77 \pm 5.2\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [280.790]\ kJ{\cdot}mol^{-1}$

Electonic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1P_0$	0	1
$^3P_0$	26	3
$^3P_2$	76	5
$^1D_2$	2678	5

Enthalpy of Formation

$\Delta_f H°(Al^-, g, 0\ K)$ is calculated from $\Delta_f H°(Al, g, 0\ K)$[1] using the adopted election affinity of $EA(Al) = 0.441 \pm 0.010$ eV (42.550 ± 0.965 $kJ{\cdot}mol^{-1}$). This value, recommended by Hotop and Lineberger[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on $Al^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.* [5] and Massey.[6]

$\Delta_f H°(Al^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Al, g, 0\ K)$ by using EA(Al) with JANAF [1] enthalpies, $H°(0\ K){-}H°(298.15\ K)$, for $Al^-(g)$, Al(g), and e^-(ref). $\Delta_r H°(Al^- \rightarrow Al + e^-, 298.15\ K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by $+6.197\ kJ{\cdot}mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for $Al^-(g)$ is given by Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6] The fine–structure separation has been calculated via an isoelectronic extrapolation of ratios of fine structure separations[4] and is that recommended by Hotop and Lineberger.[2]

A comparison of the isoelectronic sequence – $Al^-(g)$, Si(g), $P^+(g)$, and $S^{++}(g)$ – would suggest that two states, $^1D_2$ and $^1S_0$, may exist at low wave numbers. Feigirle *et al.*[3] using laser photodetachment electron spectrometry, observed the bound state, $^1D_2$, at 0.332 eV. The $^1S_0$ state would correspond to a metastable state.

References

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.756	284.770		
100	22.297	144.748	186.955	−4.221			
200	21.171	159.730	170.057	−2.065			
250	21.031	164.437	168.480	−1.011			
298.15	20.960	168.135	168.135	0.	280.790	245.345	−42.983
300	20.958	168.265	168.135	0.039	280.745	245.125	−42.680
350	20.921	171.492	168.390	1.086	279.518	239.285	−35.711
400	20.913	174.285	168.957	2.131	278.251	233.624	−30.508
450	20.933	176.749	169.688	3.177	276.954	228.123	−26.480
500	20.983	178.957	170.506	4.225	275.633	222.768	−23.272
600	21.163	182.797	172.244	6.332	272.926	212.448	−18.495
700	21.421	186.078	173.992	8.460	270.129	202.588	−15.117
800	21.715	188.957	175.686	10.617	267.226	193.136	−12.610
900	22.006	191.532	177.306	12.803	264.192	184.055	−10.682
1000	22.270	193.864	178.847	15.017	250.412	176.081	−9.198
1100	22.493	195.998	180.311	17.256	247.397	168.794	−8.015
1200	22.670	197.963	181.701	19.514	244.402	161.780	−7.042
1300	22.804	199.783	183.023	21.788	241.422	155.016	−6.229
1400	22.897	201.477	184.281	24.074	238.454	148.481	−5.540
1500	22.955	203.058	185.481	26.367	235.493	142.157	−4.950
1600	22.985	204.541	186.626	28.664	232.537	136.031	−4.441
1700	22.991	205.935	187.721	30.963	229.582	130.090	−3.997
1800	22.978	207.249	188.770	33.261	226.627	124.323	−3.608
1900	22.950	208.490	189.776	35.558	223.670	118.720	−3.264
2000	22.912	209.666	190.741	37.851	220.709	113.273	−2.958
2100	22.865	210.783	191.669	40.140	217.744	107.974	−2.686
2200	22.812	211.846	192.562	42.424	214.775	102.816	−2.441
2300	22.756	212.859	193.423	44.702	211.799	97.794	−2.221
2400	22.697	213.826	194.253	46.975	208.818	92.901	−2.022
2500	22.636	214.751	195.054	49.241	205.831	88.133	−1.841
2600	22.576	215.638	195.829	51.502	202.838	83.484	−1.677
2700	22.515	216.489	196.579	53.757	199.839	78.950	−1.527
2800	22.455	217.306	197.304	56.005	−97.067	75.496	−1.408
2900	22.397	218.093	198.008	58.248	−98.983	81.692	−1.471
3000	22.340	218.852	198.690	60.485	−100.904	87.955	−1.531
3100	22.285	219.583	199.352	62.716	−102.831	94.282	−1.589
3200	22.231	220.290	199.996	64.942	−104.764	100.672	−1.643
3300	22.180	220.973	200.621	67.162	−106.703	107.121	−1.696
3400	22.130	221.635	201.229	69.378	−108.647	113.630	−1.746
3500	22.082	222.275	201.822	71.588	−110.597	120.196	−1.794
3600	22.036	222.897	202.398	73.794	−112.552	126.818	−1.840
3700	21.992	223.500	202.961	75.996	−114.514	133.494	−1.885
3800	21.950	224.086	203.509	78.193	−116.480	140.223	−1.928
3900	21.910	224.656	204.044	80.386	−118.453	147.004	−1.969
4000	21.871	225.210	204.566	82.575	−120.432	153.836	−2.009
4100	21.834	225.749	205.076	84.760	−122.417	160.717	−2.048
4200	21.799	226.275	205.575	86.942	−124.409	167.647	−2.085
4300	21.765	226.788	206.062	89.120	−126.407	174.624	−2.121
4400	21.733	227.288	206.539	91.295	−128.413	181.648	−2.156
4500	21.702	227.776	207.005	93.466	−130.424	188.717	−2.191
4600	21.672	228.252	207.462	95.635	−132.446	195.832	−2.224
4700	21.644	228.718	207.909	97.801	−134.476	202.990	−2.256
4800	21.617	229.174	208.348	99.964	−136.515	210.192	−2.287
4900	21.591	229.619	208.777	102.124	−138.564	217.436	−2.318
5000	21.566	230.055	209.198	104.282	−140.624	224.722	−2.348
5100	21.543	230.482	209.612	106.438	−142.696	232.050	−2.377
5200	21.520	230.900	210.017	108.591	−144.780	239.418	−2.405
5300	21.498	231.310	210.415	110.742	−146.878	246.826	−2.433
5400	21.477	231.711	210.806	112.890	−148.990	254.275	−2.460
5500	21.457	232.105	211.189	115.037	−151.117	261.762	−2.486
5600	21.438	232.492	211.566	117.182	−153.260	269.288	−2.512
5700	21.419	232.871	211.937	119.325	−155.421	276.853	−2.537
5800	21.401	233.243	212.301	121.466	−157.597	284.455	−2.562
5900	21.384	233.609	212.659	123.605	−159.795	292.096	−2.586
6000	21.368	233.968	213.011	125.743	−161.991	299.771	−2.610

PREVIOUS: June 1979 (1 atm)   CURRENT: June 1983 (1 bar)

Aluminum Borate (AlBO$_2$) **IDEAL GAS** **M_r = 69.79034** **Aluminum Borate (AlBO$_2$)** **Al$_1$B$_1$O$_2$(g)**

$\Delta_f H°(0\ \text{K}) = -539.0 \pm 17\ \text{kJ·mol}^{-1}$

$S°(298.15\ \text{K}) = [269.6 \pm 10]\ \text{J·K}^{-1}\text{·mol}^{-1}$ $\Delta_f H°(298.15\ \text{K}) = -541.4 \pm 17\ \text{kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
[2000](1)	[600](1)
[1000](1)	[350](1)
[600](1)	[800](1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: [C$_s$]
Bond Distances: Al–O = [1.66] Å; O–B = [1.36] Å; B=O = [1.20] Å
Bond Angles: Al–O–B = [145]°; O–B=O = [180]°
Product of the Moments of Inertia: $I_A I_B I_C = [6.527732] \times 10^{-115}\ \text{g}^3\ \text{cm}^6$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(\text{AlBO}_2,\ \text{g},\ 298.15\ \text{K}) = -129.4 \pm 4\ \text{kcal·mol}^{-1}$ is calculated from the enthalpy of reaction, $\Delta_r H°(1500\ \text{K}) = -14.7 \pm 3.2\ \text{kcal·mol}^{-1}$ for 1/2 $Al_2O(g)$ + 1/2 $B_2O_3(g)$ = $AlBO_2(g)$ with all JANAF auxiliary data. The value of $\Delta_r H°(1500\ \text{K})$ was obtained from the mass spectrometric determination of ion intensity ratios by Buchler *et al.*[1]

Heat Capacity and Entropy

The bent molecular structure, the bond distances O–B and B=O, and the bond angle O–B–O are assumed to be the same as those in $LiBO_2(g)$. The bond distance Al–O and the bond angle Al–O–(BO) are estimated to be the same as those in $Al_2O(g)$. The principal moments of inertia are $I_A = 0.7404 \times 10^{-19}$, $I_B = 29.3249 \times 10^{-39}$, and $I_C = 30.0653 \times 10^{-39}\ \text{g cm}^2$.

The vibrational frequencies were estimated by comparison with those in $LiBO_2(g)$, $Al_2O(g)$, $B_2O_3(g)$, and $AlCl(g)$.

Reference

[1] A. Buchler, P. E. Blackburn, and J. L. Stauffer, ARPA Order No. 315–62, Arthur D. Little, Inc., Cambridge, MA.

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	−12.008	−538.981	−538.981	INFINITE
100	34.879	223.687	310.212	−8.653	−539.038	−543.346	283.815
200	43.736	250.340	274.120	−4.756	−540.187	−547.246	142.926
250	48.632	260.633	270.413	−2.445	−540.819	−548.937	114.694
298.15	52.833	269.567	269.567	0.	−541.410	−550.447	96.436
300	52.982	269.894	269.568	0.098	−541.432	−550.503	95.851
350	56.680	278.347	270.227	2.842	−542.026	−551.967	82.377
400	59.785	286.124	271.734	5.756	−542.616	−553.347	72.260
450	62.400	293.321	273.738	8.812	−543.207	−554.653	64.382
500	64.622	300.014	276.035	11.989	−543.805	−555.893	58.074
600	68.173	312.125	281.062	18.638	−545.033	−558.196	48.595
700	70.861	322.845	286.280	25.596	−546.332	−560.288	41.809
800	72.936	332.449	291.462	32.790	−547.739	−562.188	36.707
900	74.562	341 137	296.506	40.168	−549.289	−563.902	32.728
1000	75.853	349.062	301.371	47.691	−561.605	−564.675	29.496
1100	76.890	356.342	306.042	55.330	−563.180	−564.906	26.825
1200	77.731	363.070	310.518	63.062	−564.761	−564.993	24.594
1300	78.420	369.320	314.804	70.871	−566.352	−564.948	22.700
1400	78.991	375.153	318.908	78.743	−567.958	−564.780	21.072
1500	79.468	380.620	322.842	86.666	−569.585	−564.497	19.658
1600	79.870	385.761	326.615	94.634	−571.236	−564.104	18.416
1700	80.211	390.614	330.239	102.638	−572.915	−563.606	17.318
1800	80.503	395.207	333.722	110.674	−574.624	−563.010	16.338
1900	80.754	399.567	337.073	118.737	−576.367	−562.317	15.459
2000	80.972	403.715	340.303	126.824	−578.146	−561.532	14.666
2100	81.162	407.670	343.417	134.931	−579.962	−560.657	13.946
2200	81.328	411.449	346.424	143.056	−581.818	−559.694	13.289
2300	81.475	415.068	349.331	151.196	−583.714	−558.646	12.687
2400	81.605	418.538	352.142	159.350	−635.911	−556.446	12.111
2500	81.721	421.872	354.865	167.517	−637.970	−553.093	11.556
2600	81.824	425.079	357.505	175.694	−640.039	−549.657	11.043
2700	81.916	428.169	360.065	183.881	−642.119	−546.141	10.566
2800	81.999	431.150	362.551	192.077	−938.112	−541.580	10.103
2900	82.074	434.028	364.966	200.280	−939.120	−527.401	9.500
3000	82.142	436.812	367.315	208.491	−940.141	−513.186	8.935
3100	82.204	439.506	369.600	216.709	−941.174	−498.937	8.407
3200	82.260	442.117	371.826	224.932	−942.220	−484.655	7.911
3300	82.312	444.649	373.995	233.161	−943.278	−470.340	7.445
3400	82.359	447.107	376.109	241.394	−944.348	−455.992	7.005
3500	82.402	449.495	378.172	249.632	−945.431	−441.614	6.591
3600	82.442	451.817	380.185	257.875	−946.525	−427.203	6.199
3700	82.479	454.077	382.152	266.121	−947.632	−412.763	5.827
3800	82.513	456.277	384.074	274.370	−948.752	−398.291	5.475
3900	82.544	458.420	385.953	282.623	−949.883	−383.790	5.140
4000	82.573	460.511	387.791	290.879	−951.027	−369.261	4.822
4100	82.600	462.550	389.589	299.138	−952.184	−354.702	4.519
4200	82.625	464.541	391.350	307.399	−1433.203	−333.091	4.143
4300	82.649	466.485	393.075	315.663	−1433.298	−306.897	3.728
4400	82.671	468.385	394.765	323.929	−1433.410	−280.701	3.332
4500	82.691	470.243	396.422	332.197	−1433.536	−254.502	2.954
4600	82.710	472.061	398.047	340.467	−1433.682	−228.300	2.592
4700	82.728	473.840	399.640	348.739	−1433.846	−202.094	2.246
4800	82.745	475.582	401.204	357.012	−1434.031	−175.884	1.914
4900	82.761	477.288	402.740	365.288	−1434.237	−149.670	1.596
5000	82.776	478.960	404.248	373.565	−1434.466	−123.452	1.290
5100	82.790	480.600	405.729	381.843	−1434.720	−97.229	0.996
5200	82.804	482.208	407.184	390.123	−1435.002	−71.002	0.713
5300	82.816	483.785	408.614	398.404	−1435.312	−44.768	0.441
5400	82.828	485.333	410.021	406.686	−1435.653	−18.529	0.179
5500	82.840	486.853	411.404	414.969	−1436.027	7.717	−0.073
5600	82.850	488.346	412.765	423.254	−1436.437	33.972	−0.317
5700	82.860	489.812	414.104	431.539	−1436.885	60.233	−0.552
5800	82.870	491.253	415.421	439.826	−1437.370	86.502	−0.779
5900	82.879	492.670	416.719	448.113	−1437.900	112.779	−0.998
6000	82.888	494.063	417.996	456.402	−1438.455	139.065	−1.211

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

Aluminum Borate (AlBO$_2$) **Al$_1$B$_1$O$_2$(g)**

Aluminum Bromide (AlBr) **IDEAL GAS** **M_r = 106.88554** **Aluminum Bromide (AlBr)** **$Al_1Br_1(g)$**

$S°(298.15\ K) = 239.62 \pm 0.21\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 23.13 \pm 12.55\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = 15.90 \pm 12.55\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
	23663.	2
$a^3\Pi$	23795.3	2
	[23920]	[2]
$A^1\Pi$	35837.8	2
$[b^3\Sigma^+]$	[43000]	[3]

$\omega_e = 377.61\ cm^{-1}$ $\omega_ex_e = 1.3239\ cm^{-1}$ $\sigma = 1$
$B_e = 0.15871\ cm^{-1}$ $\alpha_e = 0.0008583\ cm^{-1}$ $r_e = 2.294803$ Å

Enthalpy of Formation

Ram,[1] Gaydon,[2] Singh,[3] Rosen[4] and Barrow[5] reference possible spectroscopic values for the dissociation energy of AlBr(g). The $A^1\Pi$ state yielded three values for the dissociation energy: 106.9 kcal·mol^{-1} by a short extrapolation, a minimum of 104.4 kcal·mol^{-1} as indicated by the highest observed vibrational level, and a maximum of 105.7 kcal·mol^{-1} as determined by predissociation which sets in at $v' = 4$. Ram[1] has observed rotational predissociation in the AlBr band system and reports the dissociation energy at 105.85 ± 0.46 kcal·mol^{-1}. Gaydon[2] reports a value of 86.5 kcal mol^{-1} based on a ground state linear Birge–Sponer extrapolation (v, 0–11). However, substituting the values tabulated above for ω_e and $x_e\omega_e$ into the equation $D° = \omega_e^2/4X_e\omega_e - 0.5\omega_e$, a value of 76.5 kcal·mol^{-1} is obtained for the dissociation energy. A value of 105 kcal·mol^{-1} is suggested by Barrow[5] based on wavelengths for maximum photoionization.

Semenkovich[6] measured the vapor pressure of the reaction $Al(l) + NaBr(l) \rightarrow Na(g) + AlBr(g)$ at 1175 K. By the 3rd law method $\Delta_rH°(298\ 15\ K)$ is equal to 108.134 kcal·mol^{-1}. Using JANAF auxiliary data,[7] $\Delta_fH°(AlBr, g, 298.15\ K)$ is equal to 3.829 kcal·mol^{-1} and the dissociation energy is 100.87 kcal·mol^{-1}.

Gross[8] studied the equilibrium involved in the reaction $2\ Al(l) + AlBr_3(g) \rightarrow 3\ AlBr(g)$ in the range 550 – 1300°C. The reported $\Delta_rH°(298.15\ K)$ is 106.27 kcal·mol^{-1}. Using auxiliary JANAF data,[7] $\Delta_fH°(298.15\ K)$ is 4.43 kcal·mol^{-1} and $D_0°$ is 100.26 kcal·mol^{-1}.

It should be noted that the highest observed vibrational level in the $A^1\Pi$ state lies approximately 4 kcal·mol^{-1} above the thermochemical dissociation energy of Semenkovich[6] and Gross.[8] This suggests a potential maximum in the $A^1\Pi$ state as mentioned by Barrow.[5] A similar maximum is suggested for AlF(g) and AlCl(g).[7,9,5] In addition, Wyse and Gordy,[10] from nuclear quadrupole coupling, deduce that the ionic character of the AlBr bond is ≥8%. Thus the value of $D_0° = 76.5$ kcal·mol^{-1} as obtained by a linear Birge–Sponer extrapolation is undoubtedly too low.[2] This ground state extrapolation was adjusted to 99.5 kcal·mol^{-1} and 102.2 kcal·mol^{-1} using two ionic character correction factors as suggested by Hildenbrand.[9] The former value is more suitable for metal fluorides while the latter is for the more general case. A comparison of $D_0°$ values[7,2,4] for the group IIIA gaseous monohalides suggests a value of 96–103 kcal·mol^{-1}, which is consistent with the value obtained by Semenkovich[6] and Gross.[8]

Due to the high ionic character in the AlBr bond and the possible unreliability of extrapolations of excited states which contain a potential maximum, the spectroscopic data is suspect as to the determination of $\Delta_fH°(298.15\ K)$. The chosen value for $\Delta_fH°(298.15\ K)$, 15.90 kJ·mol^{-1}, is a rounded value from the vapor pressure work of Semenkovich.[6]

Heat Capacity and Entropy

The spectroscopic constants for $Al^{79}Br$ and $Al^{81}Br$ were taken from Wyse and Gordy[10] and averaged according to the natural isotopic abundance of bromine. The electronic states are taken from Rosen[4] with the exception of the upper $^3\Pi$ state and the $b^3\Sigma^+$ state. The upper $^3\Pi$ state is estimated to be approximately in a linear relationship with the two lower $^3\Pi$ state. The $b^3\Sigma^+$ state is assigned by analogy with AlF and AlCl.[7] Lakshminarayana and Haranath[11] also reported values for two of the $a^3\Pi$ states which are in excellent agreement with Rosen's values.[4]

References

[1] R. S. Ram, Spectroscopy Lett. 9, 435 (1976); Opt. Pura. Y. Appli (Spain) 6, 38 (1973).
[2] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules" 3rd ed.. Chapman and Hall, Ltd., London, 330 pp. (1968); refer to p. 260.
[3] J. Singh, K. P. R. Nair and D. K. Rai, J. Mol. Struct. 6, 328 (1970).
[4] B Rosen (ed.), "Donnes Spectroscopiques Relatives Aux Molecules Diatomiques," Pergamon Press, New York, 515 pp. (1970).
[5] R. F. Barrow, Trans. Faraday Soc. 56, 952 (1960); Nature 189, 480 (1961).
[6] S. A. Semenkovich, Zh. Prikl. Khim. 30, 933 (1957).
[7] JANAF Thermochemical Tables: Al(l), Al(g), AlCl(g), AlF(g), and AlI(g), 9–30–79; NaBr(l), 9–30–64; Na(g), 6–30–62; Br(g), 6–30–74.
[8] P. Gross, Fulmer Research Institute, Ltd., personal communication to H. Prophet, (July, 1966).

Continued on page 171

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.568	23.125	23.125	INFINITE
100	30.226	203.571	269.949	−6.638	24.175	7.209	−3.766
200	33.855	225.727	242.827	−3.420	23.141	−9.434	2.464
250	34.918	233.404	240.199	−1.699	22.340	−17.488	3.654
298.15	35.600	239.616	239.616	0.	15.899	−24.422	4.279
300	35.622	239.836	239.617	0.066	15.850	−24.672	4.296
350	36.102	245.366	240.052	1.860	0.084	−30.552	4.560
400	36.443	250.210	241.026	3.674	−0.290	−34.903	4.558
450	36.695	254.518	242.290	5.503	−0.685	−39.207	4.551
500	36.887	258.394	243.710	7.342	−1.100	−43.465	4.541
600	37.162	265.146	246.736	11.046	−1.992	−51.855	4.514
700	37.351	270.889	249.787	14.772	−2.982	−60.089	4.484
800	37.492	275.886	252.743	18.514	−4.097	−68.173	4.451
900	37.605	280.309	255.565	22.269	−5.365	−76.108	4.417
1000	37.700	284.276	258.241	26.035	−17.402	−83.132	4.342
1100	37.783	287.873	260.774	29.809	−18.695	−89.643	4.257
1200	37.858	291.164	263.172	33.591	−19.983	−96.036	4.180
1300	37.927	294.197	265.443	37.380	−21.269	−102.321	4.111
1400	37.992	297.010	267.599	41.176	−22.553	−108.508	4.048
1500	38.054	299.634	269.648	44.979	−23.835	−114.602	3.991
1600	38.114	302.091	271.600	48.787	−25.117	−120.612	3.938
1700	38.171	304.404	273.462	52.601	−26.398	−126.541	3.888
1800	38.228	306.587	275.242	56.421	−27.680	−132.395	3.842
1900	38.283	308.656	276.947	60.247	−28.964	−138.177	3.799
2000	38.337	310.621	278.582	64.078	−30.251	−143.892	3.758
2100	38.391	312.492	280.152	67.914	−31.541	−149.542	3.720
2200	38.445	314.280	281.663	71.756	−32.837	−155.131	3.683
2300	38.499	315.990	283.119	75.603	−34.137	−160.661	3.649
2400	38.553	317.629	284.523	79.456	−35.443	−166.134	3.616
2500	38.609	319.204	285.879	83.314	−36.755	−171.552	3.584
2600	38.666	320.720	287.190	87.178	−38.073	−176.918	3.554
2700	38.725	322.180	288.459	91.047	−39.397	−182.233	3.526
2800	38.788	323.590	289.689	94.923	−334.626	−186.532	3.480
2900	38.853	324.952	290.881	98.805	−334.862	−181.238	3.264
3000	38.924	326.270	292.039	102.694	−335.100	−175.937	3.063
3100	38.999	327.548	293.164	106.590	−335.340	−170.628	2.875
3200	39.081	328.787	294.258	110.494	−335.579	−165.311	2.698
3300	39.170	329.991	295.323	114 406	−335.815	−159.986	2.532
3400	39.267	331.162	296.359	118.328	−336.048	−154.654	2.376
3500	39.372	332.302	297.370	122.260	−336.274	−149.316	2.228
3600	39.487	333.412	298.356	126.203	−336.492	−143.971	2.089
3700	39.612	334.496	299.318	130.158	−336.699	−138.620	1.957
3800	39.749	335.554	300.258	134.126	−336.894	−133.265	1.832
3900	39.896	336.589	301.176	138.108	−337.074	−127.903	1.713
4000	40.056	337.601	302.074	142.105	−337.238	−122.538	1.600
4100	40.228	338.592	302.953	146.120	−337.384	−117.169	1.493
4200	40.413	339.563	303.813	150.152	−337.509	−111.796	1.390
4300	40.612	340.517	304.656	154.203	−337.612	−106.421	1.293
4400	40.823	341.453	305.481	158.274	−337.692	−101.043	1.200
4500	41.048	342.373	306.291	162.368	−337.744	−95.664	1.110
4600	41.286	343.277	307.085	166.484	−337.772	−90.284	1.025
4700	41.537	344 168	307.865	170.625	−337.772	−84.904	0.944
4800	41.801	345.045	308.630	174.792	−337.744	−79.524	0.865
4900	42.078	345.910	309.382	178.986	−337.685	−74.145	0.790
5000	42.368	346.763	310.121	183.208	−337.596	−68.768	0.718
5100	42.669	347.605	310.848	187.460	−337.477	−63.392	0.649
5200	42.982	348.436	311.563	191.743	−337.326	−58.019	0.583
5300	43.305	349.258	312.266	196.057	−337.144	−52.650	0.519
5400	43.639	350.071	312.959	200.404	−336.930	−47.284	0.457
5500	43.983	350.875	313.641	204.785	−336.684	−41.922	0.398
5600	44.336	351.670	314.313	209.201	−336.407	−36.566	0.341
5700	44 697	352.458	314.975	213.652	−336.099	−31.214	0.286
5800	45.066	353.239	315.628	218.141	−335.757	−25.868	0.233
5900	45.441	354.012	316.272	222 666	−335.388	−20.528	0.182
6000	45.822	354.779	316.908	227.229	−334.967	−15.197	0.132

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

Aluminum Bromide ($AlBr_3$) **CRYSTAL** **M_r = 266.69354** **Aluminum Bromide ($AlBr_3$)** **$Al_1Br_3(cr)$**

$\Delta_f H°(0\ K) = -491.90 \pm 0.84\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 180.22 \pm 1.05\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = -511.28 \pm 0.84\ kJ{\cdot}mol^{-1}$

$T_{fus} = 370.6 \pm 0.2\ K$ $\Delta_{fus}H° = 11.25 \pm 0.84\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The value chosen for the enthalpy of formation is the weighted average of the direct combination value reported by Gross *et al.*[1] and the solution calorimetry value given by Efimov, Kislova and Medvedev.[2]

Gross, Hayman, and Stuart[1] measured calorimetrically the standard enthalpy of formation of $AlBr_3$(cr) at 25°C by reacting Al with liquid bromine in a glass combustion vessel. They reported $\Delta_f H°(AlBr_3$, cr, 298.15 K) = -122.16 ± 0.10 kcal·mol^{-1}.

Efimov *et. al.*[2] measured the heat of solution of $AlBr_3$(cr) in an aqueous HCl solution containing KCl(cr) and the heat of solution of $AlCl_3$(cr) in an aqueous HCl solution containing KBr(cr). From these heats of solution measurements and using the heats of formation of $AlCl_3$(cr),[3] KCl(cr)[4,5] and KBr(cr)[4,6] as auxiliary data, they obtained $\Delta_f H°(AlBr_3$, cr, 298.15 K) = -122.5 ± 0.5 kcal·mol^{-1}.

Anthony *et al.*[10] measured the heat of solution of $AlBr_3$(cr) and $AlCl_3$(cr) in an aqueous alkaline solution containing dissolved sodium halides. They reported $\Delta_f H°(AlBr_3$, cr, 298.15 K) = -118.3 ± 0.6 kcal·mol^{-1}. Eley and Watts,[11] in studying heats of solution of $AlBr_3$ and its complexes with pyridine, trimethylamine, and triethylamine in HCl, reported $\Delta_f H°(AlBr_3$,cr,298.15K) -125.6 kcal·mol^{-1}. Klemm and Tanke[12] measured the heat of solution of $AlBr_3$(cr) at 0°C in aqueous HCl. Using auxiliary data, including estimated heat capacities, Klemm and Tanke[11] reported $\Delta_f H°(AlBr_3$, cr, 298.15 K) = -121 kcal mol^{-1}. Gross, Hayman, and Stuart[1] have re–examined the data of Klemm and Tanke[12] and have calculated $\Delta_f H°(AlBr_3$, cr, 298.15 K) = -122.4 kcal·mol^{-1}. This latter value was based on the heat of solution measurements,[13] $\Delta_f H°(AlCl_3$, cr, 298.15 K) = -168.65 kcal·mol^{-1}, and on the enthalpies of formation difference of chloride and bromide ions at the proper concentration.

A number of other studies on the enthalpies of formation of $AlBr_3$(cr) are based on solution calorimetry. The earliest measurements in water[7 8 9] are probably not reliable because of hydrolysis of the aluminum halide, but estimates of the enthalpy of formation of $AlBr_3$(cr) based on measurements in aqueous acid or base are also in disagreement.

Heat Capacity and Entropy

The heat capacities, 11.6 − 308 K, have been measured by Webb, Justice, and Prophet.[13] Above 308 K they are derived[13] from the enthalpy data measured by Fischer.[14] The entropy of the crystal is based on a value of $S°(12\ K) = 4.021\ J{\cdot}K^{-1}{\cdot}mol^{-1}$, as discussed in Webb *et al.*[13]

Fusion Data

Fischer[14] determined the melting temperature (T_{fus}) for $AlBr_3$(cr) The heat of melting ($\Delta_{fus}H°$) is calculated from the enthalpies of $AlBr_3$(cr) and $AlBr_3$(l) at the melting temperature. The enthalpy of the crystal at T_{fus} was determined from the curve use'uccircld for the heat capacity calculations. The enthalpy of the liquid at T_{fus} was determined from a linear least squares fit to the enthalpy data for $AlBr_3$(l) reported by Fischer.[14] See Webb *et al.*[13] for details.

Sublimation Data

The enthalpy of sublimation is calculated from the enthalpies of formation of the dimer and the crystal for the sublimation process, 2 $AlBr_3$(cr) = Al_2Br_6(g), $\Delta_{sub}H°(298.15\ K) = +85.4 \pm 4.2\ kJ{\cdot}mol^{-1}$. Also refer to the Al_2Br_6(g) table for additional comments.

References

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.915	−491.896	−491.896	INFINITE
100	70.819	86.415	261.717	−17.530	−492.185	−492.051	257.021
200	89.947	142.206	189.044	−9.368	−493.176	−491.562	128.383
298 15	100.578	180.216	180.216	0.	−511.285	−488.515	85.586
300	100.816	180.839	180.218	0.186	−511.353	−488.374	85.033
370.600	113.078	203.294	182.510	7.703	--- CRYSTAL <--> LIQUID ---		
400	117.780	211.773	184.330	10.977	−554.791	−471.592	61.584
500	123.846	238.919	192.612	23.154	−550.784	−451.247	47.141
600	124.265	261.541	202.271	35.562	−546.690	−431.725	37.585
700	124.348	280.703	212.142	47.993	−542.715	−412.880	30.810
800	124.432	297.313	221.773	60.432	−538.885	−394.596	25.764
900	124.516	311.974	230.997	72.879	−535.225	−376.781	21.868
1000	124.600	325.097	239.762	85.335	−542.346	−358.604	18.732
1100	124.683	336.977	248.068	97.799	−538.731	−340.405	16.164
1200	124.767	347.829	255.936	110.272	−535.122	−322.535	14.040
1300	124.851	357.819	263.394	122.753	−531.517	−304.965	12.254
1400	124.934	367.075	270.473	135.242	−527.917	−287.674	10.733
1500	125.018	375.697	277.204	147.739	−524.323	−270.639	9.424

PREVIOUS: June 1972 CURRENT· September 1979

Aluminum Bromide (AlBr$_3$) LIQUID $M_r = 266.69354$ Aluminum Bromide (AlBr$_3$) Al$_3$Br$_3$(l)

$S°(298.15\ K) = [206.481]\ J·K^{-1}·mol^{-1}$

$T_{fus} = 370.6 \pm 0.2\ K$

$\Delta_f H°(298.15\ K) = [-501.381]\ kJ·mol^{-1}$

$\Delta_{fus} H° = 11.25 \pm 0.84\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(AlBr$_3$, l, 298.15 K) is calculated from $\Delta_f H°$(AlBr$_3$, cr, 298.15 K) by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(370.6\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Fischer[1] has measured the enthalpy of AlBr$_3$(l) from 374 K to 406 K. The heat capacity is derived from a linear least squares fit to his data. The resulting constant value for the heat capacity is adopted for temperatures above 400 K.

$S°$(AlBr$_3$, l, 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

Refer to the Al$_2$Br$_6$(g) table for details.

Reference

[1] W. Fischer, Z. anorg. allgem. Chem. **200**, 332 (1931).

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	124.965	206.481	206.481	0.	−501.381	−486.442	85.223
300	124.965	207.254	206.483	0.231	−501.404	−486.350	84.681
370.600	124.965	233.664	209.234	9.054	--- CRYSTAL <--> LIQUID ---		
400	124.965	243.204	211.385	12.728	−543.136	−472.510	61.703
500	124.965	271.089	220.641	25.224	−538.810	−455.357	47.571
600	124.965	293.873	231.005	37.721	−534.628	−439.062	38.224
700	124.965	313.136	241.397	50.217	−530.587	−423.455	31.599
800	124.965	329.823	251.431	62.714	−526.700	−408.418	26.667
900	124.965	344.542	260.975	75.210	−522.990	−393.858	22.859
1000	124.965	357.708	270.001	87.707	−530.070	−378.940	19.794
1100	124.965	369.618	278.525	100.203	−526.424	−364.003	17.285
1200	124.965	380.492	286.576	112.699	−522.790	−349.398	15.209
1300	124.965	390.494	294.190	125.196	−519.170	−335.096	13.464
1400	124.965	399.755	301.403	137.692	−515.562	−321.072	11.979
1500	124.965	408.377	308.251	150.189	−511.969	−307.305	10.701

PREVIOUS. June 1972 CURRENT: September 1979

Aluminum Bromide ($AlBr_3$) CRYSTAL–LIQUID

0 to 370.6 K	crystal	
above	370.6 K	liquid

Refer to the individual tables for details.

M_r = 266.69354 Aluminum Bromide ($AlBr_3$) $Al_1Br_3(cr,l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−21.915	−491.896	−491.896	INFINITE
100	70.819	86.415	261.717	−17.530	−492.185	−492.051	257.021
200	89.947	142.206	189.044	−9.368	−493.176	−491.562	128.383
298.15	100.578	180.216	180.216	0.	−511.285	−488.515	85.586
300	100.816	180.839	180.218	0.186	−511.353	−488.374	85.033
370 600	113.078	203.294	182.510	7.703	____ CRYSTAL <--> LIQUID ____		
370.600	124.965	233.664	182.510	18.958	TRANSITION		
400	124.965	243.204	186.625	22.632	−543.136	−472.510	61.703
500	124.965	271.089	200.833	35.128	−538.810	−455.357	47.571
600	124.965	293.873	214.498	47.625	−534.628	−439.061	38.224
700	124.965	313.136	227.249	60.121	−530.587	−423.455	31.599
800	124.965	329.823	239.051	72.618	−526.700	−408.418	26.667
900	124.965	344.541	249.970	85.114	−522.990	−393.857	22.859
1000	124.965	357.708	260.097	97.610	−530.070	−378.939	19.794
1100	124.965	369.618	269.521	110.107	−526.424	−364.003	17.285
1200	124.965	380.492	278.322	122.603	−522.790	−349.398	15.209
1300	124.965	390.494	286.571	135.100	−519.170	−335.095	13.464
1400	124.965	399.755	294.329	147.596	−515.562	−321.071	11.979
1500	124.965	408.377	301.648	160.093	−511.969	−307.305	10.701

PREVIOUS: CURRENT: September 1979

Aluminum Bromide ($AlBr_3$) $Al_1Br_3(cr,l)$

$\Delta_a H°(0\ K) = 1068.2 \pm 2.1\ kJ\cdot mol^{-1}$
$S°(298.15\ K) = 349.44 \pm 1.26\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -387.16 \pm 1.7\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -410.45 \pm 1.7\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}
228(1)	508.4(2)
155(1)	93.0(2)

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: D_{3h}
Bond Distance: Al–Br = [2.27 ± 0.10] Å
Bond Angle: Br–Al–Br = 120°
Product of the Moments of Inertia: $I_AI_BI_C = [2.157410 \times 10^{-111}]\ g^3\ cm^6$

Enthalpy of Formation

Fischer, Rahlfs, and Benze[1] have determined the equilibrium constants for the reaction $Al_2Br_6(g) = 2\ AlBr_3(g)$ from vapor density measurements. The heats of reaction are calculated from these data using both 2nd law and 3rd law methods. The results of the calculations are as follows, where the $\Delta_f H°(298.15\ K)$ is based on the 3rd law value of $\Delta_r H°(298.15\ K)$, for the reaction as written above, and $\Delta_f H°(Al_2Br_6, g, 298.15\ K) = -224.0\ kcal\cdot mol^{-1}$.

T/K	Data Points	$\Delta_r H°(298.15\ K)$, $kcal\cdot mol^{-1}$ Al_2Br_6 2nd law	3rd law	Drift $cal\cdot K^{-1}\cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal\cdot mol^{-1}$
613–846	4	29.6 ± 1.0	27.78 ± 0.6	−2.6 ± 1.3	−98.11
605–854	7	29.4 ± 0.5	27.73 ± 0.5	−2.2 ± 0.7	−98.14

The adopted value for the enthalpy of formation is $\Delta_f H°(AlBr_3, g, 298.15\ K) = -98.1 \pm 0.4\ kcal\cdot mol^{-1} (-410.45 \pm 1.7\ kJ\cdot mol^{-1})$.

Heat Capacity and Entropy

Beattie and Horder[2] studied the gas phase Raman spectra of monomeric $AlBr_3$. The results are consistent with a planar structure of D_{3h} symmetry with $\nu_1 = 228\ cm^{-1}$(polarized) and $\nu_4 = 93\ cm^{-1}$. The weak antisymmetric stretching mode was tentatively assigned as $\nu_3 = 360\ cm^{-1}$.

Pong *et al.*,[3] *in examining the infrared spectrum of the monomeric* $AlBr_3$ isolated in solid argon, reported $\nu_2 = 155.0\ cm^{-1}$, $\nu_3 = 510\ cm^{-1}$ and $\nu_4 = 92\ cm^{-1}$ for $AlBr_3$ isolated in xenon.

The adopted values for ν_1 and ν_4 are taken from Beattie and Horder[2] while ν_2 and ν_3 are taken from Pong *et al.*[3] The Al–Br bond distance was estimated by Heise and Weiland[5] and is consistent with the trend of experimentally known bond distances in the gaseous molecules AlF_3, $AlCl_3$, and AlI_3.[6] The principal moments of inertia are $I_A = I_B = 102.5575 \times 10^{-39}$, and $I_C = 205.1151 \times 10^{-39}\ g\cdot cm^2$.

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[6] JANAF Thermochemical Tables: $AlF_3(g)$, $AlCl_3(g)$, and $AlI_3(g)$, 9–30–79.

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

T/K	$C_p°$ ($J\cdot K^{-1}mol^{-1}$)	$S°$ ($J\cdot K^{-1}mol^{-1}$)	$-[G°-H°(T_r)]/T$ ($J\cdot K^{-1}mol^{-1}$)	$H°-H°(T_r)$ ($kJ\cdot mol^{-1}$)	$\Delta_f H°$ ($kJ\cdot mol^{-1}$)	$\Delta_f G°$ ($kJ\cdot mol^{-1}$)	log K_f
0	0.	0.	INFINITE	−18.015	−387.162	−387.162	INFINITE
100	57.421	276.467	412.068	−13.560	−387.381	−406.252	212.204
200	69.507	320.454	356.177	−7.144	−390.119	−424 154	110.778
250	73.019	336.366	350.669	−3.576	−391.887	−432.465	90.359
298.15	75.376	349.441	349.441	0.	−410.450	−438.135	76.759
300	75.451	349.907	349.442	0.140	−410.566	−438.307	76.316
350	77.155	361.673	350.367	3.957	−456.958	−440.380	65.723
400	78.376	372.060	352.443	7.847	−457.086	−438.002	57.197
450	79.271	381.346	355.147	11.789	−457.209	−435.609	50.564
500	79 943	389.734	358.193	15.770	−457.333	−433.203	45.256
600	80.861	404.398	364.707	23.814	−457.604	−428.352	37.291
700	81.439	416.909	371.293	31.931	−457.942	−423.451	31.598
800	81.825	427.810	377.691	40.096	−458.387	−418.495	27.325
900	82.094	437.464	383.806	48.293	−458.977	−413.475	23.997
1000	82.289	446.124	389.612	56.512	−470.334	−407.620	21.292
1100	82.434	453.975	395.112	64.749	−470.948	−401.319	19.057
1200	82.546	461.152	400.321	72.998	−471.561	−394.962	17.192
1300	82.633	467.763	405.258	81.257	−472.178	−388.554	15.612
1400	82.703	473.889	409.944	89.524	−472.800	−382.098	14.256
1500	82 759	479.597	414.399	97.797	−473.431	−375.597	13.079
1600	82.805	484.940	418.643	106.075	−474.071	−369.054	12.048
1700	82.844	489.961	422.692	114.358	−474.725	−362.470	11.137
1800	82.876	494.697	426.562	122.644	−475.395	−355.848	10.326
1900	82.903	499.179	430.267	130.933	−476.084	−349.188	9.600
2000	82.927	503 432	433.820	139.225	−476.796	−342.490	8.945
2100	82.947	507.479	437.232	147.518	−477.534	−335.757	8.352
2200	82.964	511.338	440.513	155.814	−478.299	−328.988	7.811
2300	82.979	515.026	443.673	164.111	−479.095	−322.184	7.317
2400	82.993	518.558	446.720	172.410	−479.923	−315.344	6.863
2500	83.005	521.946	449.662	180.709	−480.783	−308.469	6.445
2600	83.015	525.202	452.505	189.010	−481.677	−301.559	6.058
2700	83.024	528.335	455.256	197.312	−482.603	−294.613	5.700
2800	83.033	531.354	457.920	205.615	−777.462	−286.666	5.348
2900	83.040	534.268	460.503	213.919	−777.353	−269.139	4.848
3000	83.047	537.084	463.009	222.223	−777.272	−251.616	4.381
3100	83.053	539.807	465.443	230.528	−777.214	−234.095	3.944
3200	83.059	542.444	467.808	238.834	−777.177	−216.576	3.535
3300	83 064	545.000	470.109	247.140	−777.157	−199.057	3.151
3400	83.069	547.479	472.348	255.447	−777.150	−181.540	2.789
3500	83.073	549.887	474.529	263.754	−777.154	−164.022	2.448
3600	83.077	552.228	476.655	272.061	−777.163	−146.503	2.126
3700	83.080	554.504	478.728	280.369	−777.174	−128.985	1.821
3800	83.084	556.720	480.752	288.677	−777.184	−111.466	1.532
3900	83.087	558.878	482.728	296.986	−777.188	−93.947	1.258
4000	83.089	560.981	484.658	305.295	−777.185	−76.428	0.998
4100	83.092	563.033	486.544	313.604	−777.171	−58.910	0.751
4200	83.095	565.035	488.389	321.913	−777.144	−41.391	0.515
4300	83.097	566.991	490.195	330.223	−777.102	−23.874	0.290
4400	83.099	568.901	491.962	338.532	−777.042	−6.358	0.075
4500	83 101	570.769	493.693	346.842	−776.960	11.157	−0.130
4600	83.103	572.595	495.388	355.153	−776.860	28.670	−0.326
4700	83.105	574.382	497.050	363.463	−776.738	46.180	−0.513
4800	83.106	576.132	498.679	371.773	−776.595	63.687	−0.693
4900	83.108	577.846	500.277	380.084	−776.428	81.191	−0.866
5000	83.109	579.525	501.846	388.395	−776.239	98.692	−1.031
5100	83.110	581.170	503.385	396.706	−776.028	116.189	−1.190
5200	83.112	582.784	504.896	405.017	−775.795	133.681	−1.343
5300	83.113	584.367	506.381	413.328	−775.540	151.169	−1.490
5400	83.114	585.921	507.840	421.640	−775.265	168.651	−1.631
5500	83.115	587.446	509.273	429.951	−774.970	186.128	−1.768
5600	83.116	588.944	510.682	438.263	−774.656	203.600	−1.899
5700	83.117	590.415	512.068	446.574	−774.325	221.066	−2.026
5800	83.118	591.860	513.432	454.886	−773.975	238.525	−2.148
5900	83.119	593.281	514.773	463.198	−773.613	255.979	−2.266
6000	83.120	594.678	516.093	471.510	−773.215	273.424	−2.380

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

Aluminum Chloride (AlCl) IDEAL GAS $M_r = 62.43454$ Aluminum Chloride (AlCl) $Al_1Cl_1(g)$

$S°(298.15\ K) = 227.957 \pm 0.08\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -51.66 \pm 6.3\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -51.46 \pm 6.3\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
	24541.65	2
$a^3\Pi$	24615.31	2
	24680.00	2
$A^1\Pi$	38237.70	2
$b^3\Sigma^+$	43590.00	3

$\omega_e = 480.2903\ cm^{-1}$ $\omega_e x_e = 2.064\ cm^{-1}$ $\sigma = 1$
$B_e = 0.24255\ cm^{-1}$ $\alpha_e = 0.001598\ cm^{-1}$ $r_e = 2.130113$ Å

Enthalpy of Formation

Equilibrium constants as a function of temperature for the reaction 2 Al(l) + $AlCl_3(g) \rightarrow$ 3 AlCl(g) have been reported by many investigators. The heats of reaction are calculated from these data using second and third law methods. Unfortunately, most of the data are very discordant and of no help in defining $\Delta_f H°$(AlCl, g, 298.15 K). The results of Rao and Dadape[1] cover a temperature range of 300 K, show good compatibility with the thermodynamic functions, are near an average of all the data, and are judged most acceptable. The third-law heat of reaction derived from their data is adopted and combined with the heat of formation of $AlCl_3(g)$[12] to give $\Delta_f H°$(AlCl, g, 298.15 K) = −12.30 ± 1.5 kcal·mol^{-1} (−51.46 ± 6.3 kJ·mol^{-1}).

Source	T/K	Data Points	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Rao and Dadape[1]	1125–1425	11	97.25 ± 1.6	97.71 ± 0.8	0.4 ± 1.3	−12.30
Frish *et al.*[2]	931–1034	9	94.58 ± 1.0	101.64 ± 0.5	7.2 ± 1.0	−10.99
Gross *et al.*[3]	1225–1278[a]	7	--	104.60 ± 2.8	--	−10.00
Ginsberg *et al.*[4]	1423–1500	8	86.34 ± 1.8	99.66 ± 0.8	9.1 ± 1.2	−11.65
Semenkovich[5]	1223–1473	6	84.19 ± 0.4	93.42 ± 1.3	6.9 ± 0.3	−13.73
Heimgartner[6]	978–1383	13	55.52 ± 2.6	94.90 ± 9.5	33.0 ± 2.2	−13.24
Weiss[7]	1273–1473	3	88.29 ± 3.7	81.26 ± 1.2	−5.1 ± 2.7	−17.78
Pinchuk *et al.*[8]	1173–1373	3	80.20 ± 7.4	89.92 ± 1.9	7.6 ± 5.8	−14.90
Mitani *et al.*[9]	1273–1473[b]	2	81.29 ± 0.0	94.18 ± 2.7	9.4 ± 0.0	−13.48
Tanabe *et al.*[10]	1173–1573[b]	2	88.23 ± 0.0	89.49 ± 0.5	0.9 ± 0.0	−15.04
Kikuch *et al.*[11]	1273–1523[b]	2	73.61 ± 0.0	93.60 ± 5.1	14.3 ± 0.0	−13.67

[a] Temperature range too small for significant second law calculation.
[b] Individual points not reported, calculation based on reported equation at extremes of temperature range cited.

Gross *et al.*[3] and Pinchuk *et al.*[8] have studied the reaction of sodium and potassium chloride with liquid aluminum to form aluminum monochloride. These studies lead to $\Delta_f H°$(298.15 K) values for AlCl(g) in the range of −12.69 ± 1.0 to −13.60 ± 1.5 kcal·mol^{-1}.

The adopted enthalpy of formation yields a dissociation energy of 498.57 kJ·mol^{-1} for AlCl(g). Barrow[13] and Ram[14] reference possible spectroscopic values for the dissociation energy. A short extrapolation of vibrational levels yields $D_0° = 519.2$ kJ·mol^{-1} but Barrow[13] speculates that a potential maximum in the A^1 state of AlF and AlCl causes extrapolation of levels to give erroneous heats of dissociation. Ram *et al.* has observed rotational predissociation in the AlCl bond system and reports the dissociation energy at 507.5 ± 0.97 kJ·mol^{-1}. This yields $\Delta_f H°$(AlCl, g, 298.15 K) = −60.42 kJ·mol^{-1} in reasonable agreement with the selected value.

Heat Capacity and Entropy

The spectrum of AlCl has been observed and analyzed by a number of investigators.[14 15 16 17] The spectroscopic constants for $Al^{35}Cl$ and $Al^{37}Cl$ are taken from the microwave study of Wyse and Gordy[17] and averaged according to the natural isotopic abundance of chlorine. The electronic levels are those reported by Sharma;[18] the value for the $b^3\Sigma^+$ state is somewhat uncertain. The assignment of electronic states is supported by theoretical calculations.[19]

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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	−9.323	−51.656	−51.656	INFINITE
100	29.527	193.170	257.245	−6.407	−50.681	−59.849	31.262
200	32.545	214.524	231.068	−3.309	−50.903	−68.982	18.016
250	33.787	221 927	228.523	−1.649	−51.166	−73.473	15.351
298.15	34.660	227 957	227.957	0.	−51.463	−77.743	13.620
300	34.689	228.171	227.957	0.064	−51.475	−77.906	13.565
350	35.338	233.570	228.382	1.816	−51.818	−82.284	12.280
400	35.814	238.321	229.334	3.595	−52.188	−86.611	11 39
450	36.170	242.561	230.572	5.395	−52.579	−90.891	10.550
500	36.445	246.387	231.965	7.211	−52.990	−95.126	9.938
600	36.835	253.068	234.942	10.876	−53.876	−103.472	9.008
700	37.099	258.768	237.948	14.574	−54.862	−111.661	8.332
800	37.291	263.735	240.868	18.294	−55.973	−119.701	7.816
900	37.439	268.136	243.658	22.030	−57.237	−127.593	7.405
1000	37.559	272.087	246.306	25.780	−69.271	−134.575	7.029
1100	37.660	275 671	248.815	29.541	−70.560	−141.042	6.698
1200	37.749	278.952	251.192	33.312	−71.846	−147.393	6.416
1300	37.829	281.977	253.445	37.091	−73.128	−153.637	6.173
1400	37.901	284.783	255.585	40.878	−74.407	−159.782	5.962
1500	37.969	287.400	257.619	44.671	−75.684	−165.835	5.775
1600	38.033	289.853	259.558	48.471	−76.959	−171.804	5.609
1700	38.095	292.160	261.409	52.278	−78.232	−177.693	5.460
1800	38.153	294.340	263.178	56.090	−79.503	−183.507	5.325
1900	38.211	296.404	264.873	59.908	−80.774	−189.250	5.203
2000	38.266	298.365	266.499	63.732	−82.044	−194.926	5 091
2100	38.321	300.234	268.061	67.562	−83.314	−200.539	4.988
2200	38.375	302.018	269.565	71.396	−84.584	−206.092	4.893
2300	38.428	303.725	271.013	75.236	−85.856	−211.586	4.805
2400	38.482	305.361	272.410	79.082	−87.130	−217.025	4.723
2500	38.536	306.933	273.760	82.933	−88.407	−222.411	4.647
2600	38.590	308.446	275.065	86.789	−89.687	−227.746	4.575
2700	38.647	309.903	276.329	90.651	−90.970	−233.032	4.508
2800	38.705	311.310	277.553	94.519	−386.158	−237.302	4.427
2900	38.766	312.669	278.741	98.392	−386.353	−231.983	4.178
3000	38.830	313.984	279.894	102.272	−386.552	−226.656	3.946
3100	38 898	315.258	281.014	106.158	−386.754	−221.323	3.729
3200	38.971	316.495	282.103	110.052	−386.959	−215.983	3.526
3300	39.050	317.695	283.164	113.953	−387.165	−210.637	3.334
3400	39.135	318.862	284.197	117.862	−387.372	−205.284	3.154
3500	39.228	319.998	285.203	121.780	−387.579	−199.926	2.984
3600	39.328	321.104	286.185	125.708	−387.783	−194.561	2.823
3700	39.437	322.183	287.144	129.646	−387.984	−189.191	2.671
3800	39.556	323.237	288.080	133.595	−388.179	−183.816	2.527
3900	39.684	324.266	288.995	137.557	−388.367	−178.436	2.390
4000	39.823	325.272	289.889	141.533	−388.546	−173.050	2.260
4100	39.973	326.257	290.764	145.522	−388.713	−167.661	2.136
4200	40.134	327.222	291.621	149.528	−388.868	−162.268	2.018
4300	40.308	328.169	292.460	153.550	−389.006	−156.871	1.906
4400	40.493	329.098	293.282	157.589	−389.128	−151.471	1.798
4500	40.690	330.010	294.088	161.649	−389.229	−146.068	1.696
4600	40.900	330.906	294.878	165.728	−389.311	−140.664	1.597
4700	41.122	331.788	295.654	169.829	−389.370	−135.258	1.503
4800	41.357	332.656	296.416	173.953	−389.405	−129.851	1.413
4900	41 603	333.512	297.165	178.101	−389.414	−124.443	1.327
5000	41.862	334.355	297.900	182.274	−389.397	−119.036	1.244
5100	42.132	335.186	298.623	186.473	−389.352	−113.629	1.164
5200	42.414	336.007	299.334	190.701	−389.278	−108.224	1.087
5300	42.706	336.818	300.034	194.957	−389 174	−102.820	1.013
5400	43.010	337.619	300.722	199.242	−389.040	−97.418	0.942
5500	43.323	338.411	301.400	203.559	−388.876	−92.019	0.874
5600	43.645	339.195	302.068	207.907	−388.680	−86.623	0.808
5700	43.977	339.970	302.726	212.288	−388.454	−81.231	0.744
5800	44.317	340.738	303.375	216.703	−388.193	−75.844	0.683
5900	44.665	341.498	304.015	221.152	−387.903	−70.461	0.624
6000	45.019	342.252	304.646	225.636	−387.560	−65.086	0.567

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

Aluminum Chloride (AlCl) $Al_1Cl_1(g)$

Aluminum Chloride, Ion ($AlCl^+$) IDEAL GAS $M_r = 62.43399$ Aluminum Chloride, Ion ($AlCl^+$) $Al_1Cl_1^+(g)$

$S°(298.15\ K) = [232.19 \pm 1.7]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 855.7 \pm 40\ kJ{\cdot}mol^{-1}$

$\Delta_f H°(298.15\ K) = [861.904]\ kJ\ mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$[^2\Sigma]$	0	[2]
$[^2\Pi]$	[10000]	[4]

$\omega_e = [570]\ cm^{-1}$ $\omega_e x_e = [2]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.2618]\ cm^{-1}$ $\alpha_e = [0.0015]\ cm^{-1}$ $r_e = [2.05]$ Å

Enthalpy of Formation

We adopt $\Delta_f H°(0\ K) = 204.5 \pm 10\ kcal{\cdot}mol^{-1}$ based on that of AlCl(g)[1] combined with the ionization potential IP(AlCl) = 9.4 ± 0.4 eV ($216.8 \pm 9\ kcal{\cdot}mol^{-1}$). IP(AlCl) is assumed to be equal to the electron–impact appearance potential of $AlCl^+$ measured as 9.4 ± 0.4,[2] 9.5 ± 0.3[3] and 9.3 ± 0.6 eV.[4] Theoretical values include IP = 8.83 eV from an extended *Huckel calcualtion*[5] and *from ab initio calculations*[6,7] either 8.4 eV (direct value) or 9.8 eV derived from $D_0°(AlCl^+)$. Electron–impact formation of $AlCl^+$ from $AlCl_3$[8] apparently yields fragment ions with excess energy; i.e., we derive the upper limit IP<11.7 eV.

For the dissociation process $AlCl^+(X^2\Sigma) \rightarrow Al^+(^1S) + Cl(^2P)$, our adopted $\Delta_f H°$ yields $D_0°(AlCl^+) = 39 \pm 10\ kcal{\cdot}mol^{-1}$. This compares with $-31\ kcal{\cdot}mol^{-1}$ *derived from the theoretical potential energy curve*[6,7] which, however, has a maximum of $-8\ kcal{\cdot}mol^{-1}$ arising from an avoided crossing with another $^2\Sigma$ state.

Heat Capacity and Entropy

Bonding in Group III monohalides and their ions was characterized by Berkowitz and Dehmer[7] from photoelectron spectra and theoretical calculations.[6,7] They concluded that ionization removes an electron from an antibonding orbital centered mainly on the metal. This shortens the bond length and enhances the ionic nature of the bond. A decrease in bond length is observed for BF^+,[9] predicted for AlF^+[1] from Rydberg states of AlF, and predicted for $AlCl^+$ from theoretical calculations.[6,7]

For $AlCl^+$, we adopt $r_e = 2.05$ Å based mainly on the theoretical prediction.[6,7] This may be compared with 2.13 Å for AlCl and 2.06 Å for $AlCl_3$.[1] Lacking data for Rydberg states of AlCl, we estimate ω_e from $k(AlCl^+)/k(MgCl) = 1.7$ *transferred from the similar isoelectronic pair* AlF^+ and MgF.[1] B_e is calculated from r_e, while α_e and $\omega_e x_e$ are estimated by comparison with AlF^+, AlF and AlCl.[1]

The electronic ground state and an approximate value for the $^2\Pi$ level are based on theoretical calculations.[6,7] These suggest that $^2\Pi$ has only a shallow minimum (r_e>3.6 Å) or possibly is repulsive They also indicate the presence of a $^2\Sigma$ state having a double minimum above 30000 cm^{-1}. *We include only the* $^2\Pi$ *state. If it is repulsive,* our thermodynamic functions are upper–limit values. The bias would be quite small even at 3000 K.

References

[1] JANAF Thermochemical Tables: AlCl(g), $AlCl_3$(g) 6–30–70; AlF^+(g) 12–31–76; AlF(g), MgF(g) 6–30–76.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	-9.154	855.682		
100	29.269	198.245	260.674	-6.243			
200	31.566	219.136	235.214	-3.216			
250	32.825	226.319	232.738	-1.605			
298.15	33.794	232.187	232.187	0.	861.904	828.108	-145.081
300	33.826	232.396	232.188	0.063	861.929	827.899	-144.150
350	34.588	237.671	232.603	1.774	862.585	822.175	-122.703
400	35.165	242.329	233.533	3.518	863.220	816.358	-106.605
450	35.606	246.497	234.746	5.288	863.838	810.463	-94.076
500	35.948	250.267	236.112	7.077	864.439	804.500	-84.046
600	36.436	256.867	239.037	10.698	865.587	792.404	-68.985
700	36.762	262.510	241.997	14.359	866.643	780.121	-58.213
800	36.993	267.435	244.875	18.047	867.580	767.696	-50.125
900	37.166	271.802	247.629	21.756	868.365	755.161	-43.828
1000	37.302	275.725	250.246	25.479	858.384	743.309	-38.826
1100	37.415	279.286	252.727	29.215	859.148	731.764	-34.749
1200	37.516	282.546	255.078	32.962	859.917	720.150	-31.347
1300	37.612	285.553	257.308	36.718	860.691	708.471	-28.467
1400	37.711	288.344	259.426	40.485	861.470	696.733	-25.995
1500	37.818	290.949	261.442	44.261	862.254	684.939	-23.852
1600	37.939	293.394	263.363	48.049	863.046	673.092	-21.974
1700	38.077	295.698	265.198	51.849	863.846	661.195	-20.316
1800	38.235	297.878	266.954	55.665	864.656	649.251	-18.841
1900	38.414	299.950	268.636	59.497	865.478	637.262	-17.520
2000	38.615	301.926	270.252	63.348	866.314	625.229	-16.329
2100	38.837	303.815	271.805	67.221	867.166	613.154	-15.251
2200	39.079	305.627	273.302	71.116	868.034	601.038	-14.270
2300	39.338	307.370	274.745	75.037	868.922	588.882	-13.374
2400	39.613	309.050	276.140	78.984	869.828	576.687	-12.551
2500	39.901	310.673	277.489	82.960	870.755	564.454	-11.794
2600	40.199	312.244	278.796	86.965	871.702	552.183	-11.093
2700	40.503	313.766	280.063	91.000	872.671	539.875	-10.445
2800	40.811	315.245	281.293	95.066	579.760	528.499	-9.859
2900	41.120	316.682	282.489	99.162	581.866	526.631	-9.486
3000	41.428	318.082	283.652	103.290	583.994	524.691	-9.136
3100	41.732	319.445	284.785	107.448	586.142	522.679	-8.807
3200	42.029	320.775	285.889	111.636	588.310	520.597	-8.498
3300	42.319	322.072	286.965	115.853	590.499	518.447	-8.206
3400	42.600	323.340	288.017	120.099	592.707	516.230	-7.931
3500	42.870	324.579	289.044	124.373	594.935	513.949	-7.670
3600	43.127	325.790	290.048	128.673	597.181	511.603	-7.423
3700	43.373	326.975	291.030	132.998	599.446	509.195	-7.189
3800	43.604	328.135	291.991	137.347	601.729	506.725	-6.965
3900	43.823	329.270	292.932	141.718	604.029	504.195	-6.753
4000	44.027	330.383	293.855	146.111	606.346	501.606	-6.550
4100	44.217	331.472	294.759	150.523	608.680	498.958	-6.357
4200	44.393	332.540	295.646	154.954	611.030	496.254	-6.172
4300	44.555	333.586	296.516	159.401	613.395	493.493	-5.995
4400	44.703	334.612	297.370	163.864	615.775	490.677	-5.825
4500	44.838	335.618	298.209	168.341	618.171	487.807	-5.662
4600	44.961	336.605	299.033	172.831	620.578	484.884	-5.506
4700	45.071	337.573	299.843	177.333	622.999	481.907	-5.356
4800	45.169	338.523	300.639	181.845	625.430	478.880	-5.211
4900	45.256	339.456	301.422	186.367	627.874	475.801	-5.072
5000	45.333	340.371	302.191	190.896	630.326	472.673	-4.938
5100	45.399	341.269	302.949	195.433	632.786	469.496	-4.809
5200	45.456	342.151	303.694	199.976	635.255	466.270	-4.684
5300	45.504	343.017	304.428	204.524	637.729	462.996	-4.563
5400	45.543	343.868	305.151	209.076	640.208	459.676	-4.446
5500	45.575	344.704	305.862	213.632	642.690	456.310	-4.334
5600	45.600	345.526	306.563	218.191	645.175	452.899	-4.224
5700	45.618	346.333	307.254	222.752	647.660	449.444	-4.119
5800	45.630	347.127	307.934	227.314	650.148	445.944	-4.016
5900	45.636	347.907	308.605	231.878	652.630	442.402	-3.917
6000	45.637	348.674	309.267	236.441	655.131	438.816	-3.820

PREVIOUS June 1976 (1 atm) CURRENT June 1976 (1 bar)

Aluminum Chloride Fluoride (AlClF) IDEAL GAS $M_r = 81.432943$ Aluminum Chloride Fluoride (AlClF) $Al_1Cl_1F_1(g)$

$S°(298.15\ K) = [282.9 \pm 4]\ J{\cdot}K^{-1}\ mol^{-1}$

$\Delta_f H°(0\ K) = [-488.1 \pm 63]\ kJ{\cdot}mol^{-1}$

$\Delta_f H°(298\ 15\ K) = [-489.5 \pm 63]\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i
0	2
[20000]	2
[25000]	2

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[750](1)
[200](1)
[550](1)

Point Group: C_s $\sigma = 1$

Bond Distances: Al–F = [1.65] Å; Al–Cl = [2.10] Å

Bond Angle: Cl–Al–F = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.440958 \times 10^{-114}]\ g^3{\cdot}cm^6$

	Enthalpy Reference Temperature = T_r = 298.15 K					Standard State Pressure = $p°$ = 0.1 MPa	
	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.133	−488.119	−488.119	INFINITE
100	37.818	236.245	322.865	−8.662	−488.041	−492.998	257.516
200	43.971	264.376	287.217	−4.568	−488.732	−497.717	129.990
250	46.668	274.486	283.688	−2.300	−489.139	−499.916	104.452
298.15	48.806	282.895	282.895	0.	−489.528	−501.957	87.941
300	48.879	283.198	282.896	0.090	−489.543	−502.034	87.412
350	50.619	290.869	283.498	2.580	−489.942	−504.084	75.230
400	51.969	297.720	284.855	5.146	−490.340	−506 077	66.087
450	53.019	303.904	286.634	7.772	−490.739	−508.020	58.969
500	53.842	309.534	288.647	10.444	−491.143	−509.919	53.271
600	55.016	319.463	292.977	15.891	−491.984	−513.596	44.712
700	55.785	328.005	297.386	21.434	−492.901	−517.126	38.588
800	56.312	335.491	301.690	27 040	−493.930	−520.518	33.986
900	56.686	342.146	305.823	32.691	−495.107	−523.773	30.399
1000	56.961	348.134	309.759	38.374	−507.053	−526.127	27.482
1100	57.168	353.573	313.499	44.081	−508.256	−527.976	25.072
1200	57.328	358.554	317.049	49.806	−509.460	−529.716	23.058
1300	57.454	363 148	320.421	55.546	−510.666	−531.355	21.350
1400	57.554	367.410	323.627	61.296	−511.877	−532.901	19.883
1500	57.636	371.383	326 679	67.056	−513.093	−534.361	18.608
1600	57.703	375.105	329.591	72.823	−514.316	−535.739	17.490
1700	57.759	378.605	332.372	78.596	−515.544	−537.040	16.501
1800	57.806	381.908	335.033	84.374	−516.780	−538.269	15.620
1900	57.846	385 034	337.583	90.157	−518.022	−539.429	14.830
2000	57.881	388.002	340.031	95.943	−519.270	−540.523	14.117
2100	57.911	390.827	342.383	101.733	−520.523	−541.555	13.470
2200	57.938	393.522	344.647	107.526	−521.781	−542.527	12.881
2300	57.963	396.098	346.828	113.321	−523.042	−543.442	12.342
2400	57.985	398.565	348.933	119.118	−524.306	−544.302	11.846
2500	58.007	400.933	350.966	124.918	−525.571	−545.109	11.389
2600	58.028	403.208	352.932	130.719	−526.836	−545.865	10.967
2700	58.049	405.399	354.834	136.523	−528.101	−546.573	10.574
2800	58.070	407.510	356 678	142.329	−823.264	−546.267	10.191
2900	58.093	409.548	358.466	148.137	−823.427	−536.371	9.661
3000	58.117	411.518	360.202	153.948	−823.586	−526.470	9.167
3100	58.143	413.424	361.888	159.761	−823.739	−516.563	8.704
3200	58.172	415.271	363.528	165.576	−823.884	−506.652	8.270
3300	58.204	417.061	365.123	171.395	−824.021	−496.736	7.863
3400	58.238	418.799	366.676	177.217	−824.147	−486.817	7.479
3500	58.276	420.488	368.190	183.043	−824.262	−476.894	7.117
3600	58.318	422.130	369.666	188.873	−824.364	−466.967	6.776
3700	58.364	423.729	371.105	194.707	−824.451	−457.038	6.452
3800	58.414	425.286	372.511	200.546	−824.522	−447.108	6.146
3900	58 468	426.804	373.883	206.390	−824.576	−437.175	5.855
4000	58.526	428.285	375.225	212.239	−824.612	−427.241	5.579
4100	58.589	429.731	376.537	218.095	−824.627	−417.306	5.317
4200	58.655	431.143	377.820	223.957	−824.622	−407.372	5.066
4300	58.727	432.524	379.076	229.826	−824.594	−397.437	4.828
4400	58.802	433.875	380.307	235.703	−824.544	−387.504	4.600
4500	58.881	435.198	381.512	241.587	−824.468	−377.572	4.383
4600	58.965	436.493	382.693	247.479	−824.369	−367.642	4.175
4700	59.052	437.762	383.851	253.380	−824.246	−357.715	3.976
4800	59.143	439.006	384.987	259.290	−824.097	−347.790	3.785
4900	59.237	440.226	386.102	265.209	−823.922	−337.869	3.602
5000	59.335	441.424	387.197	271.137	−823.723	−327.951	3.426
5100	59.436	442.600	388.272	277.076	−823.498	−318.038	3.257
5200	59.539	443.755	389.327	283.024	−823.248	−308.130	3.095
5300	59.645	444.890	390.365	288.984	−822.974	−298.226	2.939
5400	59.754	446.006	391.385	294.954	−822.675	−288.328	2.789
5500	59.865	447.104	392.388	300.935	−822.354	−278.435	2.644
5600	59.977	448.183	393.375	306.927	−822.010	−268.549	2.505
5700	60.091	449.246	394.346	312.930	−821.644	−258.669	2.370
5800	60.207	450.292	395.302	318.945	−821.255	−248.796	2.241
5900	60.323	451.322	396.242	324.971	−820.849	−238.929	2.115
6000	60.441	452.337	397.169	331.010	−820.403	−229.072	1.994

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

Enthalpy of Formation

We tentatively adopt $\Delta_f H°(298.15\ K) = -117 \pm 15\ kcal{\cdot}mol^{-1}$ and $\Delta_a H°(0\ K) = 241 \pm 15\ kcal{\cdot}mol^{-1}$ based on our average bond energies for $AlF_2(g)$ and $AlCl_2(g)$.[1] Mass–spectrometric data[2,3] yield $\Delta_f H°(298.15\ K) = -142.6$ and $\Delta_a H°(0\ K) = 267\ kcal{\cdot}mol^{-1}$, corresponding to an enhancement of 26 $kcal{\cdot}mol^{-1}$ in the stability of AlClF(g). The same study[2,3] indicated stability enhancements of 22 (or 13) $kcal{\cdot}mol^{-1}$ for AlF_2, 19 $kcal{\cdot}mol^{-1}$ for $AlClF_2$, and 22 $kcal{\cdot}mol^{-1}$ for $AlCl_2F$. See the appropriate tables[1] for further details.

Farber *et al.*[2,3] used molecular flow effusion of vapors of AlF_3 and $AlCl_3$ over Al(l) in $Al_2O_3(cr)$ to study the reaciton Al-Cl(g) + AlF(g) = AlClF(g) + Al(g). They calculated *Kp* (5 points, 1338−1537 K) directly from mass–spectrometric ion intensities. Using JANAF auxiliary data,[1] we derive $[\Delta_r S°(2nd\ law) - \Delta_r S°(3rd\ law)] = 0.8 \pm 18\ cal\ K^{-1}{\cdot}mol^{-1}$, $\Delta_r H°(298.15\ K) = 12 \pm 25$ (2nd law) or 11.2 ± 5 (3rd law) and $\Delta_f H°(298.15\ K) = -142.6 \pm 5\ kcal{\cdot}mol^{-1}$. These results are internally consistent but, as in the case of AlF_2,[2,3] we suspect that common problems may cause a negative bias in $\Delta_f H°$. The ionizing energy is ambiguous: 20 eV[3] or AP + 3 eV.[2] The appearance potential $AP(AlClF^+) = 11 \pm 1$ eV is biased by ~2 eV, raising several questions about interpretation of the data (see $AlCl_2^+$).[1] It is conceivable that $AlClF^+$ arises from a process other than direct ionization of AlClF.

We conclude from these speculations that the experimental data[2,3] are insufficient to establish the enhanced stability of AlClF. Mass–spectrometric data indicate very little enhanced stability in BClF,[4] in agreement with average bond energies summarized on the table for $AlCl_2$.[1]

Heat Capacity and Entropy

The electronic ground state, excited levels, bond distances and bond angle are assumed to be the same as in $AlCl_2$ and AlF_2.[1] Vibrational frequencies are estimated by comparison with $AlCl_2$ and AlF_2.[1] The principal moments of inertia are $I_A = 2.3419 \times 10^{-39}$, $I_B = 23.6618 \times 10^{-39}$ and I_C $26.0037 \times 10^{-39}\ g{\cdot}cm^2$.

References

[1] JANAF Thermochemical Tables: $AlCl_2(g)$, $AlCl_2$,(g), $AlF_2(g)$, $AlClF_2(g)$, $AlCl_2F(g)$ 6–30–76; AlF(g) 12–31–75; AlCl(g) 6–30–70; Al(g) 12–31–65; Cl(g) 6–30–72; F(g) 9–30–65.

[2] M. Farber and S. P. Harris, High Temp. Sci. 3, 231 (1971).

[3] M. Farber, R. D. Srivastava and O. M. Uy, Space Sciences, Inc., AFRPL–TR–70–97, (July, 1970).

[4] R. D. Srivastava and M. Farber, Trans. Faraday Soc. 67, 2298 (1971).

Aluminum Chloride Fluoride (AlClF) $Al_1Cl_1F_1(g)$

Aluminum Chloride Fluoride, Ion ($AlClF^+$) IDEAL GAS $M_r = 81.432394$ Aluminum Chloride Fluoride, Ion ($AlClF^+$) $Al_1Cl_1F_1^+(g)$

$S°(298.15\ K) = [259.72 \pm 63]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = 271 \pm 126\ kJ{\cdot}mol^{-1}$

$\Delta_fH°(298.15\ K) = [276.144]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[850](1)
[170](2)
[500](1)

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

Point Group: [$C_{\infty v}$]

Bond Distances: Al–F = [1.60] Å; Al–Cl = [2.05] Å

Bond Angle: F–Al–Cl = [180]°

Rotational Constant: $B_0 = [0.095960]\ cm^{-1}$

Enthalpy of Formation

We adopt $\Delta_fH°(298.15\ K) = 66 \pm 30\ kcal{\cdot}mol^{-1}$ based on $\Delta_fH°$ of AlClF[1] combined with the ionization potential IP(AlClF) = 182 ± 23 $kcal{\cdot}mol^{-1}$ (7.9 ± 1 eV). IP is estimated by comparison with IP($AlCl_2$) = 7.8 ± 0.9 eV and IP(AlF_2) = 8.1 ± 0.9 eV.[1] Farber and Harris[2] reported an appearance potential of AP($AlClF^+$) = 11 ± 1 eV which appears to be seriously biased. This is discussed *on the tables for* $AlCl_2^+(g)$ and AlClF(g).

Heat Capacity and Entropy

We assume the electronic ground state to be linear $^1\Sigma^+$ and neglect excited states.[1] Bond distances are estimated to be the same as in $AlCl_2^+$ and AlF_2^+.[1] Vibrational frequencies are estimated by comparison with AlClF, $AlCl_2^+$ and AlF_2^+.[1]

References

[1] JANAF Thermochemical Tables: AlClF(g), $AlCl_2^+(g)$, $AlF_2^+(g)$ 6–30–76.

[2] M. Farber and S. P. Harris, High Temp. Sci. 3, 231 (1971).

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_fH°$ (kJ·mol⁻¹)	$\Delta_fG°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−12.635	270.854		
100	39.763	209.503	302.848	−9.334			
200	47 610	239 743	264.378	−4.927			
250	50.330	250.669	260.574	−2.476			
298.15	52.450	259.722	259.722	0.	276.144	264.370	−46.316
300	52.522	260.047	259.723	0.097	276.174	264.297	−46.018
350	54.264	268.279	260.369	2.768	276.996	262.252	−39.139
400	55.638	275.618	261.825	5.517	277.820	260.090	−33.964
450	56.723	282.237	263.731	8.327	278.645	257.824	−29.927
500	57.585	288.259	265.887	11.186	279.466	255.466	−26.688
600	58.835	298.877	270.525	17.011	281.082	250.513	−21.809
700	59 668	308 013	275.243	22.939	282.629	245.295	−18.304
800	60.245	316.020	279.850	28.936	284.070	239.862	−15.661
900	60.658	323.141	284.272	34.983	285.366	234.256	−13.596
1000	60.963	329.549	288.484	41.064	275.898	229.276	−11.976
1100	61.194	335.370	292.486	47.173	277.175	224.551	−10.663
1200	61.372	340.703	296.285	53.301	278.453	219.711	−9.564
1300	61.513	345.621	299.893	59.446	279.730	214.764	−8.629
1400	61.626	350.184	303.325	65.603	281.005	209.719	−7.825
1500	61.718	354.439	306.592	71.770	282.275	204.583	−7.124
1600	61 794	358.425	309.708	77.946	283.540	199.362	−6.508
1700	61.857	362.173	312.685	84.129	284.799	194.062	−5.963
1800	61.910	365.710	315.534	90.317	286.052	188.689	−5.476
1900	61.955	369.059	318.264	96.511	287.300	183.245	−5.038
2000	61 994	372.237	320.883	102.708	288.542	177.737	−4.642
2100	62.027	375.263	323 401	108.909	289 778	172.166	−4.282
2200	62.056	378.149	325.825	115.113	291.011	166.537	−3.954
2300	62.082	380.908	328.160	121.320	292.240	160.851	−3.653
2400	62.104	383.551	330.414	127.530	293.467	155.112	−3.376
2500	62.124	386.087	332.590	133.741	294.692	149.322	−3.120
2600	62.141	388.523	334.695	139.954	295.917	143 483	−2.883
2700	62.157	390.869	336.732	146.169	297.142	137.597	−2.662
2800	62.171	393.130	338.706	152.386	4.468	132.633	−2.474
2900	62.184	395.312	340.621	158.603	6 793	137.170	−2.471
3000	62.195	397.420	342.479	164.822	9.121	141.626	−2.466
3100	62.205	399.459	344.284	171.042	11.454	146.004	−2.460
3200	62.215	401.435	346.040	177.263	13.793	150.307	−2.454
3300	62.223	403.349	347.748	183.485	16.138	154.537	−2.446
3400	62.231	405.207	349.410	189.708	18.491	158.696	−2.438
3500	62.238	407.011	351.030	195.931	20.852	162.785	−2.429
3600	62.245	408.764	352.610	202.156	23.223	166.807	−2.420
3700	62.251	410.470	354.151	208.380	25.605	170.762	−2.411
3800	62.256	412 130	355.655	214.606	27.999	174.653	−2.401
3900	62.261	413.747	357.124	220.832	30.406	178.481	−2.390
4000	62.266	415.323	358.559	227.058	32.826	182.248	−2.380
4100	62.270	416.861	359.962	233.285	35.260	185.953	−2.369
4200	62.275	418.362	361.335	239.512	37.709	189.599	−2.358
4300	62.278	419.827	362.678	245.740	40.173	193.186	−2.347
4400	62.282	421.259	363.993	251.968	42.654	196.716	−2.335
4500	62.285	422.659	365.282	258.196	45.153	200.189	−2.324
4600	62.288	424.028	366.544	264.425	47.667	203.607	−2.312
4700	62.291	425.367	367.781	270.654	50.197	206.969	−2.300
4800	62.294	426.679	368.995	276.883	52.744	210.278	−2.288
4900	62.297	427.963	370.185	283.113	55.308	213.534	−2.276
5000	62.299	429.222	371.353	289.342	57.887	216.736	−2.264
5100	62.301	430.455	372.500	295.572	60.482	219.888	−2.252
5200	62.304	431.665	373.626	301.803	63.092	222.988	−2.240
5300	62.306	432.852	374.733	308.033	65.716	226.038	−2.228
5400	62.307	434.017	375.820	314.264	68.354	229.038	−2.216
5500	62.309	435.160	376.888	320.495	71.004	231.989	−2.203
5600	62.311	436.283	377.939	326.726	73.666	234.892	−2.191
5700	62.313	437.386	378.972	332.957	76.338	237.747	−2.179
5800	62.314	438.469	379.989	339.188	79.022	240.556	−2.166
5900	62.316	439.535	380.989	345.420	81.711	243.318	−2.154
6000	62.317	440.582	381.973	351.651	84.429	246.032	−2.142

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

Aluminum Chloride Fluoride ($AlClF_2$) IDEAL GAS $M_r = 100.431346$ Aluminum Chloride Fluoride ($AlClF_2$) $Al_1Cl_1F_2(g)$

$S°(298.15 K) = [297.8 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -995.98 \pm 6.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -999.14 \pm 6.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm⁻¹	ν, cm⁻¹
[800](1)	[910](1)
[520](1)	[210](1)
[240](1)	[260](1)

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

Point Group: [C_{2v}]

Bond Distances: Al–F = [1.63] Å; Al–Cl = [2.06] Å

Bond Angles: Cl–Al–F = [120]°; F–Al–F = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.281169] \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -238.8 \pm 1.5$ kcal mol⁻¹ and $\Delta_{at} H° = 380.8 \pm 3$ kcal·mol⁻¹ based on $\Delta_r H°(298.15\ K) = 0.5 \pm 1$ kcal·mol⁻¹ for 1/3 $AlCl_3(g)$ + 2/3 $AlF_3(g)$ = $AlClF_2(g)$. Krause and Douglas[1] obtained this result by an entrainment method which measured enhanced volatility of AlF_3 in the presence of $AlCl_3$ Corrections were made for all the possible dimers which can form in this system. The entrainment data establish that aluminum fluoride–chloride exchange reactions are almost thermoneutral.

Our adopted $\Delta_f H°$ is compared below with an approximate mass–spectrometric K_p for reaciton of AlF_2 with $AlCl_2$.[2] The discrepancy in $\Delta_f H°(AlClF_2)$ is −19 kcal·mol⁻¹ if we use $\Delta_f H° = -180$ (AlF_2) and −71 ($AlCl_2$) derived from the mass–spectrometric data.[2,3] The discrepancy disappears if we use $\Delta_f H° = -166$ (AlF_2) and −67 ($AlCl_2$) derived from average bond energies in AlF_3 and $AlCl_3$.[4] This favors the latter values of $\Delta_f H°$ for AlF_2 and $AlCl_2$,[4] although the discrepancy might arise from the observed ion intensity of $AlClF_2^+$. The signal from $AlClF_2^+$ was very weak at 40 eV,[5] this high ionizing energy might bias K_p and cause considerable fragmentation. We can eliminate AlF_2 and $AlCl_2$ by taking the difference between the mass–spectrometric reactions for $AlClF_2$ and $AlCl_2F$.[4] This yields $[\Delta_f H°(AlClF_2) - \Delta_f H°(AlCl_2F)] = -47$ kcal·mol⁻¹ which agrees with −49.8 kcal mol⁻¹ from entrainment data.[1] Thus, we tentatively ascribe the discrepancy to AlF_2[4] and $AlCl_2$.

Source	Method	Reaction	T/K	kcal·mol⁻¹ $\Delta_r H°(T)$	$\Delta_r H°(298.15\ K)$	$\Delta_f H°(298.15\ K)$
1	Entrainment	1/3 $AlCl_3(g)$ + 2/3 $AlF_3(g)$ = $AlClF_2(g)$	1196–1257	0.5 ± 1	0.5 ± 1	−238.8
2	Mass Spec.	$AlF_2(g) + AlCl_2(g) = AlCl(g) + AlClF_2(g)$	1491	—	−19.2	−240[a] or −258[b]

[a] Assuming $\Delta_f H°(298.15\ K) = -166$ (AlF_2) and −67 ($AlCl_2$) kcal·mol⁻¹

[b] Assuming $\Delta_f H°(298.15\ K) = -180$ (AlF_2) and −71 ($AlCl_2$) kcal·mol⁻¹

Heat Capacity and Entropy

We adopt a C_{2v} structure with bond angles and bond distances assumed equal to those in AlF_3 and $AlCl_3$.[4] We assume a singlet electronic ground state and neglect excited states. Vibrational frequencies are estimated by comparison of AlF_3 and $AlCl_3$ with the series BF_3, $BClF_2$, BCl_2F and Bcl_3.[6,7] The principal moments of inertia are $I_A = 12.5730 \times 10^{-39}$, $I_B = 26.2481 \times 10^{-39}$, and $I_C = 38.8212 \times 10^{-39}$ g·cm².

References

[1] R. F. Krause and T. B. Douglas, J. Phys. Chem. 72, 3444 (1968).

[2] M. Farber and S. P. Harris, High Temp. Sci. 3, 231 (1971).

[3] O. M. Uy, R. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972).

[4] JANAF Thermochemical Tables: $AlF_2(g)$, $AlCl_2(g)$, $AlCl_2F(g)$, 6–30–76; $AlF_3(g)$, $AlCl_3(g)$, 6–30–70.

[5] M. Farber, Space Sciences, Inc., Monrovia, Calif., personal communication, (August 30, 1976).

[6] D. F. Wolfe and G. L. Humphrey, J. Mol Struct. 3, 293 (1969).

[7] L. P Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956).

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

T/K	J·K⁻¹mol⁻¹ $C_p°$	$S°$	$-[G°-H°(T_r)]/T$	kJ·mol⁻¹ $H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.795	−995.980	−995.980	INFINITE
100	43.865	238.385	350.065	−11.168	−997.199	−993.852	519.135
200	57.230	273.348	303.584	−6.047	−998.328	−990.042	258.572
250	61.827	286.629	298.897	−3.067	−998.774	−987.917	206.414
298.15	65.447	297.839	297.839	0.	−999.139	−985.793	172.707
300	65.572	298.245	297 841	0.121	−999.152	−985.710	171.627
350	68.588	308.588	298.651	3.478	−999.479	−983.443	146.771
400	70.996	317.910	300.485	6.970	−999.766	−981.132	128.123
450	72.917	326.387	302.899	10.569	−1000.025	−978.787	113.615
500	74 454	334.152	305.642	14.255	−1000.265	−976.414	102.005
600	76 700	347.939	311.571	21.821	−1000.724	−971.601	84.585
700	78.209	359.883	317.639	29.571	−1001.209	−966.709	72.137
800	79.259	370.399	323.590	37.447	−1001.773	−961.744	62.795
900	80.014	379.780	329.322	45.413	−1002.462	−956.700	55.525
1000	80.573	388.241	334.797	53.444	−1013.906	−950.811	49.665
1100	80.997	395.941	340.011	61.523	−1014.596	−944.469	44.849
1200	81.325	403.003	344.970	69.640	−1015.281	−938.063	40.833
1300	81.584	409.524	349.688	77.786	−1015.966	−931.600	37.432
1400	81.792	415.577	354.181	85.955	−1016.653	−925.085	34.515
1500	81.962	421.227	358.465	94.143	−1017.346	−918.520	31.986
1600	82.101	426.521	362.554	102.346	−1018.047	−911.909	29.771
1700	82.218	431.502	366 465	110.562	−1018.755	−905.254	27.815
1800	82.316	436.204	370.210	118.789	−1019.472	−898.556	26.075
1900	82.399	440.657	373.802	127.025	−1020.197	−891.819	24.518
2000	82.471	444.885	377.251	135.269	−1020.928	−885.044	23.115
2100	82.532	448.911	380.568	143.519	−1021.664	−878.231	21.845
2200	82.586	452.751	383.763	151.775	−1022.403	−871.384	20.689
2300	82.633	456.423	386.843	160.036	−1023.143	−864.503	19.633
2400	82.674	459.941	389.816	168.301	−1023.880	−857.590	18.665
2500	82.711	463.317	392.689	176.570	−1024.613	−850.646	17.773
2600	82.743	466.561	395.468	184.843	−1025.338	−843.673	16.950
2700	82.772	469.685	398.159	193.119	−1026.054	−836.672	16.186
2800	82.798	472.695	400.768	201.398	−1320.659	−828.677	15.459
2900	82.821	475.601	403.298	209.678	−1320.252	−811.113	14.610
3000	82.842	478.409	405.756	217.962	−1319.829	−793.564	13.817
3100	82.861	481.126	408.143	226.247	−1319.386	−776.029	13.076
3200	82.879	483.757	410.465	234.534	−1318.924	−758.509	12.381
3300	82.894	486.308	412.725	242.823	−1318.438	−741.003	11.729
3400	82.909	488.783	414.926	251.113	−1317.929	−723.513	11.115
3500	82.922	491.186	417.071	259.404	−1317.394	−706.038	10.537
3600	82.934	493.522	419.162	267.697	−1316.831	−688.578	9.991
3700	82.945	495.795	421.203	275.991	−1316.241	−671.135	9.475
3800	82.955	498.007	423.195	284.286	−1315.621	−653.708	8.986
3900	82.965	500.162	425.141	292.582	−1314.972	−636.298	8.522
4000	82.974	502.262	427.043	300.879	−1314.291	−618 904	8.082
4100	82.982	504.311	428.902	309.177	−1313.579	−601.528	7.664
4200	82.990	506.311	430.722	317.475	−1312.834	−584.170	7.265
4300	82.997	508.264	432.502	325 775	−1312.057	−566.830	6.886
4400	83.003	510.172	434.246	334.075	−1311.248	−549.509	6.523
4500	83.009	512.038	435.954	342.375	−1310.403	−532.206	6.178
4600	83.015	513.862	437.628	350.677	−1309.528	−514.922	5.847
4700	83.021	515.647	439.269	358.978	−1308.621	−497.658	5.531
4800	83.026	517.395	440.879	367.281	−1307.682	−480.413	5.228
4900	83.030	519.107	442 458	375.583	−1306.710	−463.188	4 938
5000	83.035	520.785	444.007	383.887	−1305.709	−445.984	4.659
5100	83.039	522.429	445.529	392.190	−1304.678	−428.800	4.392
5200	83.043	524.042	447.023	400.495	−1303.619	−411.636	4.135
5300	83.047	525 624	448.492	408.799	−1302.531	−394.493	3.888
5400	83.050	527 176	449 934	417.104	−1301.418	−377.370	3.650
5500	83.054	528 700	451.353	425 409	−1300.279	−360.269	3 422
5600	83.057	530.196	452.747	433.715	−1299.117	−343.188	3.201
5700	83.060	531.666	454.119	442.021	−1297.932	−326.129	2.989
5800	83.063	533.111	455.469	450.327	−1296.724	−309.090	2.784
5900	83.066	534.531	456.797	458.633	−1295.500	−292.072	2.586
6000	83.068	535 927	458.104	466.940	−1294.236	−275.078	2.395

PREVIOUS June 1976 (1 atm) CURRENT June 1976 (1 bar)

Aluminum Chloride Fluoride ($AlClF_2$) $Al_1Cl_1F_2(g)$

Aluminum Chloride Oxide (OAlCl) CRYSTAL $M_r = 78.43394$

$S°(298.15 \text{ K}) = [54.4 \pm 4] \text{ J·K}^{-1}\text{·mol}^{-1}$

T_{fus} = Unknown

T_{dcm} = [500] K

$\Delta_f H°(0 \text{ K})$ = Unknown

$\Delta_f H°(298.15 \text{ K}) = -793.3 \pm 1.3 \text{ kJ·mol}^{-1}$

$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

$\Delta_f H°$(AlOCl, cr, 298.15 K) is calculated from $\Delta_r H°(298.15 \text{ K}) = 21.05 \text{ kcal·mol}^{-1}$ for the reaction $AlOCl(cr) + Cl_2(g) = AlCl_3(cr) + 1/2\ O_2(g)$ reported by Schafer *et al.*[1] This reaction is the overall reaction of the following four separate reactions:

Reaction	$\Delta_r H°(298.15 \text{ K})$, kcal·mol^{-1}
$AlOCl(cr) + 2(HCl299.5\ H_2O) = AlCl_3·600\ H_2O(l)$	−46.9
$AlCl_3·600\ H_2O(l) = AlCl_3(cr) + 600\ H_2O(l)$	+79.3
$H_2O(l) = H_2(g) + 1/2\ O_2(g)$	+68.32
$H_2(g) + Cl_2(g) + 599\ H_2O(l) = 2(HCl·299.5\ H_2O)$	−79.67
$AlOCl(cr) + Cl_2(g) = AlCl_3(cr) + 1/2\ O_2(g)$	+21.05

Heat Capacity and Entropy

The heat capacities for AlOCl(cr) are estimated based on the assumption that $\Delta C_p = 0$ for the reaction $AlCl_3(cr) + Al_2O_3(cr) = 3\ AlOCl(cr)$. $S°(298.15 \text{ K}) = 13 \text{ cal·K}^{-1}\text{·mol}^{-1}$ was estimated by Schafer *et al.*[1]

Decomposition Data

T_{dcm} is calculated as the temperature at which the Gibbs energy change of the reaction $6\ AlOCl(cr) \rightarrow 2\ Al_2O_3(cr) + Al_2Cl_6(g)$ is zero.

References

[1] H. Schafer, F. E. Wittig and W. Wilborn, Z. anorg. allgem. Chem. **297**, 48 (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							
250							
298.15	56.902	54.392	54.392	0.	−793.286	−737.235	129.161
300	57.112	54.745	54.393	0.105	−793.284	−736.888	128.304
400	64.308	72.215	56.726	6.196	−792.923	−718.130	93.778
500	69.203	87.118	61.351	12.883	−792.183	−699.511	73.077
600	72.634	100.052	66.748	19.983	−791.215	−681.065	59.292
700	74.977	111.431	72.335	27.367	−790.141	−662.791	49.458
800	76.860	121.570	77.867	34.963	−789.045	−644.673	42.093
900	78.168	130.701	83.239	42.716	−787.995	−626.691	36.372
1000	79.245	138.995	88.406	50.589	−797.638	−608.060	31.762
1100	80.040	146.586	93.355	58.554	−796.477	−589.158	27.977
1200	80.709	153.580	98.086	66.592	−795.269	−570.363	24.827
1300	81.243	160.062	102.607	74.691	−794.023	−551.672	22.166
1400	81.672	166.099	106.929	82.837	−792.749	−533.077	19.889
1500	81.961	171.744	111.064	91.019	−791.459	−514.574	17.919
1600	82.216	177.041	115.024	99.228	−790.158	−496.157	16.198
1700	82.435	182.033	118.820	107.461	−788.850	−477.822	14.682
1800	82.620	186.750	122.464	115.714	−787.539	−459.564	13.336
1900	82.770	191.221	125.966	123.984	−786.228	−441.379	12.134
2000	82.885	195.470	129.336	132.267	−784.920	−423.263	11.055
2100	82.958	199.515	132.582	140.560	−783.619	−405.212	10.079
2200	83.011	203.376	135.713	148.858	−782.330	−387.223	9.194
2300	83.036	207.067	138.736	157.161	−781.055	−369.292	8.387
2400	83.052	210.601	141.657	165.465	−779.797	−351.417	7.648
2500	83.052	213.991	144.483	173.770	−778.557	−333.593	6.970
2600	83.052	217.249	147.220	182.075	−777.335	−315.819	6.345
2700	83.052	220.383	149.872	190.381	−776.134	−298.091	5.767
2800	83.052	223.403	152.444	198.686	−1068.853	−279.439	5.213
2900	83.052	226.318	154.942	206.991	−1066.595	−251.286	4.526
3000	83.052	229.133	157.368	215.296	−1064.357	−223.210	3.886

PREVIOUS: CURRENT: March 1964

Aluminum Chloride Oxide (OAlCl) $Al_1Cl_1O_1(cr)$

Aluminum Chloride Oxide (OAlCl) IDEAL GAS $M_r = 78.43394$

$S°(298.15\text{ K}) = [248.9 \pm 20]\ \text{J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0\text{ K}) = [-346.0 \pm 20]\ \text{kJ·mol}^{-1}$

$\Delta_f H°(298.15\text{ K}) = [-348.1 \pm 20]\ \text{kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[450](1)
[350](2)
[900](1)

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

Point Group: $C_{\infty v}$

Bond Distance: O–Al = [1.62] Å; Al–Cl = [2.14] Å

Bond Angle: O–Al–Cl = 180°

Rotational Constant: $B_0 = [0.097704]\ \text{cm}^{-1}$

Enthalpy of Formation

The Gibbs energy change of the reaction $1/3\ Al_2O_3(l) + 1/3\ AlCl_3(g) = AlOCl(g)$, $\Delta_r G°(2400\text{ K}) = 28 \pm 3\ \text{kcal·mol}^{-1}$, has been determined by Greenbaum *et al.*[1] Incorporating appropriate auliliary data, the enthalpy of reaction is derived to be 82.9 kcal·mol^{-1}, yielding $\Delta_f H°(\text{AlOCl, g, 298.15 K}) = -82.2 \pm 5\ \text{kcal·mol}^{-1}$.

Heat Capacity and Entropy

Point group, ground state quantum weight and vibrational frequencies are obtained from Hilsenrath *et al.*[2] The bond distances of r(O–Al) and r(Al–Cl) are assumed to be the same as those in AlO(g) and AlCl(g) molecules, respectively. The three principal moments of inertia are: $I_A = 0$ and $I_B = I_C = 2.86467 \times 10^{-38}\ \text{g·cm}^2$.

References

[1] M. A. Greenbaum *et al.*, Marimont Corporation, California, personal communication, (August 26, 1964).
[2] J. Hilsenrath, W. H. Evans and H. W. Wooley, U. S. Nat. Bur. Stand. Report 6484, 115 (July 1, 1959).

Aluminum Chloride Oxide (OAlCl) $Al_1Cl_1O_1(g)$

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	−11.407	−346.045	−346.045	INFINITE
100	32.420	204.221	288.567	−8.435	−346.464	−348.072	181.814
200	43.404	230.239	253.322	−4.617	−347.422	−349.296	91.227
250	47.248	240.357	249.740	−2.346	−347.803	−349.719	73.070
298.15	50.068	248.931	248.931	0.	−348.109	−350.059	61.329
300	50.162	249.241	248.932	0.093	−348.120	−350.071	60.953
350	52.394	257.148	249.551	2.659	−348.386	−350.375	52.291
400	54.118	264.262	250.953	5.324	−348.617	−350.643	45.789
450	55.464	270.717	252.796	8.065	−348.826	−350.884	40.730
500	56.527	276.618	254.887	10.865	−349.023	−351.102	36.679
600	58.059	287.069	259.403	16.600	−349.420	−351.481	30.599
700	59.076	296.101	264.015	22.460	−349.871	−351 789	26.251
800	59.780	304.038	268.532	28.405	−350.425	−352.027	22.985
900	60.284	311.110	272.877	34.410	−351.124	−352.187	20.440
1000	60.656	317.482	277.024	40.458	−362.591	−351.500	18.360
1100	60.938	323.276	280.969	46.538	−363.316	−350.356	16.637
1200	61.155	328.588	284 719	52.643	−364.041	−349.146	15.198
1300	61.327	333.491	288.285	58.767	−364.769	−347.875	13.978
1400	61.465	338.041	291.678	64.907	−365.502	−346.548	12.930
1500	61.577	342.285	294.912	71.060	−366.241	−345.169	12.020
1600	61.670	346.262	297.999	77.222	−366.987	−343.740	11.222
1700	61.747	350.003	300.949	83.393	−367.741	−342.263	10.516
1800	61.811	353.535	303.773	89.571	−368.505	−340.743	9.888
1900	61.867	356.878	306.481	95.755	−369.279	−339.180	9.325
2000	61.914	360.053	309.081	101.944	−370.065	−337.575	8.817
2100	61.955	363.075	311.581	108.137	−370.864	−335.931	8.356
2200	61.990	365.958	313.987	114.335	−371.676	−334.248	7.936
2300	62.021	368.714	316.307	120.535	−372.503	−332.529	7.552
2400	62.048	371.354	318.546	126.739	−373.346	−330.773	7.199
2500	62.072	373.887	320.709	132.945	−374.204	−328.981	6.874
2600	62.094	376.322	322.802	139.153	−375.080	−327.155	6.573
2700	62.113	378.666	324.828	145.363	−375.974	−325.295	6.293
2800	62.130	380.925	326.791	151.576	−670.786	−322.433	6.015
2900	62.145	383.106	328.696	157.789	−670.620	−309.995	5.584
3000	62.159	385.213	330.545	164.005	−670.471	−297.563	5.181
3100	62.172	387.251	332.341	170.221	−670.341	−285.134	4.804
3200	62.183	389.225	334.088	176.439	−670.229	−272.710	4.452
3300	62.193	391.139	335.788	182.658	−670.133	−260.289	4.120
3400	62.203	392.996	337.444	188.878	−670.053	−247.871	3.808
3500	62.212	394.799	339.057	195.098	−669.989	−235.455	3.514
3600	62.220	396.552	340.629	201.320	−669.939	−223.040	3.236
3700	62.227	398.256	342.164	207.542	−669.903	−210.627	2.974
3800	62.234	399.916	343.662	213.765	−669.879	−198.215	2.725
3900	62.240	401.533	345.125	219.989	−669.866	−185.802	2.489
4000	62.246	403.109	346.555	226.213	−669.863	−173.391	2.264
4100	62.251	404.646	347.953	232.438	−669.870	−160.979	2.051
4200	62.256	406.146	349.321	238.663	−669.885	−148.567	1.848
4300	62.261	407.611	350.660	244.889	−669.907	−136.154	1.654
4400	62.265	409.042	351.970	251.116	−669.935	−123.741	1.469
4500	62.269	410.441	353.254	257.342	−669.967	−111.328	1.292
4600	62.273	411.810	354.512	263.569	−670.006	−98.913	1.123
4700	62.277	413.149	355.746	269.797	−670.050	−86.497	0.961
4800	62.280	414.461	356.955	276.025	−670.099	−74.081	0.806
4900	62.283	415.745	358.142	282.253	−670.151	−61.663	0.657
5000	62.286	417.003	359.307	288.481	−670.209	−49.244	0.514
5100	62.289	418.237	360.450	294.710	−670.272	−36.824	0.377
5200	62.292	419.446	361.573	300.939	−670.341	−24.404	0.245
5300	62.294	420.633	362.676	307.168	−670.415	−11.981	0.118
5400	62.296	421.797	363.760	313.398	−670.497	0.443	−0.004
5500	62.299	422.940	364.826	319.628	−670.586	12.869	−0.122
5600	62.301	424.063	365.874	325.858	−670.685	25.296	−0.236
5700	62.303	425.165	366.904	332.088	−670.793	37.725	−0.346
5800	62.305	426.249	367.918	338.318	−670.910	50.157	−0.452
5900	62.306	427.314	368.916	344.549	−671.043	62.589	−0.554
6000	62.308	428.361	369.898	350.779	−671.167	75.023	−0.653

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

Aluminum Chloride Oxide (OAlCl) $Al_1Cl_1O_1(g)$

Aluminum Chloride (AlCl$_2$) IDEAL GAS M_r = 97.88754 Aluminum Chloride (AlCl$_2$) Al$_1$Cl$_2$(g)

$\Delta_fH°(0\text{ K}) = -279.4 \pm 20\text{ kJ·mol}^{-1}$
$\Delta_fH°(298.15\text{ K}) = -280.3 \pm 20\text{ kJ·mol}^{-1}$

$S°(298.15\text{ K}) = [289.42 \pm 2.4]\text{ J·K}^{-1}\text{·mol}^{-1}$

Electronic Levels and Quantum Weights State	ϵ_i, cm^{-1}	g_i
$^2A_1$	0	2
$^2B_1$	[20000]	2
$^2B_2$	[25000]	2

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[430](1)
[160](1)
[570](1)

Point Group: [C$_{2v}$] $\sigma = 2$
Bond Distance: Al–Cl = [2.10] Å
Bond Angle: Cl–Al–Cl = [120]°
Product of the Moments of Inertia: $I_AI_BI_C = [5.925281 \times 10^{-114}]\text{ g}^3\text{·cm}^6$

Enthalpy of Formation

We adopt $\Delta_fH°(298.15\text{ K}) = -67 \pm 5\text{ kcal·mol}^{-1}$ and $\Delta_{at}H° = 201.4 \pm 6\text{ kcal·mol}^{-1}$; i.e., the average bond energy $\Delta_{at}H°/2 = 101\text{ kcal·mol}^{-1}$ is taken equal to that of AlCl$_3$.[1] $\Delta_fH°$ is consistent with experimental results of -66 ± 3[2] and $\geq -71 \pm 5\text{ kcal mol}^{-1}$[3,4] but there may be significant bias in these values.

Chai *et al.*[2] derived $\Delta_fH°(298.15\text{ K}) = -66 \pm 3\text{ kcal·mol}^{-1}$ from study of reactions of Al(c,l) with the vapor of AlCl$_3$ in an argon carrier gas. Weight–loss data (800–1000 K) for Al and AlCl$_3$ were analyzed assuming five vapor species (AlCl, AlCl$_2$, AlCl$_3$, Al$_2$Cl$_4$, Al$_2$Cl$_6$) in four simultaneous equilibrium reactions. Experimental data were combined with auxiliary data, including $S°$(AlCl$_2$) and K_p for two reactions, to derive $\Delta_fH°$(AlCl$_2$) and K_p for another reaction involving Al$_2$Cl$_4$. Despite minor changes in $S°$(AlCl$_2$), $\Delta_fH° = -66$ is till appropriate for the AlCl$_2$ equilibrium.[2] We suspect, however, that this equilibrium is strongly dependent on the other equilibria, particularly that involving Al$_2$Cl$_4$(g).

Farber and Harris[3,4] reported K_p (5 points, 1150–1430 K) for the reaction AlCl(g) + AlCl$_3$(g) = 2 AlCl$_2$(g). We obtain [$\Delta_rS°$(2nd law)$-\Delta_rS°$(3rd law)] = $-35 \pm 10\text{ cal·K}^{-1}\text{·mol}^{-1}$, $\Delta_rH°(298.15\text{ K}) = -36 \pm 13$(2nd law) or 10.5 ± 9(3rd law) and $\Delta_fH°(298.15\text{ K}) \geq -70.7 \pm 5\text{ kcal·mol}^{-1}$. We consider $\Delta_fH°$ to be a negative limit due to possible bias arising from the ionizing energy. Energy of the ionizing electrons was variously reported as 20 eV[4] or as 3 eV above the AP.[3] If 20 eV was used, we expect AlCl$_2^+$ to be enhanced due to fragmentation of AlCl$_3$. The alternative ionizing energy leads to another problem, since the authors[3,4] used literature values for the AP of AlCl$^+$ but their own value for AlCl$_2^+$. Their value has a bias of -3 eV which is discussed in detail on the table for AlCl$_2^+$(g).[1] We suspect that the mass spectrometer had a biased energy scale during the measurments.[3,4] This would induce negative bias in the ionizing energy used for AlCl$^+$ and AlCl$_3^+$, since the AP's were not based on the experimental energy scale. Again we expect AlCl$_2^+$ to be enhanced relative to AlCl$^+$ and AlCl$_3^+$. The large discrepancy in $\Delta_rS°$ is symptomatic of a temperature–dependent error; we expect that bias in K_p is greatest at low T. NO$_2$, and NO Although [BE(MX)–BE(MX$_3$)] = -20 kcal·mol^{-1}, only the mass–spectrometric data of Farber *et al.*[3-6] yield BE(MX$_2$)>BE(MX$_3$). Other data[1,2,7] and theoretical calculations[8] suggest that BE(MX$_2$)≤BE(MX$_3$).

Source	Method	Species	Average Bond Energy ($\Delta_{at}H°$/n), kcal·mol^{-1} AlCl$_n$	BCl$_n$	AlF$_n$	BF$_n$	NO$_n$
JANAF[1]	Review	MX	118.4	127.1	159.3	179.4	150.0
JANAF[1]	Review	MX$_3$	100.8	104.5	140.2	152.5	90.3
JANAF[1]	Review	MX$_2$	101	—	140	—	111.0
Farber *et al.*[3,4]	Mass spec.	MX$_2$	102.6	—	146.5, 151	—	—
Srivastava *et al.*[5,6]	Mass spec.	MX$_2$	—	104.0	147.0	155.0	—
Dibeler *et al.*[7]	Photoionization	MX$_2$	—	102.6	—	145.6	—
Others[2,1]	Various	MX$_2$	100.2[2]	103.5[1]	132.4[1]	—	—

Heat Capacity and Entropy

The electronic ground state and excited levels are assumed to be the same as in AlF$_2$.[1] Vibrational frequencies are calculated from the estimated force constants $f_r = 2.2$ and $f_\alpha/r^2 = 0\ 13$ mdyn/Å. Frequencies and force constants are estimated from simultaneous consideration of AlCl$_2^+$, AlCl$_2$, AlCl$_2^-$ and the analogous boron species. We assume that frequency changes are qualitatively similar to those of NO$_2^+$, NO$_2$, and NO$_2^-$. Thus, in going from AlCl$_2^+$ to AlCl$_2$, we expect a large decrease in ν_3, an increase in ν_2 and a small increase in ν_1. By analogy with BF$_2$,[8] the odd electron of AlCl$_2$ should occupy an anti–bonding orbital which increases the bond length but decreases the bond angle and stretching force constant. We assume a bond length 0.05 Å longer than in AlCl$_2^+$ [1] and a bond angle equal to that in BF$_2$.[8] The principal moments of inertia are $I_A = 3.5781 \times 10^{-39}$, $I_B = 38.9438 \times 10^{-39}$ and $I_C = 42.5220 \times 10^{-39}\text{ g·cm}^2$.

Continued on page 171

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−12.764	−279.371	−279.371	INFINITE
100	39.512	239.866	331.991	−9.212	−279.216	−283.603	148.139
200	47.065	269.680	294.017	−4.867	−279.710	−287.825	75.172
250	49.753	280.487	290.260	−2.443	−280 019	−289.818	60.554
298.15	51.635	289.420	289.420	0.	−280.328	−291.677	51.101
300	51.696	289 739	289.421	0.096	−280.340	−291.748	50.798
350	53.093	297.819	290.056	2.717	−280.672	−293.623	43.821
400	54.109	304.979	291.482	5.399	−281.015	−295.450	38.582
450	54.863	311.397	293.345	8.124	−281.369	−297.233	34.502
500	55.434	317.209	295.445	10.882	−281.736	−298.976	31.234
600	56.219	327.391	299.945	16.468	−282.518	−302.351	26.322
700	56.716	336.097	304.502	22.116	−283.389	−305.590	22.803
800	57.050	343.693	308.937	27.805	−284.380	−308.695	20.156
900	57.284	350.427	313.180	33.523	−285.524	−311.668	18.089
1000	57.453	356.472	317.212	39.260	−297.439	−313.743	16.388
1100	57.580	361.954	321.034	45.012	−298.612	−315.317	14.973
1200	57.677	366.968	324.656	50.775	−299.786	−316.784	13.789
1300	57.754	371.588	328.091	56.547	−300.961	−318.153	12.784
1400	57.814	375.870	331.352	62.325	−302.140	−319.431	11.918
1500	57.864	379.861	334.455	68.109	−303.322	−320.625	11.165
1600	57.904	383.597	337.411	73.898	−304.508	−321.740	10.504
1700	57.938	387.108	340.232	79.690	−305.700	−322.780	9.918
1800	57.966	390.421	342.929	85.485	−306.897	−323.751	9.395
1900	57.990	393.555	345.512	91.283	−308.102	−324.654	8.925
2000	58.011	396.530	347.989	97.083	−309.314	−325.494	8.501
2100	58.030	399.361	350.368	102.885	−310.535	−326.273	8.116
2200	58.046	402.061	352.657	108.689	−311.767	−326.993	7.764
2300	58.062	404.642	354.862	114.494	−313.011	−327.658	7.441
2400	58.076	407.113	356.988	120.301	−314.268	−328.268	7.145
2500	58.091	409.484	359.040	126.110	−315.540	−328.825	6.870
2600	58.105	411.763	361.025	131.919	−316.827	−329.331	6.616
2700	58.121	413.956	362.945	137.731	−318.131	−329.787	6.380
2800	58.137	416.070	364.805	143.544	−613.353	−329.227	6.142
2900	58.155	418.111	366.608	149.358	−613.596	−319.075	5.747
3000	58.175	420.082	368.358	155.175	−613.857	−308.915	5.379
3100	58.198	421.990	370.057	160.993	−614.135	−298.746	5.034
3200	58.223	423.838	371.709	166.814	−614.430	−288.567	4.710
3300	58.252	425.631	373.316	172.638	−614.741	−278.379	4.406
3400	58.284	427.370	374.880	178.465	−615.066	−268.182	4.120
3500	58.319	429.060	376.404	184.295	−615 403	−257.974	3.850
3600	58.359	430.703	377.890	190.129	−615.751	−247.757	3.595
3700	58.403	432.303	379.339	195.967	−616.107	−237.530	3.353
3800	58.450	433.861	380.753	201.810	−616.469	−227.294	3.124
3900	58.503	435.380	382.135	207.657	−616.833	−217.047	2.907
4000	58.559	436.862	383.484	213.510	−617.199	−206.792	2.700
4100	58.620	438.309	384.804	219.369	−617.563	−196.527	2.504
4200	58.685	439.722	386.095	225.234	−617.922	−186.254	2.316
4300	58.755	441.104	387.358	231.106	−618.273	−175.972	2.138
4400	58.829	442.455	388.595	236.986	−618.616	−165.682	1.967
4500	58.907	443.778	389.807	242.872	−618.944	−155.384	1.804
4600	58.990	445.074	390.994	248.767	−619.260	−145.079	1.647
4700	59.076	446.343	392.158	254.670	−619.559	−134.768	1.498
4800	59.166	447.588	393.300	260.582	−619.841	−124.450	1.354
4900	59.259	448.809	394.421	266.504	−620.103	−114.127	1.217
5000	59.356	450.007	395.520	272.434	−620.345	−103.798	1.084
5100	59.456	451.184	396.600	278.375	−620.564	−93.465	0.957
5200	59.559	452.339	397.661	284.326	−620.762	−83.128	0.835
5300	59.664	453.475	398.703	290.287	−620.935	−72.787	0.717
5400	59.772	454.591	399.728	296.259	−621.086	−62.443	0 604
5500	59.882	455.689	400.736	302.241	−621.212	−52.096	0.495
5600	59.994	456.769	401.727	308.235	−621.314	−41.748	0.389
5700	60.107	457.831	402.702	314.240	−621.393	−31.398	0.288
5800	60.222	458.878	403.661	320.257	−621.445	−21.047	0.190
5900	60.338	459.908	404.606	326.285	−621.477	−10.695	0.095
6000	60.455	460.923	405.536	332.324	−621.465	−0.345	0.003

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

Aluminum Chloride (AlCl$_2$) Al$_1$Cl$_2$(g)

Aluminum Chloride, Ion ($AlCl_2^+$) IDEAL GAS $M_r = 97.88699$ Aluminum Chloride, Ion ($AlCl_2^+$) $Al_1Cl_2^+(g)$

$S°(298.15\ K) = [268.26 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 475 \pm 75\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [481.160]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[390](1)
[120](2)
[690](1)

Ground State Quantum Weight: [1]

Point Group: [$D_{\infty h}$]

Bond Distance: Al–Cl = [2.05] Å

Bond Angle. Cl–Al–Cl = [180]°

Rotational Constant: B_0 = [0 056573] cm^{-1}

$\sigma = 2$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = 115 \pm 18$ kcal·mol^{-1} and IP($AlCl_2$) = 7.8 ± 0.9 eV. Electron–impact studies gave 13.4 ± 0.5 eV[1] and 13.4 ± 0.7 eV[2] for the appearance potential (AP) of $AlCl_2^+$ from $AlCl_3$. The analogous process for onset of BCl_2^+ from BCl_3 has been studied by both photoionization[3] and electron impact.[2] Comparison indicates that BCl_2^+ from electron impact[2] carried an excess energy (E*) of ~0.9 eV. We estimate the excess energy for $AlCl_2^+$ as 1.2 ± 0.6 eV. Thus, we take AP–E* = $\Delta_f H°$ = 12.2 ± 0.8 eV (281.3 ± 18 kcal mol^{-1}) for the reaction $AlCl_3(g) + e^-(g) = AlCl_2^+(g) + Cl(g) + 2\ e^-(g)$. With JANAF auxiliary data[4] this yields $\Delta_f H°(AlCl_2^+) = 113.5 \pm 18$, $\Delta_f H°(298.15\ K) = 115 \pm 18$ and IP($AlCl_2$) = 180 ± 20 kcal·mol^{-1} (7.8 ± 0.9 eV).

Electron impact studies[5-7] of $AlCl_2$ and BCl_2 gave approximate appearance potentials AP(MCl_2^+) = 12 ± 1 eV. This is ~4 eV greater than our adiabatic IP values. Such a difference could arise from several factors including bias in the ionizing–energy scale, bias in threshold detection, excess energy in MCl_2^+ and misassignment of the ionization process. The studies[5-7] make no mention of a calibrant gas for the energy scale. Reactive radicals (e.g. $AlCl_2$ from a reducing environment) may induce a bias in the energy scale. Consistent with this hypothesis, the values reported[6,7] for AP(BCl^+/BCl) and AP(BCl_2^+/BCl_3) are ~2 and 3–4 eV higher than other electron–impact data.[2,8] AP(MCl_2^+/MCl_2) was obtained[5-7] by a vanishing current (or initial break) method. We expect this to have a positive bias which increases as the pressure of MCl_2 decreases.[9] Electron impact on MCl_2 should yield a vertical AP corresponding to a nonlinear (excited) configuration of MCl_2^+. Excitation energies of >1 eV are expected if MCl_2^+ is similar to BF_2^+ and AlF_2^+.[4] Alternatively, AP(MCl_2^+) = 12 ± 1 eV[5-7] is a magnitude which may not exclude processes such as fragmentation or ion–molecular reactions of MCl_3. AP(MCl_2^+) almost overlaps with the onset of MCl_2^+ from MCl_3; i.e., 12.30 eV[1] (photoionization) or 13.0–13.2 eV[2,8] (electron impact) from BCl_3 and 13.4 ± 0.5 eV[1,2] (electron impact) from $AlCl_3$. On the other hand, the coincidence of AP(BCl^+) = AP(BCl_2^+) = 12 ± 1 eV[6,7] suggests that the two ions might be related, possibly via $BCl^+ + BCl_3 = BCl_2^+$. The authors[5,6] did not measure AP($AlCl^+$), but the analogous ion–molecular reaction is also energetically feasible. In summary, there are three plausible factors which may contribute to positive bias in the observed AP($AlCl_2^+$) and some conceivable alternative interpretations of the data.[5-7] This precludes use of AP($AlCl_2^+$) in calculating $\Delta_f H°$ of $AlCl_2^+$.

Hastie and Margrave[10] used an extended Hucket method to calculate IP($AlCl_2$) = 6.65 eV. This result should approximate the vertical IP which we expect at ~9 eV.

Heat Capacity and Entropy

We assume the electronic ground state to be linear $^1\Sigma^+$ and neglect excited states by analogy with $MgCl_2$[4,11] and other triatomic species having sixteen valence electrons.[12] We estimate the bond distance to be almost the same as in $AlCl_3$ and 0.05 Å shorter than in $AlCl_2$[4] 0 Likewise, we transfer the stretching force constant from $AlCl_3$ and the ratio f_r/f_α = 19 Å−2 from $MgCl_2$.[11] Thus, we calculate vibrational frequencies from the estimated force constants $f_r = 2.9$, $f_{rr} = 0\ 2$ and $f_\alpha/r^2 = 0.036$ mdyn/Å. The resulting values have been rounded upward.

References

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.481	475.202		
100	43.152	214.688	314.010	−9.932			
200	50.669	247.132	273.173	−5.208			
250	53.206	258.723	269.158	−2.609			
298.15	55.063	268.261	268.261	0.	481.160	469.865	−82.318
300	55.124	268.602	268.262	0.102	481.193	469.794	−81.798
350	56.563	277.213	268.939	2.896	482.072	467.825	−69.819
400	57.646	284.840	270.459	5.752	482.944	465.730	−60.818
450	58.470	291.679	272.443	8.656	483.807	463.526	−53.805
500	59.106	297.874	274.681	11.596	484.662	461.227	−48.184
600	60.000	308.736	279.477	17.555	486.332	456.382	−39.732
700	60.579	318.031	284.337	23.586	487.922	451.264	−33.674
800	60.971	326.147	289.067	29.665	489.399	445.924	−29.116
900	61.249	333.346	293.594	35.776	490.728	440.408	−25.561
1000	61.452	339.810	297.898	41.912	481.290	435.514	−22.749
1100	61 604	345.674	301.979	48.065	482.596	430.873	−20.460
1200	61 721	351.040	305.847	54.232	483.905	426.113	−18.548
1300	61.813	355.984	309.516	60.408	485.213	421.244	−16.926
1400	61.887	360.568	313.001	66.594	486.520	416.275	−15.531
1500	61.946	364.840	316.316	72.785	487.824	411.211	−14.320
1600	61 996	368.839	319.475	78.983	489.125	406.062	−13.257
1700	62.036	372.599	322.490	85.184	490 422	400.830	−12.316
1800	62.071	376.146	325.374	91.390	491.713	395.523	−11.478
1900	62.100	379.503	328.135	97.598	492.998	390.144	−10.726
2000	62.125	382.688	330.784	103.809	494.275	384.698	−10.047
2100	62.146	385.720	333.328	110.023	495.544	379.187	−9.432
2200	62.165	388.612	335.776	116.239	496.802	373.617	−8.871
2300	62.181	391.375	338.134	122.456	498.049	367.990	−8.357
2400	62.196	394.022	340.408	128.675	499.282	362.309	−7.885
2500	62.208	396.561	342.603	134.895	500.501	356.576	−7.450
2600	62.219	399.001	344.726	141.116	501.704	350 795	−7.048
2700	62.230	401.350	346 780	147.339	502.890	344 969	−6 674
2800	62.238	403.613	348.769	153.562	210.157	340.066	−6.344
2900	62.247	405.797	350.698	159.786	212.402	344.666	−6.208
3000	62.254	407.908	352.570	166.012	214.629	349.189	−6.080
3100	62.260	409.949	354.389	172.237	216.836	353.638	−5.959
3200	62.266	411.926	356.156	178.464	219.025	358.016	−5.844
3300	62.272	413.842	357.875	184.690	221.196	362.326	−5.735
3400	62.277	415.701	359.549	190.918	223.350	366.570	−5.632
3500	62.281	417.506	361.179	197.146	225.489	370.751	−5.533
3600	62.286	419.261	362.768	203.374	227.615	374.871	−5.439
3700	62.289	420.967	364.318	209.603	229.728	378.933	−5.350
3800	62.293	422.629	365.831	215.832	231.832	382.937	−5.264
3900	62.296	424.247	367.308	222.062	233.927	386.886	−5.182
4000	62.299	425.824	368.751	228.291	236.017	390.782	−5.103
4100	62.302	427.362	370.162	234.521	238.103	394 625	−5.028
4200	62.305	428.864	371.542	240.752	240.188	398 417	−4.955
4300	62.307	430.330	372.892	246.982	242.273	402.160	−4.885
4400	62.309	431.762	374.214	253.213	244.361	405.854	−4.818
4500	62.312	433.163	375.508	259.444	246.456	409.501	−4.753
4600	62.314	434.532	376.777	265.676	248.555	413.101	−4.691
4700	62.315	435.872	378.020	271.907	250.662	416.655	−4.631
4800	62.317	437.184	379.239	278.139	252.778	420.165	−4.572
4900	62.319	438.469	380.434	284.370	254.906	423.630	−4.516
5000	62.320	439.728	381.608	290.602	257.044	427.051	−4.461
5100	62.322	440.962	382.759	296.834	259.194	430.430	−4.409
5200	62.323	442.173	383.890	303.067	261.357	433.767	−4.357
5300	62.325	443.360	385.001	309.299	263.533	437.061	−4.307
5400	62.326	444.525	386.093	315.532	265.723	440.315	−4.259
5500	62.327	445.668	387.166	321.764	267.925	443.528	−4.212
5600	62.328	446.791	388.220	327.997	270.140	446.701	−4.167
5700	62.329	447.895	389.258	334.230	272.368	449.834	−4.122
5800	62.330	448.979	390.278	340.463	274.611	452.928	−4.079
5900	62.331	450.044	391.282	346.696	276.862	455.983	−4 037
6000	62.332	451.092	392.270	352.929	279.147	458.997	−3.996

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

$\Delta_fH°(0\ K) = [-474 \pm 105]\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = [285.8 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = [-481.160]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	[23000]	3
$^1B_1$	[30000]	1

Vibrational Frequencies and Degeneracies

ν, cm^{-1}
[430](1)
[160](1)
[460](1)

Point Group: [C_{2v}] $\sigma = 2$
Bond Distance: Al–Cl = [2.15] Å
Bond Angle: Cl–Al–Cl = [105]°
Product of the Moments of Inertia: $I_AI_BI_C = [7.583526 \times 10^{-114}]\ g^3\ cm^6$

Enthalpy of Formation

We adopt $\Delta_fH°(298.15\ K) = -115 \pm 25\ kcal \cdot mol^{-1}$ based on an estimated electron affinity of $EA(AlCl_2) = 46 \pm 23\ kcal \cdot mol^{-1}$ (2.0 ± 1 eV) and a fluoride–ion affinity of $IA(AlCl) = 46 \pm 25\ kcal \cdot mol^{-1}$. JANAF auxiliary data[1] are used in converting from one quantity to another. If AlX_2 radicals were analogous to X atoms,[2,3] then $EA(AlCl_2)$ should be approximately equal to $EA(AlF_2) = 0.2 \pm 0.4$ eV.[1] This analogy may not be justified, since the pertinent orbitals are quite different. An electron added to AlX_2 presumably occupies a molecular orbital centered mainly on the metal opposite the two halogens. We assume that the orbital energy is characteristic of the metal Al and is perturbed relatively little by substitution of Cl for F. This implies that $EA(AlCl_2) \approx EA(AlF_2)$.

The energy for the self–ionization process, $2\ AlF_2 = AlF_2^+ + AlF_2^-$, is $\Delta_rH° = [IP(AlF_2) - EA(AlF_2)] = 5.9 \pm 1$ eV.[1] Assuming $AlCl_2$ is similar, we estimate $EA(AlCl_2) = 1.9$ eV. The energy difference between the reactions $AlF_2^- = AlF + F^-$ and $AlF_2 = AlF + F$ is $\Delta_rH° = [IA(AlF) - D_0°(AlF_2)] = -29\ kcal \cdot mol^{-1}$. Assuming $AlCl_2^-$ is analogous, we estimate $EA(AlCl_2) = 2.3$ eV. We adopt the intermediate value $EA(AlCl_2) = 2.0 \pm 1$ eV but emphasize that all estimates depend on AlF_2.[1]

Heat Capacity and Entropy

Electronic levels and quantum weights are assumed equal to those of isoelectronic $SiCl_2$[1] calculated from the estimated force constants $f_r = 1.73$, $f_\pi = 0.07$ and $f_\alpha/r^2 = 0.156$ mdyn/Å. Frequencies and force constants are estimated from simultaneous consideration of $AlCl_2$, $AlCl_2$, $AlCl_2^-$ and the analogous boron species. We assume that frequency changes are qualitatively similar in the two series $AlCl_2^+$, $AlCl_2$, $AlCl_2^-$ and NO_2^+, NO_2, NO_2^- [1] which have the same number of valence electrons. Furthermore, we expect isoelectronic $SiCl_2$[1] to provide upper–limit frequencies for $AlCl_2^-$. Thus, in going from $AlCl_2$ to $AlCl_2^-$, we assume little change in ν_1 and ν_2 but a significant decrease in ν_3.

By analogy with BF_2,[4,5] we expect that the odd electron in $AlCl_2$ occupies a molecular orbital centered mainly on the metal opposite the two chlorides. This orbital should be antibonding[4] in the sense that addition of an electron increases the bond length but decreases the bond angle and stretching force constant. We assume that the bond length is 0.05 Å longer and the bond angle is 15° smaller than in $AlCl_2$.[1] The principal moments of inertia are: $I_A = 5.5597 \times 10^{-39}$, $I_B = 34.2573 \times 10^{-39}$ and $I_C = 39.8170 \times 10^{-39}\ g \cdot cm^2$.

References

[1] JANAF Thermochemical Tables: $AlCl_2(g)$, $AlCl_2^+(g)$, $AlF_2(g)$, $AlF_2^+(g)$ and $AlF_2^-(g)$, 6–30–76; $NO_2^-(g)$, 6–30–72; $SiCl_2(g)$, 12–31–70; $AlCl(g)$, 6–30–70; $Cl^-(g)$, 6–30–65.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1}mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−12.969	−474.211		
100	39.846	235.193	329.316	−9.412			
200	48.255	265.583	290.476	−4.979			
250	50.901	276.654	286.636	−2 496			
298.15	52.650	285.778	285.778	0.	−481.160	−485.169	85.000
300	52.706	286.104	285.779	0.097	−481.209	−485.193	84.480
350	53.953	294.328	286.426	2.766	−482.533	−485.753	72.495
400	54.836	301.593	287.877	5 487	−483.876	−486.122	63.481
450	55.478	308.091	289.768	8.245	−485.236	−486.321	56.451
500	55.957	313.962	291.899	11.032	−486.614	−486.368	50.810
600	56.606	324.227	296.456	16.663	−489.429	−486.055	42.315
700	57 013	332.985	301.064	22.345	−492.345	−485.264	36.211
800	57.283	340.617	305.541	28.061	−495.388	−484.047	31.605
900	57.471	347.376	309.821	33.799	−498.590	−482.439	28.000
1000	57.607	353.438	313.885	39.553	−512.566	−479.704	25.057
1100	57.708	358.934	317.734	45.319	−515.804	−476.261	22.616
1200	57.786	363.958	321.380	51.094	−519.045	−472.524	20.568
1300	57.847	368.586	324.836	56.876	−522.289	−468.515	18.825
1400	57.895	372.875	328.116	62.663	−525.537	−464.257	17.322
1500	57.934	376.871	331.234	68.455	−528.790	−459.767	16.010
1600	57.966	380.611	334.205	74.250	−532.049	−455.059	14.856
1700	57.993	384.126	337.039	80.048	−535.313	−450.147	13.831
1800	58.015	387.441	339.748	85.848	−538.584	−445.043	12.915
1900	58.034	390.578	342.341	91.651	−541.862	−439.757	12.090
2000	58.051	393.556	344.828	97.455	−545.149	−434.298	11.343
2100	58.065	396.388	347.217	103.261	−548.445	−428.674	10.663
2200	58.078	399.090	349.514	109.068	−551.752	−422.893	10.041
2300	58.090	401.672	351.726	114.876	−555.072	−416.962	9.469
2400	58.101	404.144	353.859	120.686	−558.405	−410.886	8.943
2500	58.112	406.516	355.918	126.496	−561.753	−404.670	8.455
2600	58.124	408.796	357.908	132.308	−565.116	−398.321	8.002
2700	58 136	410.990	359.834	138 121	−568.497	−391.841	7.581
2800	58.150	413.104	361.699	143.935	−865.796	−384.269	7.169
2900	58.166	415.145	363.507	149.751	−868.117	−367.030	6.611
3000	58.184	417.117	365.261	155.569	−870.456	−349.712	6.089
3100	58.205	419.025	366.965	161.388	−872.812	−332.315	5.599
3200	58.230	420.874	368.621	167.210	−875.185	−314.842	5.139
3300	58.259	422.666	370.231	173.034	−877.574	−297.294	4.706
3400	58.293	424.406	371.799	178.862	−879.976	−279.674	4.297
3500	58.332	426.096	373.326	184.693	−882.391	−261.982	3.910
3600	58.376	427.740	374.815	190.528	−884.816	−244.222	3.544
3700	58.427	429.340	376.267	196.368	−887.248	−226.394	3.196
3800	58.484	430.899	377.685	202.214	−889.686	−208.501	2.866
3900	58.547	432.419	379.069	208.065	−892.125	−190.543	2.552
4000	58.618	433.902	380.421	213.924	−894.564	−172.523	2.253
4100	58.696	435.350	381.743	219.789	−897.000	−154.441	1.968
4200	58.782	436.766	383.036	225.663	−899 429	−136.301	1.695
4300	58.875	438.150	384.302	231.546	−901.848	−118.103	1.435
4400	58.975	439.505	385.541	237.438	−904.256	−99.848	1.185
4500	59.083	440.831	386.755	243.341	−906.647	−81.539	0.946
4600	59.199	442.131	387.945	249.255	−909.022	−63.177	0.717
4700	59.322	443.405	389.112	255.181	−911.378	−44.764	0.497
4800	59.452	444 656	390.256	261.120	−913.712	−26.301	0.286
4900	59.589	445.883	391.378	267.072	−916 021	−7.789	0.083
5000	59.733	447.088	392.481	273.038	−918.306	10.769	−0.113
5100	59.884	448.273	393.563	279.018	−920.564	29.373	−0.301
5200	60.041	449.437	394.626	285.015	−922.795	48.021	−0.482
5300	60.204	450.582	395.671	291.027	−924.996	66.712	−0.657
5400	60.372	451.709	396.699	297.056	−927.168	85.444	−0.827
5500	60.545	452.818	397.709	303.101	−929.310	104.216	−0.990
5600	60.724	453.911	398.703	309.165	−931.421	123.026	−1.148
5700	60.906	454.987	399.681	315.246	−933.502	141.874	−1.300
5800	61.093	456.048	400 644	321.346	−935.549	160.758	−1.448
5900	61.283	457.094	401.592	327.465	−937.569	179.677	−1.591
6000	61.476	458.126	402.525	333 603	−939.537	198.628	−1.729

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

Aluminum Chloride Fluoride ($AlCl_2F$) IDEAL GAS $M_r = 116.885943$

$S°(298.15\ K) = [311.4 \pm 4]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -788.4 \pm 6\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -790.8 \pm 6\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
[840](1)	[640](1)
[430](1)	[190](1)
[160](1)	[220](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distances: Al–F = [1.63] Å; Al–Cl = [2.06] Å
Bond Angles: Cl–Al–F = [120]°; Cl–Al–Cl = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.841449 \times 10^{-113}]\ g^3\cdot cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -189.0 \pm 1.5\ kcal\cdot mol^{-1}$ and $\Delta_a H° = 341.4 \pm 3\ kcal\cdot mol^{-1}$ based on $\Delta_r H°(298.15\ K) = 0.5 \pm 1\ kcal\cdot mol^{-1}$ for $2/3\ AlCl_3(g) + 1/3\ AlF_3(g) = AlCl_2F(g)$. Krause and Douglas[1] obtained this result by an entrainment method which measured enhanced volatility of AlF_3 in the presence of $AlCl_3$. Corrections were made for all the possible dimers which can form in this system. The entrainment data establish that aluminum fluoride–chloride exchange reactions are almost thermoneutral.

Our adopted $\Delta_f H°$ is compared below with an approximate mass–spectrometric K_p for reaction of AlF_2 with $AlCl_2$.[2] The discrepancy in $\Delta_f H°(AlCl_2F)$ is $-22\ kcal\cdot mol^{-1}$ if we use $\Delta_f H° = -180$ (AlF_2) and -71 ($AlCl_2$) derived from the mass–spectrometric data.[2,3] The discrepancy almost disappears if we use $\Delta_f H° = -166$ (AlF_2) and -67 ($AlCl_2$) derived from average bond energies in AlF_3 and $AlCl_3$.[4] This favors the latter values of $\Delta_f H°$ for AlF_2 and $AlCl_2$,[4] although the discrepancy might arise from the observed ion intensity of $AlCl_2F^+$. The signal from $AlCl_2F^+$ was very weak at 40 eV,[5] this high ionizing energy might bias K_p and cause considerable fragmentation. We can eliminate AlF_2 and $AlCl_2$ by taking the difference between the mass–spectrometric reactions for $AlClF_2$[4] and $AlCl_2F$. This yields $[\Delta_f H°(AlClF_2) - \Delta_f H°(AlCl_2F)] = -47\ kcal\cdot mol^{-1}$ which agrees with $-49.8\ kcal\cdot mol^{-1}$ from entrainment data.[1] Thus, we tentatively ascribe the discrepancy to AlF_2[4] and $AlCl_2$.

Source	Method	Reaction	T/K	kcal·mol^{-1} $\Delta_r H°(T)$	 $\Delta_r H°(298.15\ K)$	 $\Delta_f H°(298.15\ K)$
1	Entrainment	$2/3\ AlCl_3(g) + 1/3\ AlF_3(g) = AlCl_2F(g)$	1196–1257	0.5 ± 1	0.5 ± 1	-189.0
2	Mass Spec.	$AlF_2(g) + AlCl_2(g) = AlF(g) + AlCl_2F(g)$	1491	—	-23.4	-194^a or -211^b

[a] Assuming $\Delta_f H°(298.15\ K) = -166$ (AlF_2) and -67 ($AlCl_2$) kcal·mol^{-1}.
[b] Assuming $\Delta_f H°(298.15\ K) = -180$ (AlF_2) and -71 ($AlCl_2$) kcal·mol^{-1}.

Heat Capacity and Entropy

We adopt a C_{2v} structure with bond angles and bond distances assumed equal to those in AlF_3 and $AlCl_3$.[4] We assume a singlet electronic ground state and neglect excited states. Vibrational frequencies are estimated by comparison of AlF_3 and $AlCl_3$ with the series BF_3, $BClF_2$, BCl_2F and BCl_3.[6,7] The principal moments of inertia are: $I_A = 18.3596 \times 10^{-39}$, $I_B = 37.4744 \times 10^{-39}$ and $I_C = 55.8339 \times 10^{-39}\ g\cdot cm^2$.

References

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Aluminum Chloride Fluoride ($AlCl_2F$) $Al_1Cl_2F_1(g)$

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

T/K	J·K^{-1}mol^{-1} $C_p°$	 $S°$	 $-[G°-H°(T_r)]/T$	kJ·mol^{-1} $H°-H°(T_r)$	 $\Delta_f H°$	 $\Delta_f G°$	log K$_f$
0	0.	0.	INFINITE	−15.747	−788.390	−788.390	INFINITE
100	47.886	247.731	366.958	−11.923	−789.415	−786.070	410.601
200	61.104	285.446	317.475	−6.406	−790.202	−782.405	204.343
250	65.494	299.572	312.518	−3.236	−790.517	−780.418	163.059
298.15	68.804	311.403	311.403	0.	−790.776	−778.449	136.381
300	68.916	311.829	311.404	0.127	−790.785	−778.372	135.527
350	71.562	322.660	312.253	3.642	−791.019	−776.284	115.854
400	73.607	332.355	314.171	7.274	−791.227	−774.165	101.096
450	75.197	341.120	316.686	10.995	−791.418	−772.021	89.614
500	76.446	349.110	319.535	14.788	−791.600	−769.856	80.426
600	78.234	363.218	325.671	22.528	−791.963	−765.473	66.640
700	79.411	375.372	331.923	30.414	−792.373	−761.026	56.788
800	80.220	386.032	338.034	38.398	−792.874	−756.516	49.395
900	80.797	395.515	343.904	46.451	−793.510	−751.934	43.641
1000	81.221	404.051	349.499	54.553	−804.905	−746.513	38.994
1100	81.541	411.808	354.816	62.691	−805.551	−740.643	35.170
1200	81.788	418.914	359.866	70.858	−806.194	−734.714	31.981
1300	81.983	425.469	364.663	79.047	−806.837	−728.731	29.281
1400	82.139	431.550	369.226	87.254	−807.483	−722.698	26.964
1500	82.265	437.222	373.572	95.474	−808.134	−716.620	24.955
1600	82.370	442.534	377.718	103.706	−808.791	−710.497	23.195
1700	82.457	447.531	381.679	111.947	−809.456	−704.334	21.642
1800	82.530	452.246	385.470	120.197	−810.129	−698.131	20.259
1900	82.592	456.710	389.103	128.453	−810.811	−691.890	19.021
2000	82.645	460.948	392.590	136.715	−811.502	−685.613	17.906
2100	82.691	464.981	395.942	144.982	−812.203	−679.302	16.897
2200	82.731	468.829	399.168	153.253	−812.912	−672.956	15.978
2300	82.765	472.507	402.278	161.528	−813.631	−666.579	15.138
2400	82.796	476.030	405.278	169.806	−814.358	−660.170	14.368
2500	82.823	479.411	408.176	178.087	−815.094	−653.730	13.659
2600	82.847	482.659	410.979	186.370	−815.839	−647.261	13.004
2700	82.869	485.787	413.692	194.656	−816.591	−640.762	12.396
2800	82.888	488.801	416.321	202.944	−1111.252	−633.269	11.814
2900	82.905	491.710	418.870	211.234	−1110.923	−616.204	11.099
3000	82.921	494.520	421.345	219.525	−1110.600	−599.150	10.432
3100	82.935	497.240	423.750	227.818	−1110.282	−582.107	9.808
3200	82.948	499.873	426.088	236.112	−1109.967	−565.074	9.224
3300	82.959	502.426	428.363	244.407	−1109.654	−548.051	8.675
3400	82.970	504.902	430.578	252.704	−1109.341	−531.037	8.158
3500	82.980	507.308	432.736	261.001	−1109.027	−514.033	7.672
3600	82.989	509.645	434.840	269.299	−1108.709	−497.037	7.212
3700	82.997	511.919	436.892	277.599	−1108.386	−480.051	6.777
3800	83.005	514.133	438.896	285.899	−1108.056	−463.074	6.365
3900	83.012	516.289	440.853	294.200	−1107.715	−446.105	5.975
4000	83.018	518.391	442.765	302.501	−1107.364	−429.145	5.604
4100	83.024	520.441	444.635	310.803	−1106.998	−412.194	5.251
4200	83.030	522.441	446.464	319.106	−1106.617	−395.252	4.916
4300	83.035	524.395	448.253	327.409	−1106.218	−378.319	4.596
4400	83.040	526.304	450.006	335.713	−1105.801	−361.396	4.290
4500	83.044	528.170	451.722	344.017	−1105.359	−344.483	3.999
4600	83.049	529.996	453.404	352.322	−1104.898	−327.580	3.720
4700	83.053	531.782	455.053	360.627	−1104.413	−310.687	3.453
4800	83.057	533.530	456.669	368.932	−1103.904	−293.804	3.197
4900	83.060	535.243	458.255	377.238	−1103.368	−276.933	2.952
5000	83.063	536.921	459.812	385.544	−1102.807	−260.073	2.717
5100	83.066	538.566	461.340	393.851	−1102.220	−243.223	2.491
5200	83.069	540.179	462.841	402.158	−1101.607	−226.386	2.274
5300	83.072	541.761	464.315	410.465	−1100.967	−209.561	2.065
5400	83.075	543.314	465.764	418.772	−1100.302	−192.748	1.864
5500	83.077	544.838	467.188	427.080	−1099.610	−175.948	1.671
5600	83.080	546.335	468.588	435.388	−1098.894	−159.161	1.485
5700	83.082	547.806	469.965	443.696	−1098.153	−142.387	1.305
5800	83.084	549.251	471.319	452.004	−1097.386	−125.626	1.131
5900	83.086	550.671	472.652	460.312	−1096.599	−108.878	0.964
6000	83.088	552.068	473.964	468.621	−1095.768	−92.146	0.802

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

Aluminum Chloride (AlCl$_3$) CRYSTAL M_r = 133.34054 Aluminum Chloride (AlCl$_3$) Al$_1$Cl$_3$(cr)

$\Delta_f H°(0\ K) = -704.30 \pm 0.84\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 109.29 \pm 0.42\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = -705.63 \pm 0.84\ kJ{\cdot}mol^{-1}$

$T_{fus} = 465.7 \pm 0.2\ K$ $\Delta_{fus}H° = 35.35 \pm 0.84\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation, $\Delta_f H°$(AlCl$_3$, cr, 298.15 K) = −168.65 ± 0.20 kcal·mol^{-1} (−705.632 ± 0.84 kJ·mol^{-1}) is a weighted average of the values of Gross and Hayman[1] and of Coughlin.[3] NBS[4] recommended a value of − 704.2 kJ·mol^{-1} based on data available prior to 1968.

Gross and Hayman[1] measured the enthalpy of direct combination of "spectrographically pure" aluminum and carefully purified chlorine and derived $\Delta_f H°$(298.15 K) = −168.80 ± 0 16 kcal·mol^{-1}. Siemonsen[2] also reported the enthalpy of direct combination and is in agreement at −167.5 kcal·mol^{-1} within his relatively large uncertainty interval of ±1.1 kcal·mol^{-1}. Coughlin[3] determined the enthalpy of solution of 99.99+% pure Al in 4.360 m HCl and also the enthalpy of solution of anhydrous AlCl$_3$ in the same solvent. Enthalpies of mixing were measured to close a thermochemical cycle at 303.15 K (adjusted to 1981 relative atomic masses).

Source	Reaction	$\Delta_r H°$(303.15 K), cal·mol^{-1}
1	Al(cr) + 3H$^+$(sln) = Al^{+++}(sln) + 3/2 H$_2$(g)	−127057 ± 120
2	3(HCl·12.731 H$_2$O)(l) = 3H$^+$(sln) + 3 Cl$^-$(sln) + 38.193 H$_2$O(sln)	0 ± 10
3	AlCl$_3$(cr) = Al^{+++}(sln) + 3 Cl$^-$(sln)	−72504 ± 50
4	38.193 H$_2$O(l) = 38.193 H$_2$O(sln)	−3050 ± 20
5	Al(cr) + 3 (HCl·12.731 H$_2$O)(l) = AlCl$_3$(cr) + 38.193 H$_2$O(l) + 3/2 H$_2$(g)	−51503 ± 140

With auxiliary data from JANAF[12] and CODATA,[5] the enthalpy of reaction (5) at 298.15 K is −51910 ± 140 cal·mol^{-1} AlCl$_3$ Interpolation of data for $\Delta_f H°$(HCl, aq, 298.15 K)[4] yields $\Delta_f H°$(AlCl$_3$, cr, 298.15 K) = −168.32 kcal·mol^{-1}. The overall uncertainty is estimated as 300 cal·mol^{-1}. Semenenko *et al.*[6] also determined the enthalpy of solution of Al in (HCl, 11 13 H$_2$O) and of AlCl$_3$in (HCl, 11.26 H$_2$O). Their results yield a more negative value, $\Delta_f H°$(AlCl$_3$, cr, 298.15 K) = −170 1 ± 0.4 kcal·mol^{-1}. This discrepancy is due both to differences in the solution enthalpies measured for Al and AlCl$_3$. When adjusted to the conditions of Coughlin's experiments, Semenenko's enthalpy of reaction (1) is calculated to be −128.20 kcal·mol^{-1} which deviates more significantly than the values calculated for other authors.[7] Semenenko's enthalpy of solution of AlCl$_3$, recalculated to solution in pure water at 20°C is −77.46 kcal·mol^{-1}, a more positive value than those found for other investigators.[7] The enthalpy of solution of AlCl$_3$ measured by Krivtsov *et al.*[8] and recalculated to these same conditions is −78.66 kcal·mol^{-1}.

Heat Capacity and Entropy

Justice[9] reported low temperature heat capacity data (13 to 310 K) and presented smoothed thermodynamic functions, including $S°$(298.15 K) = 109.29 J·K^{-1}·mol^{-1} of which 0.360 J·K^{-1}·mol^{-1} is extrapolation below 13 K. Enthalpies relative to 273.15 K were measured by Fischer[10] from 298.15 K to 504 K and enthalpies relative to 298.15 K were measured by McDonald[11] from 310 K to 493 K. The enthalpy data for the crystal can be fit within about 2% by integration of $C_p°$(cr) = 64.94 + 0.088 T in J·K^{-1}·mol^{-1}, which is an extrapolation of $C_p°$ data reported by Justice.[9]

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The enthalpy of sublimation is calculated from the enthalpies of formation of the dimer and the crystal for the sublimation process, 2 AlCl$_3$(cr) = Al$_2$Cl$_6$(g), $\Delta_{sub}H°$(298.15 K) = 115.52 ± 2.3 kJ·mol^{-1}. Also refer to the Al$_2$Cl$_6$(g) table for additional comments.

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[12] JANAF Thermochemical Tables: Al(cr), 6–30–79; H$_2$(g), 3–31–77.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0	0.	0.	INFINITE	−16.979	−704.300	−704 300	INFINITE
100	47.112	30 798	180.962	−15.016	−707.189	−681.219	355.832
200	79.203	75.145	117.298	−8.431	−706.962	−655.173	171.114
298.15	91.128	109.286	109.286	0.	−705.632	−630.018	110.377
300	91.295	109.850	109.288	0.169	−705.602	−629.549	109.614
400	100.081	137.318	112.974	9.738	−703.746	−604.464	78.935
465 700	105.854	152.965	117.529	16.503	−−− CRYSTAL <−−> LIQUID −−−		
500	108.868	160.594	120.224	20.185	−701.288	−579.914	60.583
600	117.654	181.219	128.701	31.511	−698.146	−555.922	48.397
700	126.440	200.016	137.565	43.716	−694.297	−532.513	39.737
800	135.227	217.473	146.474	56.799	−689.744	−509.703	33.280
900	144.013	233.908	155.284	70.761	−684.503	−487.506	28.294
1000	152.800	249.536	163.934	85.602	−689.183	−465.168	24.298
1100	161.586	264.511	172.401	101.321	−682.264	−443.094	21.041
1200	170.372	278.948	180.682	117.919	−674.484	−421.689	18.356
1300	179 159	292.932	188.781	135.396	−665.841	−400 967	16.111
1400	187.945	306.531	196.709	153.751	−656.333	−380.943	14.213
1500	196.732	319.797	204.474	172.985	−645.961	−361.629	12.593

PREVIOUS: June 1970 CURRENT: September 1979

Aluminum Chloride ($AlCl_3$) LIQUID M_r = 133.34054 Aluminum Chloride ($AlCl_3$) $Al_1Cl_3(l)$

$S°(298.15\ K) = [172.908]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 465.7 \pm 0.2\ K$

$\Delta_fH°(298.15\ K) = [-674.805]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 35.35 \pm 0.84\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(AlCl_3, l, 298.15\ K)$ is calculated from $\Delta_fH°(AlCl_3, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(465.7\ K)-H°(298.15\ K)$, between the crystal and the liquid.

Heat Capacity and Entropy

Fischer[1] and McDonald[2] measured enthalpy data for the crystal and liquid. In each case, the liquid data extended over a short range of temperature, 473–504 K and 475–493 K, respectively. Their data can be represented within 2% by the heat capacity equation derived for the crystal [see $AlCl_3$(cr) table], a heat of fusion of 35.35 $kJ{\cdot}mol^{-1}$, and a liquid heat capacity of 125.5 $J{\cdot}K^{-1}{\cdot}mol^{-1}$. Fischer's data are high, while McDonald's points lie below the selected values.

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

Fusion Data

Kendall *et al.*[3] observed $AlCl_3$ to melt "sharply" at 463.4 K. Foster[4] noted that $AlCl_3$ began melting and melted completely in the range 465.7 ± 0.2 K. Johnson *et al.*[5], Nisel'son *et al.*,[6] and Ostrikova *et al.*[7] reported melting temperatures of 465.9 ± 0.3 K, 467.2 K, and 466 K, respectively. Smits and Meyering,[8] Treadwell and Terebesi[9] and Viola *et al.*[10] derived triple point temperatures of 465.8 K, 466.5 K, and 466.86 K, respectively, from intersection of vapor pressure curves for crystal and liquid. The value of Foster, $T_{fus} = 465.7 \pm 0.2$ K, is adopted as most accurate. The vapor pressure (monomer and dimer contributions) at the triple point is 2.3 atm. $\Delta_{fus}H°$ is based on enthalpies measured by Fischer[1] and McDonald.[2]

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	125.520	172.908	172.908	0.	−674.805	−618.161	108.299
300	125.520	173.684	172.910	0.232	−674.712	−617.809	107.570
400	125.520	209 794	177.833	12.784	−669.873	−599.581	78.297
465 700	125.520	228.883	183.723	21.031	--- CRYSTAL <--> LIQUID ---		
500	125.520	237.803	187.130	25.336	−665.311	−582.541	60.858
600	125.520	260.688	197.541	37.888	−660.942	−566.400	49.309
700	125.520	280.037	207.979	50.440	−656.746	−550.977	41.114
800	125.520	296.798	218.057	62.992	−652.724	−536.143	35.007
900	125.520	311.582	227.644	75.544	−648.894	−521.803	30.285
1000	125.520	324.807	236.710	88.096	−655.862	−507.118	26.489
1100	125.520	336.770	245.272	100.648	−652.110	−492.425	23.383
1200	125.520	347.692	253.358	113.200	−648.376	−478.074	20.810
1300	125.520	357 739	261.006	125.752	−644.658	−464.032	18.645
1400	125.520	367.041	268.252	138.304	−640.953	−450.277	16.800
1500	125.520	375.701	275.130	150.856	−637.263	−436.786	15.210

PREVIOUS: June 1970 CURRENT. September 1979

Aluminum Chloride ($AlCl_3$)

CRYSTAL–LIQUID

0 to 465.7 K crystal
above 465.7 K liquid

Refer to the individual tables for details.

M_r = 133.34054 Aluminum Chloride ($AlCl_3$) $Al_1Cl_3(cr,l)$

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−16.979	−704.300	−704 300	INFINITE
100	47.112	30.798	180.962	−15.016	−707.189	−681.219	355.832
200	79.203	75.145	117.298	−8.431	−706.962	−655.173	171.114
298.15	91.128	109.286	109.286	0.	−705.632	−630.018	110.377
300	91.295	109.850	109.288	0.169	−705.602	−629.549	109.614
400	100.081	137.318	112.974	9.738	−703.746	−604.464	78.935
465.700	105.854	152.965	117.529	16.503	CRYSTAL <−−> LIQUID		
465.700	125.520	228.883	117.529	51.857	TRANSITION		
500	125.520	237.803	125.478	56.163	−665.311	−582.541	60.858
600	125.520	260.688	146.164	68.715	−660.942	−566.400	49.309
700	125.520	280.037	163.942	81.267	−656.746	−550.977	41.114
800	125.520	296.798	179.525	93.819	−652.724	−536.144	35.007
900	125.520	311.582	193.393	106.371	−648.894	−521.803	30.285
1000	125.520	324.807	205.884	118.923	−655.862	−507.118	26.489
1100	125.520	336.770	217.248	131.475	−652.110	−492.426	23.383
1200	125.520	347.692	227.670	144.027	−648.376	−478 074	20.810
1300	125.520	357.739	237.294	156.579	−644.658	−464 033	18.645
1400	125.520	367.041	246.233	169.131	−640.953	−450.278	16.800
1500	125.520	375.701	254.579	181.683	−637.263	−436.787	15.210

PREVIOUS: CURRENT: September 1979

Aluminum Chloride (AlCl$_3$) IDEAL GAS M_r = 133.34054 Aluminum Chloride (AlCl$_3$) Al$_1$Cl$_3$(g)

$\Delta_a H°$ = 1269.0 ± 3 4 kJ·mol^{-1}
$S°$(298.15 K) = 314.49 ± 2.9 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = −582.85 ± 2.9 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = −584.59 ± 2.9 kJ·mol^{-1}

Vibrational Frequencies and Degeneracies			
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
371(1)	183(1)	610(2)	146(2)

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: D_{3h}
Bond Distance: Al–Cl = 2.06 Å
Bond Angle. Cl–Al–Cl = 120°
Product of the Moments of Inertia: $I_A I_B I_C$ = 1 052528 × 10^{-112} g^3·cm^6

Enthalpy of Formation

The enthalpy of formation is calculated from the value adopted for Al$_2$Cl$_6$(g) and the heat of dissociation of $Al_2Cl_6 \rightarrow 2AlCl_3$ derived from equilibrium *PVT* data on aluminum chloride vapor as listed below.

The four investigations are in reasonable agreement. Giving consideration also to equilibrium data on the reaction of AlCl$_3$(g) and Al(l) *to form AlCl(g) [see AlCl(g) table], there is selected as a best value* $\Delta_r H°$(298.15 K) = 30.25 kcal·mol^{-1} Al$_2$Cl$_6$, which yields $\Delta_f H°$(AlCl$_3$, g, 298.15 K) = −139.72 kcal·mol^{-1} (−584.59 ± 2.9 kJ·mol^{-1}). NBS[15] recommended a value of −139.4 kcal·mol^{-1} (−583.250 kJ·mol^{-1}) for the enthalpy of formation of AlCl$_3$(g) based on data available prior to 1968.

Source	T/K	Data Points	$\Delta_r H°$(298.15 K), kcal·mol^{-1} Al$_2$Cl$_6$ 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
Smits and Meijering[1]	669–816	6	29.45 ± 0.7	30.21 ± 0.2	1.0 ± 0.9
Fischer *et al.*[2]	647–869	17[a]	31.04 ± 0.3	30.42 ± 0.2	−0.8 ± 0.4
Vrieland and Stull[3]	669–825	19[b]	0.27 ± 0.3	30.50 ± 0.2	0.3 ± 0.4
Polyachenok *et al.*[4]	650–1100	2[c]	30.68 ± 0.0	30.03 ± 0.5	−0.7 ± 0.0

[a] Twenty–three points reported, points at 938, 881, 944, 734, 805 and 605 K rejected by statistical test.
[b] Twenty–six points reported, points at 627.9, 643.1, 671.3, 638.4, 671.6, 722.5 and 686.9 K rejected by statistical test.
[c] Individual points not reported, an equation for the equilibrium constant was used to calculate two points at the extremes of temperature.

Heat Capacity and Entropy

The structure of monomeric AlCl$_3$ has been the subject of considerable debate due to conflicting assignments made on the basis of the electron diffraction data of Zasorin and Rambidi[5] and the matrix–isolation IR study by Lesiecki and Shirk.[6] Electron diffraction of the vapor at 800 K yielded an Al–Cl bond length of 2.06 ± 0.01 Å and a Cl–Al–Cl angle of 118 ± 1.5°, which allowing for the possibility of "shrinkage" was taken to indicate a planar equilibrium D_{3h} geometry. The argon matrix spectra obtained by Lesiecki and Shirk[6] showed four infrared–active fundamentals including the symmetric stretch, implying a pyramidal C_{3v} structure, their normal coordinate analysis suggested a Cl–Al–Cl angle near 112°. Hargittai and Hargittai[7] argued, however, that the electron diffraction results for AlCl$_3$ are not compatible with a pyramidal model having an inversion frequency of 183 cm^{-1} and a barrier height equal to 2–3 vibrational quanta. Beattie *et al.*[8] were unable to reproduce the IR frequencies observed by Lesiecki and Shirk[6] in their own matrix isolation studies and it was later concluded that the earlier work by Lesiecki and Shirk was based on incorrect band assignments.[9] The D_{3h} structure is supported by the original electron diffraction work as well as theoretical calculations[10,11] and correlations[9] of the frequencies of AlCl$_3$, AlCl$_2$Br, AlClBr$_2$and AlBr$_3$.

For aluminum chloride vapor at high temperatures (monomer predominant), Klemperer[12] observed the band at 610 cm^{-1} in the IR spectrum and Beattie and Horder[13] reported Raman bands at 371 cm^{-1} and 146 cm^{-1}. The remaining fundamental is that reported by Lesiecki and Shirk;[6,9] a second experimental observation of ν_2 = 174 cm^{-1} was reported by Perov *et al.*[14] *in a xenon matrix along with* ν_1 = 350 cm^{-1}, ν_4 = 142 cm^{-1}. The principal moments of inertia are $I_A = I_B$ = 37.4744 × 10^{-39}, and I_C = 74.9488 × 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	−16.575	−582.852	−582.852	INFINITE
100	51.072	247.272	372.957	−12.568	−583.698	−579.375	302.635
200	64.468	287.225	320.862	−6 728	−584.215	−574.842	150.133
250	68.798	302.100	315.662	−3.390	−584.420	−572.475	119 612
298.15	71.876	314.494	314.494	0.	−584.588	−570.158	99.889
300	71.976	314 939	314.496	0.133	−584.594	−570.069	99.258
350	74.300	326.218	315.381	3 793	−584.748	−567.635	84.715
400	76.014	336.257	317.375	7.553	−584.888	−565.181	73.805
450	77.300	345.288	319.983	11.387	−585.021	−562.710	65.318
500	78.281	353.485	322.930	15.278	−585.152	−560.223	58.526
600	79.643	367.888	329.255	23.179	−585.435	−555.212	48.335
700	80.514	380.235	335.677	31.190	−585.779	−550.149	41.053
800	81.100	391.027	341.936	39.273	−586.227	−545.029	35.587
900	81.513	400.604	347.932	47.405	−586.816	−539.846	31.332
1000	81.813	409.209	353.637	55.572	−598.170	−533.828	27.884
1100	82.038	417.017	359.049	63.765	−598.777	−527.364	25.042
1200	82.211	424.163	364.182	71.978	−599.382	−520.846	22.672
1300	82.346	430 749	369.053	80.206	−599.987	−514.276	20 664
1400	82.454	436.856	373.680	88.446	−600.595	−507 660	18.941
1500	82.542	442.548	378.084	96.696	−601.206	−501.001	17.446
1600	82.614	447.877	382.281	104.954	−601.823	−494.300	16.137
1700	82.674	452.888	386.289	113.218	−602.447	−487.561	14.981
1800	82.724	457.615	390.121	121.488	−603.078	−480.785	13.952
1900	82.767	462.088	393.792	129.763	−603.720	−473.974	13.030
2000	82.803	466.335	397.314	138.041	−604.372	−467.128	12.200
2100	82.835	470.376	400 698	146.323	−605.038	−460.249	11.448
2200	82.862	474.230	403.953	154.608	−605.719	−453.339	10.764
2300	82.886	477.914	407.089	162.896	−606.418	−446.397	10.138
2400	82.907	481.442	410.114	171.185	−607.137	−439.424	9.564
2500	82.925	484.826	413.036	179.477	−607.877	−432.421	9.035
2600	82.942	488.079	415.860	187 770	−608.642	−425.388	8.546
2700	82.956	491.210	418.593	196.065	−609.432	−418.324	8.093
2800	82.970	494.227	421.241	204.362	−904.150	−410.264	7.654
2900	82.981	497.139	423.808	212.659	−903.900	−392.629	7.072
3000	82.992	499.952	426.299	220.958	−903.677	−375.003	6.529
3100	83.002	502.673	428.719	229.258	−903.483	−357.384	6.022
3200	83.010	505.309	431.072	237.558	−903.317	−339.771	5.546
3300	83.018	507.863	433.360	245.860	−903.177	−322.162	5.099
3400	83.026	510.342	435.588	254.162	−903.061	−304.557	4.679
3500	83.032	512.748	437.759	262.465	−902.969	−286.956	4.283
3600	83.038	515.088	439.874	270.768	−902.896	−269.356	3.908
3700	83.044	517.363	441.938	279.072	−902.841	−251.759	3.554
3800	83.049	519.578	443.952	287.377	−902.800	−234.163	3.219
3900	83.054	521.735	445.919	295.682	−902.770	−216.567	2.901
4000	83.058	523.838	447.841	303.988	−902.748	−198.973	2.598
4100	83.063	525.889	449.719	312.294	−902.730	−181.378	2.311
4200	83.066	527.890	451.557	320 600	−902.712	−163.785	2.037
4300	83.070	529.845	453.355	328.907	−902.692	−146.191	1.776
4400	83.073	531.755	455.115	337.214	−902.666	−128.599	1.527
4500	83.076	533.622	456.839	345.522	−902.629	−111.007	1.289
4600	83.079	535.448	458.528	353.829	−902.581	−93.415	1.061
4700	83.082	537.234	460.184	362.138	−902.519	−75.826	0.843
4800	83.085	538.984	461.807	370.446	−902.439	−58.237	0.634
4900	83.087	540.697	463.400	378.754	−902.340	−40.651	0.433
5000	83.089	542.375	464.963	387.063	−902.220	−23.067	0.241
5100	83.091	544.021	466.497	395.372	−902.077	−5.485	0.056
5200	83.093	545.634	468.003	403.682	−901.910	12.093	−0.121
5300	83.095	547.217	469.483	411.991	−901.719	29.669	−0.292
5400	83.097	548.770	470.937	420.301	−901.501	47.240	−0.457
5500	83.099	550.295	472.366	428.610	−901.257	64.808	−0.615
5600	83.100	551.792	473.771	436.920	−900.987	82.370	−0.768
5700	83.102	553.263	475.153	445.230	−900.690	99.927	−0.916
5800	83.103	554.709	476.512	453.541	−900.363	117.479	−1.058
5900	83.105	556 129	477.849	461.851	−900.014	135.025	−1.195
6000	83.106	557.526	479.166	470.162	−899.616	152.562	−1.328

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

Potassium Tetrachloroaluminate ($KAlCl_4$) CRYSTAL $M_r = 207.89184$ Potassium Tetrachloroaluminate ($KAlCl_4$) $Al_1Cl_4K_1(cr)$

$S°(298.15\ K) = [196.6 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$

$T_{fus} = 529\ K$

$\Delta_f H°(0\ K) =$ Unknown

$\Delta_f H°(298.15\ K) = -1196.6 \pm 10\ kJ \cdot mol^{-1}$

$\Delta_{fus} H° =$ Unknown

Enthalpy of Formation

The enthalpy of reaction of aluminum chloride and potassium chloride was measured by Baud.[1] From $\Delta_r H° = -26.38\ kcal \cdot mol^{-1}$ for the reaction: $Al_2Cl_6(cr) + 2\ KCl(cr) = 2\ KAlCl_4(cr)$, the value of $\Delta_f H°(KAlCl_4, cr, 298.15\ K)$ is calculated to be $-286\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Heat capacities are estimated by comparison with those for $KMgCl_3(cr)$ reported by Kelley.[5] $S°(298.15\ K) = 47 \pm 2\ cal \cdot K^{-1} \cdot mol^{-1}$ is estimated according to the methods suggested by Kubaschewski and Evans[2] and Kelley.[3]

References

[1] E. Baud, Ann. chim. phys. **1**, 8 (1904).

[2] O. Kubaschewski and E. Ll. Evans, Metallurgical Thermochemistry, Pergamon Press, 426 pp. (1958).

[3] K. K. Kelley, U. S. Bur. Mines, personal communication, (June, 1960).

[4] W. Fischer and A.–L. Simon, Z. anorg. allgem. Chem. **306**, 1 (1960).

[5] 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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
0							
100							
200							
250							
298.15	156.482	196.648	196 648	0.	−1196.624	−1094.521	191.755
300	156.649	197.616	196.651	0.290	−1196.559	−1093.887	190.463
400	165.477	243.891	202.901	16.396	−1195.380	−1059.743	138.388
500	174.305	281.763	214.994	33.385	−1191.274	−1026.295	107.216
600	183.176	314.346	228.897	51.269	−1186.429	−993.742	86.513
700	190.790	343.177	243.203	69.982	−1180.903	−962.056	71.789
800	196.648	369.064	257.345	89.375	−1174.867	−931.199	60.801
900	199.995	392.431	271.078	109.218	−1168.589	−901.117	52.299
1000	202.087	413.622	284 290	129.332	−1172.876	−870.976	45.495

PREVIOUS. June 1962 CURRENT: June 1963

Sodium Tetrachloroaluminate ($NaAlCl_4$) CRYSTAL $M_r = 191.78331$

$S°(298.15\ K) = [188.3 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$

$T_{fus} = 424\ K$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -1142.2 \pm 4\ kJ \cdot mol^{-1}$

$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

$\Delta_f H°(NaAlCl_4$, cr, 298.15 K) is calculated from $\Delta_r H° = -11.9\ kcal \cdot mol^{-1}$ for the reaction $Al_2Cl_6(cr) + 2\ NaCl(cr) = 2\ NaAlCl_4(cr)$, as measured by Baud.[1]

Heat Capacity and Entropy

Heat capacities are estimated by comparison with those of $KAlCl_4$(cr). $S°(298.15\ K) = 45 \pm 2\ cal \cdot K^{-1} \cdot mol^{-1}$ is estimated according to the methods suggested by Kubaschewski and Evans[2] and Kelley.[3]

Fusion Data

T_{fus} was reported by Fischer and Simon.[4]

References

[1] E. Baud, Ann chim. phys. **1**, 8 (1904).

[2] O. Kubaschewski and E. Ll. Evans, 'Metallurgical Thermochemistry', Pergamon Press, 426 pp. (1958).

[3] K. K. Kelley, U. S Bur. Mines, personal communication, (June, 1960).

[4] W. Fischer and A.–L. Simon, Z. anorg. allgem. Chem. **306**, 1 (1960).

Sodium Tetrachloroaluminate ($NaAlCl_4$) $Al_1Cl_4Na_1(cr)$

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298 15	154 975	188.280	188.280	.000	−1142.232	−1041.574	182 479
300	154.808	189.238	188.283	.287	−1142.168	−1040.950	181.245
400	164.808	235.161	194 477	16.274	−1141.251	−1007.533	131.570
500	174.054	272.947	206.498	33.224	−1137.177	−974.559	101.811
600	182.422	305.445	220.342	51.062	−1132.355	−942 476	82.050
700	189.117	334.098	234.587	69.658	−1126.902	−911.253	67.999
800	193.510	359.645	248.652	88 795	−1121.055	−880.842	57.513
900	197.276	382.673	262.285	108.350	−1114.969	−851.179	49.401
1000	199.158	403.572	275.385	128.187	−1119.408	−821.440	42.908

PREVIOUS CURRENT June 1963

Sodium Tetrachloroaluminate ($NaAlCl_4$) $Al_1Cl_4Na_1(cr)$

Potassium Hexachloroaluminate (K_3AlCl_6) CRYSTAL $M_r = 356.99444$ Potassium Hexachloroaluminate (K_3AlCl_6) $Al_1Cl_6K_3(cr)$

$S°(298.15\ K) = [376.6 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = [800 \pm 20]\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -2092 \pm 4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

$\Delta_f H°(K_3AlCl_6$, cr, 298.15 K) is recalculated from the same quantity given by Rossini *et al.*[1] The latter value was derived from the enthalpy change for the reaction $Al_2Cl_6(cr) + 6\ KCl(cr) = 2\ K_3AlCl_6(cr)$, as measured by Baud.[2]

Heat Capacity and Entropy

Heat capacities are estimated by comparison with the corresponding values of the sum of the constituent halides for $K_3AlCl_6(cr)$. In a similar manner, $S°(298.15\ K)$ is estimated to be $90 \pm 2\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

T_{fus} is estimated by comparison with that for $K_3AlF_6(cr)$.

References

[1] U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
[2] E. Baud, Ann. chem. phys. 1, 8 (1904).

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	248.906	376.560	376.560	0.	−2092.000	−1938.463	339.611
300	249.283	378.101	376.565	0.461	−2091.936	−1937.511	337.351
400	259.157	451.152	386.458	25.878	−2095.873	−1885.176	246.179
500	269.659	510.122	405.474	52.324	−2092.096	−1832.919	191.484
600	279.491	560.178	427.189	79.794	−2087.377	−1781.512	155.094
700	287.859	603.896	449.375	108.165	−2081.856	−1730.961	129.166
800	295.809	642.863	471.168	137.355	−2075.676	−1681.247	109.774
900	302.880	678.124	492.235	167.300	−2068.982	−1632.341	94.739
1000	308.779	710.343	512.458	197.885	−2072.560	−1583.440	82.710
1100	314.532	740.048	531.815	229.056	−2301.871	−1521.060	72.229
1200	319.658	767.640	550.331	260.771	−2290.853	−1450.560	63.141
1300	324.103	793.405	568.049	292.963	−2279.389	−1380.998	55.489
1400	328.026	817.571	585.018	325.574	−2267.536	−1312.333	48.964
1500	331.320	840.316	601.287	358.544	−2255.353	−1244.528	43.338
1600	334.302	861.796	616.904	391.827	−2242.885	−1177.544	38.443
1700	336.969	882.145	631.913	425.394	−2230.167	−1111.349	34.148
1800	339.322	901.473	646.356	459.211	−2217.233	−1045.908	30.351
1900	341.362	919.876	660.272	493.248	−2204.120	−981.191	26.975
2000	343.088	937.430	673.694	527.473	−2190.865	−917.169	23.954

PREVIOUS: June 1962 CURRENT: September 1963

Sodium Hexachloroaluminate (Na_3AlCl_6) CRYSTAL $M_r = 308.66885$

$\Delta_f H°(0\ K)$ = Unknown
$S°(298.15\ K) = [347.3 \pm 8]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = -1979 \pm 4\ kJ{\cdot}mol^{-1}$
$T_{fus} = [780 \pm 20]\ K$ $\Delta_{fus}H°$ = Unknown

Enthalpy of Formation

$\Delta_f H°(Na_3AlCl_6$, cr, 298.15 K) is recalculated from the same quantity given by Rossini *et al.*[1] The latter value was derived from the enthalpy change for the reaction $Al_2Cl_6(cr) + 6\ NaCl(cr) = 2\ Na_3AlCl_6(cr)$, as measured by Baud.[2]

Heat Capacity and Entropy

Heat capacities are estimated by comparison with the corresponding values of the sum of the constituent halides for Na_3AlF_6(cr). In a similar manner, $S°(298.15\ K)$ is estimated to be $83 \pm 2\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

Fusion Data

T_{fus} is estimated by comparison with that for Na_3AlF_6(cr).

References

[1] U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
[2] E. Baud, Ann. chim. phys. 1, 8 (1904).

Sodium Hexachloroaluminate (Na_3AlCl_6) $Al_1Cl_6Na_3(cr)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	244.136	347.272	347.272	0.	−1979.032	−1828.584	320.360
300	244.513	348.783	347.277	0.452	−1978.970	−1827.651	318.222
400	254.387	420.484	356.986	25.399	−1983.806	−1777.071	232.062
500	264.010	478.294	375.646	51.324	−1980.531	−1725.747	180.288
600	273.006	527.237	396.933	78.182	−1976.354	−1675.168	145.836
700	281.165	569.941	418.662	105.896	−1971.360	−1625.355	121.286
800	288.696	607.991	439.992	134.399	−1965.663	−1576.307	102.922
900	294.972	642.363	460.599	163.588	−1959.438	−1528.007	88.683
1000	300.620	673.738	480.367	193.372	−1963.442	−1479.661	77.290
1100	305.720	702.633	499.277	223.692	−1956.272	−1431.627	67.982
1200	310.453	729.439	517.353	254.503	−2239.053	−1376.941	59.937
1300	314.741	754.459	534.640	285.765	−2228.519	−1305.523	52.457
1400	318.821	777.935	551.189	317.445	−2217.595	−1234.930	46.076
1500	322.796	800.069	567.050	349.529	−2206.295	−1165.132	40.574
1600	326.352	821.018	582.274	381.990	−2194.644	−1096.100	35.784
1700	329.385	840.895	596.907	414.778	−2182.693	−1027.805	31.581
1800	332.210	859.803	610.992	447.860	−2170.477	−960.222	27.865
1900	334.825	877.835	624.565	481.213	−2158.018	−893.324	24.559
2000	337.230	895.072	637.663	514.818	−2145.341	−827.088	21.601

PREVIOUS: CURRENT September 1963

Aluminum Fluoride (AlF) IDEAL GAS $M_r = 45.979943$ **Aluminum Fluoride (AlF)** $Al_1F_1(g)$

$\Delta_fH°(0\ K) = -265.623 \pm 3.35\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 215.16 \pm 0.04\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = -265.684 \pm 3.35\ kJ{\cdot}mol^{-1}$

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

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^1\Sigma^+$	0.0	1	802.26	4.77	0.5525	0.00495	1.6544
$a^3\Pi$	27254.	6	830.30	4.60	0.55718	0.00468	1.6474
$A^1\Pi$	43949.7	2	803.94	5.99	0.55640	0.00534	1.6485
$b^3\Sigma^+$	44804.5	3	786.37	7.64	0.56280	0.00651	1.6391
$B^1\Sigma^+$	54282.5	1	866.60	7.45	0.57968	0.00560	1.6151
$c^3\Sigma^+$	55023.4	3	938.22	4.81	0.58992	0.00458	1.6010
$C^1\Sigma^+$	57755.9	1	938.22	5.09	0.58992	0.00458	1.6010

Enthalpy of Formation

We adopt $\Delta_fH°(298.15\ K) = -63.5 \pm 0.8\ kcal{\cdot}mol^{-1}$ ($-265\,684 \pm 3.35\ kJ{\cdot}mol^{-1}$) and $D_0° = 160.0 \pm 1.5\ kcal{\cdot}mol^{-1}$ ($669.440 \pm 6.3\ kJ{\cdot}mol^{-1}$) based on our analysis of numerous equilibrium data.[1-12] We only tabulate our analysis of three studies, the other analyses are essentially those which were reported earlier.[22] However, the previously calculated $D_0°$ values will differ due to a more current heat of formation for Al(g). Greatest weight is given to torsion effusion[2] and transport[5,12] data for the Al–AlF_3 system. Hildenbrand *et al.*[2] found that orifice area affected the torsion–effusion pressures of AlF from reaction A. They derived equilibrium pressures from a semi–empirical correlation of data for the four cells listed below. Mass–spectrometric studies[9] of the Al–AlF system near 950 K indicated that the vapor consists of AlF with a small amount of AlF. The adopted $D_0° = 669\,440 \pm 6.3\ kJ{\cdot}mol^{-1}$ is consistent with $D_0° > 665.6\ kJ{\cdot}mol^{-1}$ derived from the highest observed level in $A^1\Pi$.[14] The potential energy curve of this excited state may have a maximum.[14, 15]

Source	Method	Reaction[a]	T/K	Data Points	δS cal·K^{-1}·mol^{-1}	$\Delta_rH°$(298.15 K), kcal·mol^{-1} 2nd Law	3rd Law	$\Delta_fH°(_{298.15}\ K)$	$D_0°$ kcal·mol^{-1}
Hildenbrand (1963)	torsion eff.[b]								
Cell 7	$P=1.30P_t$	A	882–931	8	-2.7 ± 2.1	54.1 ± 2.0	56.60 ± 0.2	-63.73 ± 0.8	160.3
Cell 9	$P=1.72P_t$	A	856–932	8	$0 4 \pm 1.5$	57.3 ± 1.4	56.91 ± 0.2	-63.42 ± 0.8	160.0
Cell 15X	$P=2.07P_t$	A	866–931	8	1.0 ± 0.6	57.8 ± 0.5	56.85 ± 0.1	-63.48 ± 0.8	160.1
Cell 16X	$P=3.13P_t$	A	867–929	7[c]	0.5 ± 1.4	57.2 ± 1.3	56.79 ± 0.1	-63.54 ± 0.8	160.1
Semenkovitch (1960)	transport	B	1170–1373	5	-0.2 ± 0.2	55.3 ± 0.3	55.56 ± 0.1	-63.40 ± 0.8	160.0
Hildenbrand (1981)	torsion eff.[b]								
Cell G7S	$P=1.12P_t$	A	863–930	13	-1.0 ± 0.2	58.25 ± 0.21	57.37 ± 0.05	-62.96 ± 0.8	160.1
Cell G5Z	$P=1.31P_t$	A	839–928	6	-2.4 ± 0.2	57.61 ± 0.16	57.22 ± 0.04	-63.11 ± 0.8	159.7
Cell G6Z	$P=1.65P_t$	A	835–929	13	-0.4 ± 0.1	57.68 ± 0.07	57.25 ± 0.04	-63.08 ± 0.8	159.7
Cell G7L	$P=2.10P_t$	A	840–930	13	-1.0 ± 0.2	58.20 ± 0.19	57.31 ± 0.08	-63.02 ± 0.8	159.6

[a] Reactions: A: 1/3 AlF_3(cr) + 2/3 Al(cr) = AlF(g); B: 1/3 AlF_3(cr) + 2/3 Al(l) = AlF(g);

[b] P = equilibrium pressure and P_t = torsion pressure. [c] One point rejected.

Heat Capacity and Entropy

Electronic levels and molecular constants are based on the detailed analysis of electronic spectra published by Barrow, Kapp and Malmberg[16] and a follow–up to this investigation published by Kapp and coworkers.[20] Constants for the ground state are confirmed by microwave spectra.[11 17 18] The triplet–singlet separation, a^3–$X^1\Sigma^+$, calculated by Barrow *et al.*[16] is in excellent agreement with the results from the low resolution chemiluminiscence work of Rosenwaks *et al.*[21] We omit electronic states between 60000 and 68000 cm^{-1} including nine observed levels and one predicted level,[16] these would have negligible effects on the thermodynamic functions The analysis of Barrow *et al.*[16] is supported by theoretical calculations.[20,21]

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$ (kJ·mol^{-1})	$\Delta_fG°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.891	−265.623	−265.623	INFINITE
100	29.121	182.450	242.280	−5.983	−264.653	−273.680	142.956
200	30.034	202.816	218.015	−3.040	−264.976	−282.645	73.819
298.15	31.932	215.157	215.157	0.	−265.684	−291.172	51.012
300	31.967	215.354	215.157	0.059	−265.699	−291.330	50.725
400	33.602	224.787	216.432	3.342	−266.534	−299.750	39.143
500	34.734	232.415	218.890	6.763	−267.429	−307.952	32.171
600	35.502	238.820	221.692	10.277	−268.387	−315.967	27.507
700	36.037	244.335	224.542	13.855	−269.431	−323.816	24.163
800	36.423	249.174	227.325	17.479	−270.593	−331.508	21.645
900	36.712	253.481	229.996	21.137	−271.904	−339.045	19.678
1000	36.937	257.362	232.542	24.819	−283.981	−345.667	18.056
1100	37.117	260.891	234.961	28.522	−285.313	−351.771	16.704
1200	37.265	264.127	237.259	32.242	−286.642	−357.754	15.573
1300	37.390	267.115	239.442	35.975	−287.969	−363.627	14.611
1400	37.499	269.890	241.519	39.719	−289.295	−369.397	13.782
1500	37.594	272.480	243.498	43.474	−290.620	−375.072	13.061
1600	37.679	274.909	245.386	47.238	−291.946	−380.659	12.427
1700	37.757	277.196	247.190	51.010	−293.272	−386.163	11.865
1800	37.828	279.356	248.918	54.789	−294.598	−391.589	11.364
1900	37.894	281.403	250.574	58.575	−295.922	−396.941	10.913
2000	37.957	283.348	252.165	62.368	−297.245	−402.224	10.505
2100	38.016	285.202	253.694	66.166	−298.565	−407.440	10.135
2200	38.073	286.972	255.167	69.971	−299.881	−412.594	9.796
2300	38.127	288.665	256.587	73.781	−301.190	−417.688	9.486
2400	38.180	290.289	257.957	77.596	−302.491	−422.725	9.200
2500	38.232	291.849	259.282	81.417	−303.783	−427.708	8.936
2600	38.282	293.349	260.564	85.242	−305.063	−432.640	8.692
2700	38.332	294.795	261.805	89.073	−306.331	−437.522	8.464
2800	38.382	296.190	263.008	92.909	−601.485	−441.391	8.234
2900	38.432	297.538	264.176	96.750	−601.627	−435.670	7.847
3000	38.483	298.841	265.310	100.595	−601.751	−429.945	7.486
3100	38.535	300.104	266.412	104.446	−601.858	−424.217	7.148
3200	38.589	301.328	267.484	108.303	−601.945	−418.485	6.831
3300	38.645	302.517	268.527	112.164	−602.011	−412.751	6.533
3400	38.704	303.671	269.544	116.032	−602.057	−407.015	6.253
3500	38.767	304.794	270.535	119.905	−602.081	−401.278	5.989
3600	38.833	305.887	271.502	123.785	−602.083	−395.541	5.739
3700	38.904	306.952	272.446	127.672	−602.063	−389.804	5.503
3800	38.979	307.990	273.368	131.566	−602.019	−384.067	5.279
3900	39.061	309.004	274.269	135.468	−601.953	−378.333	5.067
4000	39.148	309.994	275.149	139.378	−601.863	−372.600	4.866
4100	39.242	310.962	276.011	143.298	−601.749	−366.870	4 674
4200	39.344	311.909	276.855	147.227	−601.612	−361.142	4.491
4300	39.453	312.836	277.681	151.167	−601.451	−355.419	4.317
4400	39.570	313.744	278.490	155.118	−601.267	−349.699	4.151
4500	39.695	314.635	279.283	159.081	−601.056	−343.984	3.993
4600	39.829	315.509	280.061	163.057	−600.824	−338.274	3.841
4700	39.972	316.367	280.825	167.047	−600.569	−332.569	3.696
4800	40.125	317.210	281.574	171.052	−600.290	−326.870	3.557
4900	40.286	318.039	282.310	175.072	−599.987	−321.177	3.424
5000	40.458	318.854	283.032	179.110	−599.663	−315.490	3.296
5100	40.638	319.657	283.743	183.164	−599.316	−309.810	3.173
5200	40.829	320.448	284.441	187.238	−598.947	−304.137	3.055
5300	41.029	321.228	285.128	191.330	−598.556	−298.471	2.942
5400	41.239	321.997	285.803	195.444	−598.145	−292.813	2.832
5500	41.458	322.755	286.468	199.578	−597.712	−287.163	2.727
5600	41.687	323.504	287.123	203.736	−597.260	−281.521	2.626
5700	41.925	324.244	287.768	207.916	−596.788	−275.887	2.528
5800	42.171	324.976	288.403	212.121	−596.294	−270.262	2.434
5900	42.427	325.699	289.029	216.351	−595.784	−264.644	2.343
6000	42.691	326.414	289.646	220.607	−595.234	−259.039	2.255

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

Aluminum Fluoride, Ion (AlF^+) IDEAL GAS $M_r = 45.979394$ Aluminum Fluoride, Ion (AlF^+_1) $Al_1F^+_1(g)$

$S°(298.15 \text{ K}) = [220.07 \pm 0.9] \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_fH (0 \text{ K}) = 686.0 \pm 24 \text{ kJ·mol}^{-1}$
$\Delta_fH°(298.15 \text{ K}) = [692.034] \text{ kJ·mol}^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^2\Sigma^+]$	0	[2]
$[^2\Pi]$	[5000]	[4]
$[^2\Sigma^+]$	[20000]	[2]
$[^2\Pi]$	[33000]	[4]

$\omega_e = [925]$ cm^{-1} $\omega_ex_e = [5.5]$ cm^{-1} $\sigma = 1$
$B_e = [0.587]$ cm^{-1} $\alpha_e = [0.005]$ cm^{-1} $r_e = [1.605]$ Å

Enthalpy of Formation

We adopt $\Delta_fH° = 164 \pm 6$ kcal·mol^{-1} based on IP(AlF) = 9.86 ± 0.25 eV (227.5 ± 6 kcal·mol^{-1}). Barrow, Kopp and Malmberg[1] used the observed data for BF to predict that, to a good approximation, IP(AlF) = $T°$(AlF, 3d) + IP(Al, 3d). This gave IP(AlF) = 79335 cm^{-1} (9.84 eV) which the authors[1] rounded to 80000 cm^{-1} (9 92 eV). We adopt an intermediate value corresponding to $\Delta_fH° = 164$ kcal·mol^{-1}. This yields $D_0° = 70 \pm 6$ kcal·mol^{-1} for $AlF^+(g) \rightarrow Al^+(g) + F(g)$.

IP(AlF) = 9.86 ± 0 25 eV is consistent with electron impact data which gave the following values for the appearance potential of AlF+ from AlF. 8.9 ± 0.6,[2] 9.0 ± 1,[3] 9.2,[4] 9.5 ± 0.5,[5] 9 to 10,[6] 9.7 ± 0.3,[7] 9.7 ± 0 5,[8] 9.9 ± 0.3,[8] and 10.1 ± 0.3 eV.[8]

Heat Capacity and Entropy

We assume the ground–state configuration to be the same as observed for BF^+[9] and the isoelectronic molecules AlO and AlF.[10] Theoretical calculations for $AlCl^+$[11] predict the same ground state, they also suggest that the $^2\Pi$ excited state is either repulsive or has a shallow potential minimum at a much longer bond length. We assume the $^2\Pi$ state in AlF^+ to be nonrepulsive and estimate excited state levels equal to those in AlO.[10] Comparison with $AlCl^+$ suggests that $^2\Pi$ should be in the range 5000–15000 cm^{-1}. Our thermodynamic functions would be upper–limit values if the $^2\Pi$ state were repulsive.

Bonding in Group III monohalides and their ions was characterized by Berkowitz and Dehmer[11] from photoelectron spectra and theoretical calculations. They concluded that ionization removes an electron from an antibonding orbital centered mainly on the metal This shortens the bond length and enhances the ionic nature of the bond. A decrease in bond length is observed for BF^+[9] and predicted by theroretical calculations for $AlCl^+$.[11, 10] By analogy with BF^+ and BF,[9] we expect AlF^+ to have vibrational and rotational constants similar to those of the Rydberg excited states of AlF.[1, 10] Our adopted constants are approximate avarages from the Rydberg states. The adopted bond length is 0.05 Å shorter than in ground state AlF; a similar difference is observed for BF^+.

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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	−8.813	685.976		
100	29.110	187.705	246.750	−5.905			
200	29.620	207.970	222.861	−2.978			
250	30.336	214.653	220.573	−1.480			
298.15	31.155	220.065	220.065	0.	692.034	658.828	−115.424
300	31.187	220.258	220.066	0.058	692.056	658.621	−114.676
350	32.031	225.129	220.448	1.638	692.646	653.002	−97.455
400	32.797	229.458	221.309	3.259	693.219	647.299	−84.529
450	33.463	233.360	222.435	4.916	693.778	641.526	−74.466
500	34 030	236.916	223.708	6.604	694.326	635.690	−66.410
600	34.924	243.204	226.447	10.054	695.383	623.863	−54.312
700	35.599	248.640	229.238	13.582	696.365	611.864	−45.658
800	36.167	253.431	231.968	17.170	697.247	599.731	−39.158
900	36.705	257.722	234.595	20.814	698.001	587.495	−34.097
1000	37.260	261.618	237.106	24.512	688.017	575.942	−30.084
1100	37.850	265.196	239.499	28.267	688.816	564.696	−26.815
1200	38.476	268.516	241.780	32.083	689.663	553.376	−24.088
1300	39.127	271.622	243.958	35.963	690.562	541.982	−21.777
1400	39.785	274.545	246.039	39.909	691.516	530.518	−19.794
1500	40.434	277.313	248.033	43.920	692.525	518.983	−18.073
1600	41.055	279.942	249.945	47.995	693.589	507.379	−16.564
1700	41.637	282.449	251.784	52.130	694.705	495.707	−15.231
1800	42.169	284.844	253.555	56.320	695.869	483.968	−14.044
1900	42.644	287 137	255.262	60.561	697.078	472.163	−12.981
2000	43.060	289.335	256.912	64.847	698.326	460.293	−12.022
2100	43.417	291.445	258.506	69.171	699.611	448.360	−11.152
2200	43.715	293.472	260.050	73.529	700.927	436.365	−10.361
2300	43.958	295.420	261.545	77.913	702.270	424.310	−9.636
2400	44.150	297.296	262.996	82.318	703.638	412.195	−8.971
2500	44.297	299 101	264.405	86.741	705.027	400.023	−8.358
2600	44.402	300.840	265.773	91.176	706.434	387.795	−7.791
2700	44 471	302.518	267.103	95.620	707.859	375.513	−7.265
2800	44.509	304.136	268.397	100.070	415.397	364.146	−6.793
2900	44.521	305.698	269.656	104.521	417.945	362.270	−6.525
3000	44.511	307.207	270.883	108.973	420.505	360.307	−6.273
3100	44.483	308.666	272.078	113.423	423.076	358.258	−6.037
3200	44.441	310.078	273.244	117.869	425.658	356.126	−5.813
3300	44.387	311.445	274.381	122.311	428.249	353.913	−5 602
3400	44.324	312.769	275.490	126.746	430.850	351.621	−5.402
3500	44.255	314.053	276.574	131.175	433.460	349.253	−5.212
3600	44.181	315.298	277.632	135.597	436.078	346.810	−5.032
3700	44.105	316.508	278.667	140.011	438.705	344.294	−4.861
3800	44.028	317.683	279.678	144.418	441.340	341.707	−4.697
3900	43.951	318.826	280.667	148.817	443.982	339.051	−4.541
4000	43.875	319.937	281.635	153.208	446 632	336.327	−4.392
4100	43.801	321.020	282.583	157.592	449.288	333.536	−4.249
4200	43.729	322.074	283.511	161.969	451.951	330.681	−4.113
4300	43.661	323.103	284.419	166.338	454.620	327.762	−3.982
4400	43.596	324.106	285.310	170.701	457.295	324.781	−3.856
4500	43.535	325.085	286.183	175.057	459.978	321.739	−3 735
4600	43.478	326.041	287.039	179.408	462.663	318.637	−3.618
4700	43.425	326.975	287.879	183.753	465.352	315.477	−3.506
4800	43.376	327.889	288.703	188.093	468.044	312.260	−3.398
4900	43.332	328.783	289.512	192.429	470.741	308.986	−3.294
5000	43.292	329.658	290.306	196.760	473.438	305.658	−3 193
5100	43.256	330.515	291.086	201.087	476.136	302.276	−3.096
5200	43.225	331.355	291.852	205.411	478.834	298.840	−3.002
5300	43 197	332.178	292.606	209.732	481.532	295.353	−2.911
5400	43.174	332.985	293.346	214.051	484.227	291.815	−2.823
5500	43.155	333.777	294.074	218.367	486.920	288.227	−2.737
5600	43.139	334.554	294.790	222.682	489.609	284.590	−2.655
5700	43.128	335.318	295.494	226.995	492.292	280.905	−2.574
5800	43.119	336 068	296.187	231.307	494.972	277.173	−2.496
5900	43.115	336 805	296.869	235.619	497.642	273.395	−2.420
6000	43.113	337.529	297.541	239.930	500.326	269.570	−2.347

PREVIOUS: *June 1976 (1 atm)* CURRENT. June 1976 (1 bar)

Aluminum Fluoride, Ion (AlF^+_1) $Al_1F^+_1(g)$

Aluminum Fluoride Oxide (OAlF) IDEAL GAS $M_r = 61.979343$ Aluminum Fluoride Oxide (OAlF) $Al_1F_1O_1(g)$

$\Delta_fH°(0\ K) = -579 \pm 16$ or 28 kJ·mol^{-1}

$S°(298.15\ K) = [237.3 \pm 4$ or $16]$ J·K^{-1}·mol^{-1} $\Delta_fH°(298.15\ K) = -582 \pm 16$ or 28 kJ·mol^{-1}

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[675](1)	386 (2)	1022(1)

Ground State Quantum Weight: [1] σ = 1
Point Group: [$C_{\infty v}$]
Bond Distances: O–Al = [1.61] Å; Al–F = [1.63] Å
Bond Angle: O–Al–F = [180]°
Rotational Constant: B_0 = [0.184214] cm^{-1}

Enthalpy of Formation

We adopt $\Delta_fH°(298.15\ K) = -139 \pm 4$ kcal·mol^{-1} and $\Delta_aH° = 293.2 \pm 4$ kcal·mol^{-1}, derived from effusion data for reaction A.[1] This reaction is analyzed along with limited equilibrium data for three other reactions. The latter are in satisfactory agreement with reaction A. Dissociation energies calculated from our adopted values[5] are 13.9 kcal·mol^{-1} larger than those of the corresponding diatomic molecules; i.e., $\Delta_aH°$ (FAl–O) = 133.9 ± 4, $\Delta_aH°$(OAl–F) = 173.2 ± 4, or $\Delta_rH°$ = 13.9 ± 5 kcal·mol^{-1} for the reaction OAlF(g) + Al(g) = AlF(g) + AlO(g). These values suggest that O=Al–F has enhanced stability, consistent with the observation of this reaction[4] by mass-spectrometric sampling of flames containing aluminum species. We assign $\Delta_fH°$ the alternative uncertainty of ±7 kcal·mol^{-1} in case OAlF is nonlinear. Farber and Srivastava[4] emphasized that $\Delta_fH°$ is much too negative to be compatible with the alternative arrangement Al–O–F.

Source	Method	Reaction[a]	T/K	Data Points	δS cal·K^{-1}·mol^{-1}	$\Delta_rH°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	$\Delta_fH°$(298.15 K) kcal·mol^{-1}
1	Reaction effus.	A	2203–2228[b]	8	−22 ± 26	43 ± 25	91.0 ± 1.6	−138.9 ± 3
2,3	Mass spec.[c]	B	1540–1923	8	—	107.1 ± 3.2	—	−143.6 ± 7
4	Flame mass spec.	C	2250	1	—	—	−10.2	−135.3 ± 6
	Flame mass spec.	D	2250	1	—	—	−11.7	−133.0 ± 6

[a] Reactions:
A: 1/3 $AlF_3(g)$ + 1/3 $Al_2O_3(\alpha)$ = OAlF(g)
B AlF(g) + $Al_2O(g)$ = OAlF(g) + 2 Al(g)
C: AlF(g) + AlO(g) = OAlF(g) + Al(g)
D: AlF(g) + $H_2O(g)$ = OAlF(g) + $H_2(g)$

[b] *T* converted to IPTS–68 assuming published values to be IPTS–48.

[c] Analysis based on relative ion intensities corrected [3] as follows I(OAlF) = 66 at 1773 K and I(AlF) = 120 at 1923 K. Values of K_p were not measured, thus precluding third law analysis.

Heat Capacity and Entropy

Snelson[6] observed infrared spectra of OAlF, OBF, OBCl and OBBr isolated in inert gas matrices. He proposed linear structures for OBCl and OBBr based on agreement of observed and calculated shifts in isotopic frequencies. Isotopic shifts for OBF were consistent with linearity but were less conclusive. Lacking isotopic data, Snelson[6] assumed OAlF to be linear.

For triatomics having 16 valence electrons (either BAB or BAC types), a linear ground state is predicted by Walsh's correlation[7] and related semiempirical calculations.[8] These correlations derive mainly from covalent triatomics in which the central atom is carbon or some less electropositive element. Ionic triatomics can behave differently, e.g., the alkaine earth difluorides change from linear (BeF_2)[5] to bent configurations (CaF_2, SrF_2 and BaF_2).[9] OAlF is isoelectronic with and intermediate between MgF_2 and SiO_2. Electric deflection data indicated SiO_2 to be linear.[10] Data for MgF_2[5] are contradictory, indicating either a linear or slightly bent (~158°) structure. This comparison with SiO_2 and MgF_2 favors linearity of OAlF but does not rule out a slightly bent structure.

We adopt the linear structure O=Al–F with an O–Al distance slightly shorter than in AlO[5] and an Al–F distance equal to that in AlF_3.[5] We assume the ground-state configuration to be $^1\Sigma^+$ and neglect excited states which should be relatively unimportant.[8] Vibrational frequencies are those assigned by Snelson[6] from a comparison of derived force constants for OAlF and OBX molecules. Values of ν_2 and ν_3 from IR spectra in an argon matrix. Snelson[6] used a stretching force constant transferred from AlF_3 in order to estimate ν_1 = 675 cm^{-1}. Although a weak absorption was observed at 687 cm^{-1}, this band was not assigned[6] to ν_1 because it was not conclusively associated with ν_2 and ν_3.

We estimate the uncertainty to be ~1 cal·K^{-1}·mol in the entropy and Gibbs-energy function of linear OAlF. If OAlF were nonlinear with an angle of 160°, S° would change by +3.8 (298 K) and +2.1 (2000 K) cal·K^{-1}·mol, while the Gibbs-energy function would change by +2.9 cal·K^{-1}·mol at 2000 K.

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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	−10.785	−579.067	−579.067	INFINITE
100	31 151	195.688	274.080	−7.839	−579.511	−581.198	303.586
200	40 013	219.989	241.397	−4.281	−580.675	−582.431	152.115
250	43.792	229.337	238.071	−2.183	−581.171	−582.810	121.772
298.15	46.806	237.316	237.316	0.	−581.576	−583.088	102.155
300	46 910	237.606	237.317	0.087	−581.590	−583.098	101.526
350	49 445	245.034	237.898	2.498	−581.947	−583.320	87.056
400	51.493	251.776	239.218	5.023	−582.257	−583.495	76.197
450	53.145	257.939	240.960	7.640	−582.535	−583.632	67.746
500	54.482	263.610	242.946	10.332	−582.793	−583.740	60.983
600	56.463	273.731	247.254	15.886	−583.291	−583.883	50.832
700	57.813	282.542	251.679	21.604	−583.824	−583.940	43.574
800	58.763	290.328	256.033	27.435	−584.446	−583.916	38.126
900	59 452	297.291	260.237	33.348	−585.205	−583.806	33.883
1000	59 964	303.582	264.262	39.320	−596.724	−582.842	30.445
1100	60.355	309.317	268.101	45.337	−597.497	−581.416	27.609
1200	60.658	314.582	271.758	51.388	−598.268	−579.920	25.243
1300	60.899	319.447	275.242	57.466	−599.041	−578.360	23.239
1400	61.092	323.967	278.563	63.566	−599.818	−576.740	21.518
1500	61.250	328.188	281.732	69.684	−600.602	−575.064	20.026
1600	61.380	332.145	284.760	75.815	−601.393	−573.336	18.718
1700	61 489	335.870	287.658	81.959	−602.193	−571.558	17.562
1800	61.581	339.387	290.435	88.113	−603.003	−569.733	16.533
1900	61.659	342.719	293.100	94.275	−603.821	−567.862	15.612
2000	61.726	345.883	295.661	100.444	−604.649	−565.948	14.781
2100	61.783	348.896	298.125	106.619	−605.485	−563.993	14.029
2200	61.834	351.771	300.498	112.800	−606.328	−561.997	13.344
2300	61.878	354.521	302.788	118.986	−607.177	−559.963	12.717
2400	61.916	357.155	304.999	125.176	−608.030	−557.892	12.142
2500	61.950	359.683	307.136	131.369	−608.886	−555.785	11.613
2600	61.981	362.114	309.204	137.566	−609 744	−553.644	11.123
2700	62.008	364.454	311.207	143.765	−610.602	−551.470	10.669
2800	62.032	366.709	313.149	149.967	−905.358	−548.297	10.229
2900	62.054	368.886	315.034	156.172	−905.115	−535.549	9.646
3000	62.074	370.990	316.864	162.378	−904.868	−522.810	9 103
3100	62 092	373.026	318.643	168.586	−904.614	−510.078	8.595
3200	62 108	374.998	320.374	174.796	−904.354	−497.356	8.118
3300	62.123	376.909	322.058	181.008	−904 087	−484.641	7 671
3400	62.136	378.764	323 699	187.221	−903.811	−471.935	7.250
3500	62.149	380.565	325.298	193.435	−903.526	−459.237	6.854
3600	62.160	382.316	326.858	199.651	−903.232	−446.547	6.479
3700	62.171	384.019	328.380	205.867	−902.929	−433.865	6.125
3800	62 180	385 677	329.866	212.085	−902.616	−421.192	5.790
3900	62.189	387.293	331.318	218.303	−902.294	−408.527	5.472
4000	62.198	388.867	332.737	224.523	−901.963	−395.870	5.170
4100	62.205	390.403	334.125	230.743	−901.623	−383.222	4.882
4200	62.213	391.902	335.482	236.964	−901.275	−370.583	4.609
4300	62.219	393.366	336.812	243.185	−900.919	−357.951	4.348
4400	62.225	394.797	338.113	249.407	−900.556	−345.328	4.100
4500	62.231	396.195	339.389	255.630	−900.185	−332.714	3.862
4600	62.237	397.563	340.638	261.854	−899.811	−320.108	3.635
4700	62.242	398.902	341.864	268.078	−899.433	−307.509	3.418
4800	62.247	400.212	343.066	274.302	−899.052	−294.919	3.209
4900	62.251	401.496	344.245	280.527	−898.669	−282.337	3.010
5000	62.255	402.753	345.403	286.752	−898.287	−269.763	2.818
5100	62.259	403.986	346.539	292.978	−897.906	−257.196	2.634
5200	62.263	405.195	347.656	299.204	−897.528	−244.637	2 457
5300	62.267	406.381	348.753	305.430	−897.155	−232.085	2.287
5400	62.270	407.545	349.831	311.657	−896.789	−219.540	2.124
5500	62.273	408.688	350.891	317.884	−896.432	−207.002	1.966
5600	62.276	409.810	351.933	324.112	−896.085	−194.469	1.814
5700	62.279	410.912	352.958	330.340	−895.750	−181.944	1.667
5800	62.282	411.995	353.966	336.568	−895.426	−169.424	1.526
5900	62.284	413.060	354.959	342.796	−895.122	−156.910	1.389
6000	62.287	414.107	355.936	349.024	−894.813	−144 402	1.257

PREVIOUS December 1975 (1 atm) CURRENT December 1975 (1 bar)

$S°(298.15\ K) = [264.21 \pm 2.1]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -693 \pm 40\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -695 \pm 40\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights State	ϵ_i, cm^{-1}	g_i
$^2A_1$	0	2
$^2B_1$	[20000]	2
$^2B_2$	[25000]	2

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[730](1)
[280](1)
[880](1)

Point Group: [C_{2v}] σ = 2
Bond Distance: Al–F = [1.65] Å
Bond Angle: F–Al–F = [120]°
Product of the Moments of Inertia: $I_AI_BI_C = [3.369562 \times 10^{-115}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

We tentatively adopt $\Delta_fH°(298.15\ K) = -166 \pm 10\ kcal{\cdot}mol^{-1}$ which corresponds to an average bond energy, $\Delta_aH°/2 = 140\ kcal{\cdot}mol^{-1}$, similar to that in AlF$_3$(g).[1] $\Delta_fH°$ is a compromise between discrepant results (−0 and −151 kcal·mol^{-1}) from two mass–spectrometric equilibria analyzed below. In our opinion there is possible cause to suspect K_p for either reaction. The large entropy discrepancy (δS) for reaction B suggests a temperature–dependent bias in the mass–spectrometric K_p.[5] If both AlF$_2$ and AlF$_3$ were determined from the intensity of AlF$_2^+$ at different ionizing energies, then we expect $\Delta_fH°$ [5] to be a positive limit. Reaction A was studied twice by molecular flow effusion of AlF$_3$(g) over the system Al(l)–Al$_2$O$_3$(cr). The earlier study[3,4] yields $\Delta_fH°(298.15\ K) = -188$ or $-179\ kcal{\cdot}mol^{-1}$, depending on the ionizing energy. Unfortunately, the ionizing energy in the first case is ambiguous. We conclude that $\Delta_fH°$ is quite dependent on ionizing energy. In addition, K_p and $\Delta_fH°$ may be affected by bias in the ionizing energy scale or related problems. These are discussed in more detail on tables for AlF$_2^+$, AlCl$_2^+$ and AlCl$_2$.[1] We believe that $\Delta_fH°$ [3,4] may be a negative limit.

The later study[2] of reaction A yields $\Delta_fH° = -180\ kcal{\cdot}mol^{-1}$. Internal evidence[2] gives us no reason to suspect this value. The possibility of negative bias is suggested, however, by inference from average bond energies (see AlCl$_2$),[1] and by using $\Delta_fH° = -180$ to derive $\Delta_fH°$ of other species in related mass–spectrometric studies. Effects of alternative values of $\Delta_fH°$(AlF$_2$) are discussed on the tables for Al$_2^-$, AlF$_4^-$, AlF$_2$O, AlClF, AlClF$_2$, and AlCl$_2$F.[1] Only for AlClF$_2$ and AlCl$_2$F do we have reliable, independent values of $\Delta_fH°$. These are consistent with $\Delta_fH°(AlF_2) = -166$ instead of −180. Although an alternative explanation is conceivable (see AlClF$_2$),[1] we choose $\Delta_fH°(AlF_2) = -166$ kcal·mol^{-1}.

Source	Reaction[a]	Ionizing Energy, eV	Data Points	T/K	δS cal·K^{-1}·mol^{-1}	$\Delta_rH°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	$\Delta_fH°$(298.15 K) kcal·mol^{-1}	$\Delta_aH°/2$
[2]	A	AP+(2 or 3)	7	1453–1675	4.0 ± 1.7	31.0 ± 2.6	24.6 ± 0.9	−180.4	147.0
[3,4]	A	AP+−2	1	1538	—	—	25.8	−179.2	146.5
[3,4]	A	20(or AP+3)	5	1408–1633	3.6 ± 0.6	22.5 ± 0.9	17.0 ± 0.8	−188.0	150.9
[5]	B	?	4	1243–1301	−76 ± 10	−47 ± 13	50.2 ± 3.7	<−151.2	>132.4

[a] Reactions: A) 1 AlF(g) = Al(g) + AlF$_2$(g) B) AlF$_3$(g) + AlF(g) = 2 AlF$_2$(g)

Heat Capacity and Entropy

The electronic ground state is that predicted for BF$_2$ by theoretical calculations,[6] it is consistent with semiempirical calculations[7] for BF$_2$, AlF$_2$, BCl$_2$ and AlCl$_2$. We estimate excited states of BF$_2$ at −30000 ($^2B_1$) and −40000 ($^2B_2$) by assuming that approximate theoretical calculations[6] have a bias similar to analogous calculations[8] of NO$_2$.[9] Dissociative electron–attachment data[10] yield −43000 cm^{-1} for BF$_2$($^2B_2$) confirming the estimation method. We use BF$_2$($^2B_1$) to estimate a crude correlation–energy correction for AlF$_2$($^2B_1$).[7] Dissociative electron–attachment data[11] for AlF$_2$($^2B_2$) are approximate; they yield −20000 ± 10000 ($\Delta_fH° = -166$) or −25000 ± 10000 cm^{-1} ($\Delta_fH° = -180$).

Vibrational frequencies are calculated from the estimated force constants $f_r = 4.25$ and $f_\alpha/r^2 = 0.25$ mdyn/Å. Frequencies and force constants are estimated from simultaneous consideration of AlF$_2^+$, AlF$_2$, AlF$_2^{-1}$ and the analogous boron species. We assume that frequency changes are qualitatively similar to those of NO$_2^+$, NO$_2$ and NO$_2^-$. In going from AlF$_2^+$ to AlF$_2$, we expect a large decrease in ν_3, an increase in ν_2 and some increase in ν_1. By analogy with BF$_2$,[6] the odd electron in AlF should occupy an antibonding orbital which increases the bond length but decreases the bond angle and stretching force constant. We assume a bond length 0.05 Å longer than AlF$_2^+$ [1] and a bond angle equal to that in BF$_2$.[6] The principal moments of inertia are: $I_A = 1.7832 \times 10^{-39}$, $I_B = 12.8835 \times 10^{-39}$ and $I_C = 14.6667 \times 10^{-39}\ g{\cdot}cm^2$.

Continued on page 171

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.505	−692.684	−692.684	INFINITE
100	35.777	220.448	301.626	−8.118	−692 688	−696.997	364.074
200	41.060	246.892	268.255	−4.273	−693.574	−700.993	183.081
250	43.614	256.331	264.952	−2.155	−694.073	−702.790	146.840
298.15	45.857	264.209	264.209	0.	−694.544	−704.426	123.413
300	45.937	264.493	264.210	0.085	−694.562	−704.487	122.662
350	47 921	271.728	264.777	2.433	−695.038	−706.104	105.380
400	49.558	278.237	266.059	4.871	−695.503	−707.653	92.410
450	50 888	284 154	267.746	7.384	−695.961	−709.144	82.315
500	51.967	289.573	269.662	9.956	−696.417	−710.584	74.234
600	53.559	299.199	273.803	15.237	−697.344	−713.331	62.101
700	54.637	307.541	278.040	20.651	−698.330	−715.919	53.423
800	55.391	314.889	282.196	26.154	−699.417	−718.359	46.904
900	55.935	321.446	286.199	31.722	−700.644	−720.655	41.826
1000	56.338	327.361	290.025	37.337	−712.635	−722.045	37.716
1100	56.644	332.746	293.667	42.986	−713.880	−722.925	34.329
1200	56.882	337.685	297 132	48.663	−715.124	−723.693	31.502
1300	57.070	342.246	300.429	54.361	−716.371	−724.356	29.105
1400	57.220	346.481	303.569	60.076	−717.622	−724.924	27.047
1500	57.343	350.433	306.563	65.804	−718.879	−725.401	25.261
1600	57.444	354.137	309.422	71.544	−720.143	−725.795	23.695
1700	57.529	357.622	312.156	77.292	−721.415	−726.109	22.311
1800	57.600	360.912	314.774	83.049	−722.693	−726.348	21.078
1900	57.661	364.028	317.285	88.812	−723.977	−726.517	19.973
2000	57.713	366.987	319.697	94.581	−725.264	−726.617	18.977
2100	57.759	369.804	322.016	100.355	−726.553	−726.653	18.075
2200	57.799	372.492	324.250	106.132	−727.840	−726.628	17.252
2300	57.835	375.062	326.404	111.914	−729.121	−726.544	16.500
2400	57.868	377.524	328.483	117.699	−730.394	−726.404	15.810
2500	57.898	379.887	330.492	123.488	−731.656	−726.212	15.173
2600	57.927	382.159	332.436	129.279	−732.902	−725.970	14.585
2700	57 955	384.345	334.318	135.073	−734.129	−725.680	14.039
2800	57.983	386.454	336.143	140.870	−1029.236	−724.377	13.513
2900	58.012	388.489	337.913	146.670	−1029.321	−713.487	12.851
3000	58.041	390.456	339.632	152.472	−1029.380	−702.596	12.233
3100	58.072	392.360	341.302	158.278	−1029.408	−691.702	11.655
3200	58.105	394.204	342.927	164.087	−1029.406	−680.808	11.113
3300	58.141	395.992	344.508	169.899	−1029.370	−669.915	10.604
3400	58.179	397.729	346.048	175.715	−1029.299	−659.024	10.125
3500	58.221	399.416	347.549	181.535	−1029.193	−648.135	9.673
3600	58.266	401.057	349.012	187.359	−1029.050	−637.249	9.246
3700	58.314	402.654	350.441	193.188	−1028.869	−626.368	8.843
3800	58.366	404.209	351.835	199.022	−1028.651	−615.493	8.461
3900	58.423	405.726	353.198	204.862	−1028.395	−604.623	8.098
4000	58.483	407.206	354.529	210.707	−1028.102	−593.761	7.754
4100	58.548	408.651	355.832	216.559	−1027.770	−582.907	7.426
4200	58.617	410.063	357.106	222.417	−1027.401	−572.060	7.115
4300	58.689	411.443	358.354	228.282	−1026.996	−561.224	6.818
4400	58.766	412.793	359.576	234.155	−1026.554	−550.397	6.534
4500	58.847	414.114	360.773	240.036	−1026.074	−539.581	6.263
4600	58.932	415.409	361.947	245.924	−1025.562	−528.775	6.004
4700	59.021	416.677	363.098	251.822	−1025.016	−517.981	5.757
4800	59.113	417.921	364.227	257.729	−1024.437	−507.199	5.519
4900	59.209	419.141	365.335	263.645	−1023.826	−496.430	5.292
5000	59.308	420.338	366 424	269.571	−1023.186	−485.673	5.074
5100	59.409	421.513	367.492	275.506	−1022.517	−474.930	4.864
5200	59.514	422.668	368.542	281.453	−1021.821	−464.199	4.663
5300	59 621	423.802	369.574	287.409	−1021.099	−453.482	4.469
5400	59.730	424.918	370.589	293.377	−1020.353	−442.780	4.283
5500	59.842	426.015	371.587	299.355	−1019.584	−432.091	4.104
5600	59.955	427.094	372.568	305.345	−1018.794	−421.416	3.931
5700	60.070	428.156	373.534	311.347	−1017.985	−410.757	3.764
5800	60 186	429.202	374.485	317.359	−1017.155	−400.111	3.603
5900	60.303	430.232	375.421	323.384	−1016.312	−389.479	3.448
6000	60.421	431.246	376.343	329.420	−1015.432	−378.864	3.298

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

Aluminum Fluoride, Ion (AlF_2^+) IDEAL GAS $M_r = 64.977797$ Aluminum Fluoride, Ion (AlF_2^+) $Al_1F_2^+(g)$

$S°(298.15 K) = [239.3 \pm 4]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 87 \pm 63\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [92.048]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[670](1)
[240](2)
[1000](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: $[D_{\infty h}]$
Bond Distance: Al–F = [1.60] Å
Bond Angle: F–AL–F = [180]°
Rotational Constant. $B_o = [0.173304]\ cm^{-1}$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = 22 \pm 15\ kcal{\cdot}mol^{-1}$ and $IP(AlF_2) = 8.1 \pm 0.9$ eV. Electron–impact studies[1,2] gave 15.2 ± 0.3 eV for the appearance potential (AP) of AlF_2^+ from AlF_3. The analogous process for onset of BF_2^+ from BF_3 has been studied by both photoionization[3] and electron impact.[4] Comparison indicates that BF_2^+ from electron impact[4] carried an excess energy (E*) of −0.4 to −0.9 eV. We estimate the excess energy for AlF_2^+ as 1.0 ± 0.5 eV. Thus, we take $AP{-}E^* = \Delta_r H° = 14.2 \pm 0.6$ eV ($327.5 \pm 14\ kcal{\cdot}mol^{-1}$) for the reaction $AlF_3(g) + e^-(g) = AlF_2^+(g) + F(g) + 2\ e^-(g)$. With JANAF auxiliary data[5] this yields $\Delta_f H°(AlF_2^+) = 21 \pm 15$, $\Delta_f H°(298.15\ K) = 22 \pm 15$ and $IP(AlF_2) = 187 \pm 20\ kcal{\cdot}mol^{-1}$ (8.1 ± 0.9 eV).

Electron–impact studies of AlF_2 gave approximate appearance potentials $AP(AlF_2^+) = 9 \pm 1$,[1] 10 ± 1[6] and 11 ± 1 eV.[7] We dismiss the last value[7] due to possible bias analogous to that of $AlCl_2^+(g)$.[5] Electron impact on AlF_2 should yield a vertical AP corresponding to a nonlinear (excited) configuration of AlF_2^+. Theoretical calculations for the linear $^2B_1$ state of BF_2[8] suggest an excitation energy of −1.1 eV at a bond angle of 120°. Extended Huckel calculations for AlF_2[9] suggest −1.4 eV at 130°. Thus, we combine E* = 1.2 ± 0.5 eV with the observed AP values[1,6] to get $IP(AlF_2) = 7.8 \pm 1.2$ and 8.8 ± 1.2 eV. These are consistent with the adopted value.

The extended Huckel calculation[9] gave $IP(AlF_2) = 7.8$ eV at a bond angle of 130°. This result should approximate the vertical IP which we expect at −9.3 eV.

Heat Capacity and Entropy

We assume the electronic ground state to be $^1\Sigma^+$ and neglect excited states. We expect the ground state to be linear by analogy with other triatomic species having sixteen valence electrons.[10] Although conflicting data[5] suggest that isoelectronic MgF_2 is either linear or slightly nonlinear, recent Raman data[11] favor a linear structure. We estimate the bond distance to be slightly shorter than that in AlF_3 and 0.05 Å shorter than that estimated for AlF_2.[5] We transfer the stretching force constant from AlF_3 and the ratio $f_r/f_\alpha = \sim 13$ Å^{-2} from MgF_2. This ratio is a compromise between very different values of ν_2 observed for MgF_2 in the gas[5] and matrix[11] phases. Thus, we calculate vibratonal frequencies for AlF_2^+ from the force constants $f_r = 4.9$, $f_{rr} = 0.2$ and $f_\alpha/r^2 = 0.14$ mdyn/Å. The resulting values have been rounded downward.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.730	87.485		
100	35.844	193.010	279.338	−8.633			
200	44 056	220.679	243.650	−4.594			
250	46.927	230.826	240.097	−2.318			
298.15	49.281	239.299	239.299	0.	92.048	83.338	−14.601
300	49.364	239.604	239.300	0.091	92.075	83.284	−14.501
350	51 404	247.371	239.908	2.612	92.811	81.761	−12.202
400	53 086	254.349	241.285	5.226	93.561	80.131	−10.464
450	54.463	260.684	243.094	7.916	94.319	78.407	−9.101
500	55.589	266.482	245.147	10.668	95.083	76.598	−8.002
600	57.271	276.776	249.582	16.316	96.601	72.758	−6.334
700	58.428	285.697	254.119	22.105	98.069	68.668	−5.124
800	59.245	293.555	258.567	27.991	99.443	64.372	−4.203
900	59.839	300.569	262.851	33.946	100.682	59.912	−3.477
1000	60.282	306.898	266.944	39.953	91.162	56.083	−2.929
1100	60.619	312.660	270.842	45.999	92.392	52.516	−2.494
1200	60.882	317 946	274.550	52.075	93.625	48.836	−2.126
1300	61.091	322.828	278.079	58.174	94.858	45.054	−1.810
1400	61.258	327.361	281.439	64.292	96.089	41.176	−1.536
1500	61.395	331.593	284.643	70.424	97.315	37.211	−1.296
1600	61.508	335.559	287.703	76.570	98.535	33.165	−1.083
1700	61.603	339.291	290.629	82.725	99.749	29.042	−0.892
1800	61.682	342.814	293.431	88.890	100.957	24.848	−0.721
1900	61.750	346.151	296.118	95.062	102.160	20.586	−0.566
2000	61.808	349.320	298.700	101.240	103.361	16.262	−0.425
2100	61.858	352.337	301.183	107.423	104.561	11.878	−0.295
2200	61.902	355.215	303.574	113.611	105.763	7.436	−0.177
2300	61 940	357.968	305.879	119.803	106.970	2.940	−0.067
2400	61.974	360.605	308.105	125.999	108.186	−1.609	0.035
2500	62.004	363 135	310.256	132.198	109.414	−6.209	0.130
2600	62.030	365.568	312.337	138.400	110.657	−10.859	0.218
2700	62.054	367.909	314.352	144.604	111.918	−15.556	0.301
2800	62.075	370.166	316.305	150.810	−180.700	−19.333	0.361
2900	62.094	372.345	318.200	157.019	−178.298	−13.613	0.245
3000	62.111	374.450	320.041	163.229	−175.870	−7.975	0.139
3100	62.127	376.487	321.829	169.441	−173.414	−2.419	0.041
3200	62.141	378.460	323.568	175.654	−170.928	3.057	−0.050
3300	62.154	380.372	325.260	181.869	−168.412	8.456	−0.134
3400	62.165	382.228	326.909	188.085	−165.862	13.777	−0.212
3500	62.176	384.030	328.515	194.302	−163.280	19.023	−0.284
3600	62.186	385.782	330.082	200.520	−160.665	24.195	−0.351
3700	62.195	387.486	331.610	206.739	−158.016	29.293	−0.414
3800	62.204	389.144	333.102	212.959	−155.333	34.320	−0.472
3900	62.211	390.760	334.560	219.180	−152.617	39.276	−0.526
4000	62.219	392.335	335.985	225.401	−149.869	44.161	−0.577
4100	62.225	393.872	337.378	231.623	−147.088	48.977	−0.624
4200	62.231	395.371	338.741	237.846	−144.276	53.726	−0.668
4300	62.237	396.836	340.075	244.070	−141.433	58.406	−0.709
4400	62.243	398.267	341.382	250.294	−138.562	63.020	−0.748
4500	62.248	399.665	342.661	256.518	−135.660	67.569	−0.784
4600	62.252	401.034	343.915	262.743	−132.733	72.053	−0.818
4700	62.257	402.372	345.145	268.969	−129.780	76.473	−0.850
4800	62.261	403.683	346.351	275.195	−126.804	80.830	−0.880
4900	62.265	404 967	347.534	281.421	−123.804	85.125	−0.907
5000	62.269	406.225	348.695	287.648	−120.785	89.358	−0.934
5100	62.272	407.458	349.836	293.875	−117.746	93.531	−0.958
5200	62.275	408.667	350.955	300.102	−114.690	97.644	−0.981
5300	62.278	409.854	352.056	306.330	−111.618	101.698	−1.002
5400	62.281	411.018	353.137	312.558	−108.533	105.694	−1.022
5500	62.284	412.161	354.200	318.786	−105.436	109.632	−1.041
5600	62.287	413.283	355.245	325.015	−102.328	113.515	−1.059
5700	62.289	414.385	356.272	331.243	−99.213	117.341	−1.075
5800	62.292	415.469	357.284	337.472	−96.088	121.112	−1.091
5900	62.294	416.534	358.279	343.702	−92.962	124.831	−1.105
6000	62.296	417.581	359.259	349.931	−89.810	128.494	−1.119

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

Aluminum Fluoride, Ion (AlF$_2^-$) IDEAL GAS M_r = 64.978895 Aluminum Fluoride, Ion (AlF$_2^-$) Al$_1$F$_2^-$(g)

$\Delta_fH°(0\ K) = -900 \pm 84\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = [260.05 \pm 3.3]\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = [-907.928]\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights State	ϵ_i, cm^{-1}	g_i
$^1A_1$	[0]	1
$^3B_1$	[26000]	3
$^1B_1$	[44000]	1

Vibrational Frequencies and Degeneracies ν, cm $^{-1}$
[730](1)
[280](1)
[780](1)

Point Group: [C$_{2v}$] $\sigma = 2$
Bond Distance: Al–F = [1.70] Å
Bond Angle: F–Al–F = [105]°
Product of the Moments of Inertia: $I_AI_BI_C$ = [4 600099 × 10^{-115}] g^3·cm^6

Enthalpy of Formation

We adopt $\Delta_fH°$(298.15 K) = −217 ± 20 kcal·mol^{-1} which corresponds to an electron affinity of EA(AlF$_2$) = 50 ± 8 kcal·mol^{-1} (2.2 ± 0.4 eV) and a fluoride–ion affinity of IA(AlF) = 92 ± 20 kcal·mol^{-1}. $\Delta_fH°$ is based on K_p data for the reaction AlF$_2$(g) = F(g) + AlF$_2^-$(g) reported by Srivastava *et al.*[1] The authors measured K_p with a molecular–flow–effusion method using a mass spectrometer operating in both positive– and negative–ion modes. They give three points (1705–1900 K) obtained from study of the vapor species over the system AlF$_3$(cr)–KF(cr)–Al(l). Our analysis gives [$\Delta_rS°$(2nd law)–$\Delta_rS°$(3rd law)] = −0.2 ± 4.8 cal·K^{-1}·mol^{-1} and $\Delta_rH°$(298.15 K) = 28.4 ± 8.8(2nd law) or 28.8 ± 1(3rd law) kcal·mol^{-1}. Reducing the 3rd law $\Delta_rH°$ to absolute zero and combining with EA(F) = 78.38 kcal·mol^{-1},[2] we derive EA(AlF$_2$) = 49.7 ± 8 kcal·mol^{-1}. The uncertainity of ±8 kcal·mol^{-1} is our estimate of a reasonable bound for error in $\Delta_rH°$.

Depending on the value used for $\Delta_fH°$(AlF$_2$), the above reaction yields $\Delta_fH°$(AlF$_2^-$, g, 298.15 K) = −231,[3,2] −217[2] or −202[4,2] kcal·mol^{-1}. In contrast, we derive $\Delta_fH°$(AlF$_2^-$, g, 298.15 K) = −181 ± 25 kcal·mol^{-1}, independent of $\Delta_fH°$(AlF$_2$), from $\Delta_rH°$(0 K) AP–E* = 127 kcal[5] for the reaction AlF$_3$(g) + e$^-$(g) = AlF$_2^-$(g) + F(g) Depending on $\Delta_fH°$(AlF$_2$), this yields EA(AlF$_2$) = 0 ± 25,[3,2] 14 ± 25[2] or 29 ± 25[4,2] kcal·mol^{-1}. Petty *et al.*[5] measured the appearance potential (AP) and excess translational energy of AlF$_2^-$ in the dissociative electron–attachment reaction. E*, the excess vibrational–translational energy of the products at threshold, was estimated[5] from the measured translational energy via an approximate empirical correlation. We estimate ±25 kcal·mol^{-1} as an approximate bound for error in E*.[6] The resulting $\Delta_fH°$(AlF$_2^-$) = −181 ± 25 kcal^{-1}·mol^{-1} is inconsistent with the two most likely values (−231 and −217) derived from AlF$_2$. Bias might exist in either experiment.[5,2] It is conceivable that AlF$_2^-$ is formed[5] in an excited electronic state. Thus far, electronic excitation has been observed[7] in only one negative molecular ion, AsF$_4^-$. If it occurs for AlF$_2^-$, then $\Delta_fH°$ = −181 ± 25 refers to an excited electronic state. The electronic energy of this state would be −13000 ± 9000 cm^{-1}, based on the two most likely values of $\Delta_fH°$(AlF$_2^-$). Such values are not unreasonable, so we cannot rule out electronic excitation.[5] We conclude that additional data are needed to confirm $\Delta_fH°$(AlF$_2^-$).

Heat Capacity and Entropy

Electronic levels and quantum weights are assumed equal to those of isoelectronic SiF$_2$;[2,8] however, see the above comment on excited levels. Vibrational frequencies are calculated from the estimated force constants f$_r$ = 3.7, f$_{rr}$ = 0.1 and f$_\alpha$/r^2 = 0.29 mdyn/Å. Frequencies and force constants are estimated from simultaneous consideration of AlF$_2^+$, AlF$_2$, AlF$_2^-$ and the analogous boron species. We assume that frequency changes are qualitatively similar in the two series AlF$_2^+$, AlF$_2$, AlF$_2^-$ and NO$_2^+$, NO$_2$, NO$_2^-$ [2] which have the same number of valence electrons. Furthermore, we expect isoelectronic SiF$_2^2$ to provide upper–limit frequencies for AlF$_2^-$. Thus, in going from AlF$_2$ to AlF$_2^-$, we assume little change in ν_1 and ν_2 but a significant decrease in ν_3.

By analogy with BF$_2$,[8,9] we expect that the odd electron in AlF$_2$ occupies a molecular orbital centered mainly on the metal opposite the two fluorines. This orbital should be antibonding[8] in the sense that addition of an electron increases the bond length but decreases the bond angle and stretching force constant. We assume that the bond length is 0.05 Å longer and the bond angle is 15° smaller than in AlF$_2$.[2] The principal moments of inertia are I_A = 2.8061 × 10^{-39}, I_B = 11.4773 × 10^{-39}and I_C = 14.2834 × 10^{-39} g·cm^2.

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[3] O. M. Uy, R. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972).
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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	−11.573	−899.939		
100	35.786	215.980	297 844	−8.186			
200	41.429	242.516	264.145	−4.326			
250	44.174	252.060	260.799	−2.185			
298.15	46.511	260.046	260.046	0.	−907.928	−910.314	159.483
300	46.594	260.334	260.047	0.086	−907.983	−910.329	158.502
350	48.597	267.672	260.622	2.468	−909.465	−910.602	135.900
400	50.209	274.271	261.923	4.939	−910.936	−910.664	118.921
450	51.494	280.262	263.633	7.483	−912.402	−910.542	105.693
500	52.520	285.742	265.573	10.084	−913.868	−910.257	95.094
600	54.009	295.459	269.765	15.416	−916.824	−909.258	79.158
700	55.003	303.864	274.050	20.870	−919.848	−907.759	67.738
800	55.690	311.256	278.248	26.407	−922.980	−905.820	59.144
900	56.182	317.845	282.288	32.001	−926.259	−903.480	52.437
1000	56.545	323.785	286.146	37.639	−940.306	−900.006	47.011
1100	56.820	329 187	289.817	43.308	−943.610	−895.816	42.539
1200	57.032	334.141	293.307	49.001	−946.917	−891.325	38.798
1300	57.199	338.713	296.626	54.712	−950.228	−886.558	35.622
1400	57.333	342.957	299.786	60.439	−953.545	−881.536	32.891
1500	57.442	346.916	302.797	66.178	−956.871	−876.276	30.515
1600	57.532	350.626	305.672	71.927	−960.204	−870.794	28.429
1700	57.607	354.116	308.420	77.684	−963.546	−865.104	26.581
1800	57.670	357.411	311.051	83.448	−966.896	−859.217	24.934
1900	57.724	360.530	313.574	89.218	−970.251	−853.143	23.455
2000	57.770	363.493	315.996	94.993	−973.611	−846.893	22.119
2100	57.809	366.312	318.326	100.772	−976.973	−840.474	20.906
2200	57.844	369.002	320.568	106.554	−980.334	−833.895	19.799
2300	57.874	371.574	322.731	112.340	−983.690	−827.164	18.785
2400	57.901	374.038	324.817	118.129	−987.038	−820.287	17.853
2500	57.925	376.402	326.834	123.920	−990.375	−813.270	16.992
2600	57.947	378.674	328.784	129.714	−993.697	−806.120	16.195
2700	57.967	380.862	330.673	135.510	−997.001	−798.843	15.455
2800	57.986	382.970	332.503	141.307	−1294.186	−790.476	14.747
2900	58.005	385.005	334.279	147.107	−1296.350	−772.448	13.913
3000	58.023	386.972	336.003	152.908	−1298.488	−754.346	13.134
3100	58 041	388.875	337.678	158.711	−1300.598	−736.173	12.404
3200	58.060	390.718	339.306	164.517	−1302.678	−717.932	11.719
3300	58.079	392.505	340.892	170.323	−1304.726	−699.627	11.074
3400	58.101	394.239	342.435	176.132	−1306.741	−681.261	10.466
3500	58.124	395.923	343.939	181.944	−1308.722	−662.835	9.892
3600	58.149	397.561	345.406	187.757	−1310.668	−644.353	9.349
3700	58.177	399.155	346.838	193.574	−1312.579	−625.818	8.835
3800	58.209	400.707	348.235	199.393	−1314.455	−607.232	8.347
3900	58.243	402.219	349.600	205.215	−1316.294	−588.597	7.883
4000	58.281	403 694	350.934	211.042	−1318.098	−569.915	7.442
4100	58.324	405.134	352.238	216.872	−1319.866	−551.189	7.022
4200	58.370	406.540	353.514	222.706	−1321.600	−532.419	6.622
4300	58.422	407.914	354.764	228.546	−1323.298	−513.609	6.239
4400	58.477	409.258	355.987	234.391	−1324.963	−494.760	5.874
4500	58.538	410.572	357.185	240.242	−1326.592	−475.873	5.524
4600	58.604	411.860	358.360	246.099	−1328.190	−456.951	5.189
4700	58.675	413.121	359.512	251.963	−1329.756	−437.994	4.868
4800	58.751	414.357	360.641	257.834	−1331.292	−419.004	4.560
4900	58.832	415.569	361.750	263.713	−1332.796	−399.982	4.264
5000	58.919	416.759	362.838	269.601	−1334.273	−380.930	3.980
5100	59.011	417.926	363.907	275.497	−1335.722	−361.849	3.706
5200	59.108	419.073	364.957	281.403	−1337.145	−342.739	3.443
5300	59.210	420.200	365.989	287.319	−1338.542	−323.603	3.189
5400	59.317	421.308	367.003	293.245	−1339.916	−304.440	2.945
5500	59.429	422.397	368.000	299.182	−1341.267	−285.252	2.709
5600	59.545	423.469	368.981	305.131	−1342.597	−266.040	2.482
5700	59.666	424.524	369.946	311.092	−1343.907	−246.804	2.262
5800	59.792	425.563	370.896	317.064	−1345.195	−227.546	2.049
5900	59.921	426.586	371.832	323.050	−1346.470	−208.265	1.844
6000	60.055	427.594	372.753	329 049	−1347.706	−188.965	1.645

PREVIOUS: June 1976 (1 atm) CURRENT· June 1976 (1 bar)

Aluminum Fluoride, Ion (AlF$_2^-$) Al$_1$F$_2^-$(g)

Aluminum Fluoride Oxide ($OAlF_2$) IDEAL GAS $M_r = 80.977746$ Aluminum Fluoride Oxide ($OAlF_2$) $Al_1F_2O_1(g)$

$\Delta_fH°(0\ K) = -1105.4 \pm 30\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = [292.7 \pm 13]\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -1108.8 \pm 30\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$[^2B_2]$	0	[2]
$[^2B_1]$	[1000]	[2]
$[^2B]$	[20000]	[2]

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}
[900](1)	[900](1)
[640](1)	[240](1)
[260](1)	[270](1)

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

Bond Distances: Al–F = [1.63] Å; Al–O = [1.72] Å

Bond Angles: F–Al–F = [120]°; F–Al–O = [120]°

Product of the Moments of Inertia: $I_AI_BI_C = [3.719682 \times 10^{-114}]\ g^3\cdot cm^6$

Enthalpy of Formation

We adopt $\Delta_fH°(298.15\ K) = -265 \pm 7\ kcal\cdot mol^{-1}$ and $\Delta_{at}H° = 437 \pm 8\ kcal\cdot mol^{-1}$ based on JANAF auxiliary data[1] combined with $\Delta_rH°(298.15\ K) = 15.5 \pm 5\ kcal\cdot mol^{-1}$ for the reaction $AlF(g) + AlFO(g) = Al(g) + AlF_2O(g)$. $\Delta_rH°$ is from our 3rd law analysis of K_p data reported by Uy *et al.*[2] They calculated K_p directly from ion intensities observed at 1453–1675 K in a mass–spectrometric study of vapor species over the system $AlF_3(g)$–$Al(l)$–$Al_2O_3(cr)$. 2nd law analysis gives $\Delta_rH°(298.15\ K) = 20.8 \pm 0.8\ kcal\cdot mol^{-1}$ and the difference $[\Delta_rS°(2nd\ law) - \Delta_rS°(3rd\ law)] = 3.4 \pm 0.5\ cal\cdot K^{-1}\ mol^{-1}$. Uy *et al.*[2] assigned $\Delta_rH°$(2nd law) an overall uncertainty (including contributions from T) of $\pm 5\ kcal\cdot mol^{-1}$.

The adopted $\Delta_{at}H° = 437\ kcal\cdot mol^{-1}$ implies that AlF_2O is surprisingly stable. Average bond energies from AlF_3 ($140\ kcal\cdot mol^{-1}$) and AlO, AlO_2 and Al_2O ($-120\ kcal\cdot mol^{-1}$) yield an estimate of $\Delta_{at}H°(AlF_2O) = 400\ kcal\cdot mol^{-1}$. If we attribute all of the difference to the Al–O bond, then the AlF_2O data imply an Al–O bond energy of $157\ kcal\cdot mol^{-1}$. This enhancement of $37\ kcal\cdot mol^{-1}$ contrasts with the near equality of Al–O bond energies in the oxides[1] and hydroxides.[8] An analogous treatment of AlFO(g)[1] yields an Al–O bond energy of $153\ kcal\cdot mol^{-1}$, similar to that in AlF_2O. Existing data for BF_2O and BFO imply bond energies of −166 and $-200\ kcal\cdot mol^{-1}$ compared with values of −130 (B–O) and −190 (B=O) from the oxides. There are obvious differences between the Al and B systems which we are unable to rationalize via existing knowledge of electronic structure. We feel that confirmation of the oxyfluoride data is desirable.

Heat Capacity and Entropy

Molecular parameters are all estimated by analogy with BF_2O and BF_2O^+. Two emission bands due to BF_2O or BF_2O^+ were analyzed by Mathews.[3] Vibrational analysis of the band with $\nu_\infty = 17171\ cm^{-1}$ gave the three symmetrical stretching modes of the lower state. Rotational analysis of the band with $\nu_o = 22391\ cm^{-1}$ gave structural parameters including the bond length B–O = 1.40 ± 0.05 Å. This value indicates a single bond which is longer than those of 1.36, 1.263 and 1.20 A observed for the various bond types in B_2O_3, BO_2 and BO. It is not known[3] whether the two emission bonds have a common lower state. Zahradnik and Carsky[4] used semiempirical CNDO calculations to predict the electronic transitions of BF_2O and BF_2O^+. They favored assignment of the $22391\ cm^{-1}$ transition to BF_2O^+ and the other transition to either BF_2O^+ or BF_2O.

Due to the lengthened B–O bond and the theoretical results, we tentatively attribute both observed bands to BF_2O^+. We estimate the missing vibrational frequencies of BF_2O^+ and all those of BF_2O and BF_2O^- by comparison with HBF_2, BF_3 and $ClBF_2$. We assume that addition of an electron causes a large increase in ν_1 and ν_5 but a smaller increase in ν_2 and ν_6.

Vibrational frequencies of AlF_2O are estimated from those of BF_2O by comparison of AlF_3, AlFO, AlO and Al_2O[1] with the analogous boron species. Electronic levels are crude estimates based on calculations or data for the 24–valence–electron species BF_2O,[4] BF_3^+,[5,6] and NO_3.[5,7] Bond angles are assumed to be 120° Bond distances are assumed equal to those of AlF_3 and Al_2O[1]. The principal moments of inertia are: $I_A = 12.0265 \times 10^{-39}$, $I_B = 12.5730 \times 10^{-39}$ and $I_C = 24.5995 \times 10^{-39}\ g\cdot cm^2$.

References

[1] JANAF Thermochemical Tables. AlFO(g) and $AlO_2(g)$, 12–31–75, AlF(g), AlO(g) and $Al_2O(g)$, 6–30–75; $AlF_3(g)$, 6–30–70; Al(g), 12–31–65.

[2] O. M. Uy, R. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972); AD–731303, 50 pp. (1971).

[3] C. W. Mathews and K. K. Innes, J. Mol. Spectrosc. 15, 199 (1965); ibid. 19, 203 (1966).

Continued on page 171

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

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−14.325	−1105.379	−1105.379	INFINITE
100	42.267	235.438	343.053	−10.761	−1106.659	−1103.801	576.567
200	55.050	269.080	298.254	−5.835	−1107.918	−1100.427	287.402
250	59.640	281.871	293.729	−2.964	−1108.393	−1098.497	229.518
298.15	63.390	292.705	292.705	0.	−1108.760	−1096.556	192.112
300	63.521	293.098	292.707	0.117	−1108.773	−1096.480	190.914
350	66.737	303.139	293.492	3.377	−1109.076	−1094.407	163.331
400	69.357	312.228	295.275	6.781	−1109.322	−1092.294	142.639
450	71.477	320.524	297.626	10.304	−1109.528	−1090.152	126.542
500	73.192	328 147	300.303	13.922	−1109.709	−1087.990	113.661
600	75.724	341.730	306.103	21.376	−1110.043	−1083 614	94.337
700	77.441	353.540	312.055	29.040	−1110.406	−1079.182	80.530
800	78.644	363.964	317.905	36.848	−1110.857	−1074.691	70.170
900	79.513	373.280	323.549	44.758	−1111.445	−1070.137	62.109
1000	80 158	381.693	328.950	52.743	−1122.796	−1064 748	55.617
1100	80.650	389.357	334.098	60.784	−1123.404	−1058.914	50.284
1200	81.035	396.391	339.000	68.869	−1124.015	−1053.024	45.837
1300	81.344	402.890	343.668	76.989	−1124.631	−1047.084	42.072
1400	81.600	408.928	348.116	85.136	−1125.256	−1041.095	38.844
1500	81.819	414.566	352.360	93.308	−1125.891	−1035.062	36.044
1600	82.013	419.852	356.415	101.499	−1126.537	−1028.985	33.593
1700	82.190	424.830	360.295	109.710	−1127.193	−1022.868	31.429
1800	82.358	429.532	364.012	117.937	−1127.858	−1016.712	29.504
1900	82.521	433.990	367.579	126.181	−1128.531	−1010.519	27.781
2000	82.683	438.226	371.006	134 441	−1129.208	−1004.291	26.229
2100	82.845	442.265	374.304	142.718	−1129.886	−998.028	24.825
2200	83.008	446.122	377.481	151.010	−1130.562	−991.733	23.547
2300	83.175	449 816	380.546	159.319	−1131.232	−985.408	22.379
2400	83.344	453.359	383.507	167.645	−1131.891	−979.054	21.309
2500	83.516	456.765	386.370	175.988	−1132.535	−972.672	20.323
2600	83.690	460.044	389.141	184.349	−1133.160	−966.265	19.413
2700	83.866	463.206	391.826	192.726	−1133.762	−959.834	18.569
2800	84.043	466.259	394.430	201.122	−1428.239	−952.414	17 768
2900	84.220	469.211	396.958	209.535	−1427.690	−935.430	16.849
3000	84.398	472.069	399.414	217.966	−1427.109	−918.466	15.992
3100	84.574	474.840	401.803	226.414	−1426.493	−901.521	15.191
3200	84.749	477.527	404.127	234.881	−1425.839	−884.597	14.440
3300	84.922	480.138	406.391	243.364	−1425.148	−867.694	13.734
3400	85.092	482.676	408.598	251.865	−1424.416	−850.812	13.071
3500	85.260	485.145	410.750	260.383	−1423.644	−833.952	12.446
3600	85.424	487.549	412.850	268.917	−1422.831	−817.115	11.856
3700	85.585	489.892	414.900	277.467	−1421.976	−800.302	11.298
3800	85.742	492.176	416.904	286.034	−1421.080	−783.511	10 770
3900	85.894	494.405	418.863	294.615	−1420.143	−766.745	10.269
4000	86.042	496.582	420.779	303.212	−1419.165	−750.004	9.794
4100	86.185	498.708	422.654	311.824	−1418.148	−733.287	9.342
4200	86.324	500.787	424.489	320.449	−1417.092	−716.596	8.912
4300	86.458	502.820	426.287	329.088	−1416.000	−699.931	8.502
4400	86.587	504.809	428.049	337.741	−1414.871	−683.291	8.112
4500	86.711	506.756	429 777	346.406	−1413 706	−666 677	7.739
4600	86.830	508.663	431.471	355.083	−1412.511	−650.090	7.382
4700	86.944	510.532	433.133	363.771	−1411.285	−633.529	7.041
4800	87.053	512.363	434.765	372.471	−1410.031	−616 994	6.714
4900	87.157	514.159	436.367	381.182	−1408.749	−600.485	6.401
5000	87.256	515.921	437.941	389.903	−1407.445	−584.003	6.101
5100	87.350	517.650	439.487	398.633	−1406.119	−567.547	5.813
5200	87.440	519.347	441.006	407.372	−1404.773	−551.118	5.536
5300	87.524	521.013	442.500	416.121	−1403.411	−534.714	5.270
5400	87 604	522.650	443.969	424.877	−1402.035	−518.337	5.014
5500	87.679	524.258	445.414	433.641	−1400.648	−501.985	4.767
5600	87.750	525.839	446 837	442.413	−1399.252	−485.658	4.530
5700	87.817	527.393	448.236	451.191	−1397.850	−469.357	4.301
5800	87.879	528.920	449.614	459.976	−1396.442	−453.080	4.080
5900	87.937	530 423	450.971	468.767	−1395.036	−436.827	3.867
6000	87.990	531.902	452.308	477.563	−1393.610	−420.600	3.662

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

Aluminum Fluoride Oxide, Ion ($OAlF_2^-$) IDEAL GAS $M_r = 80.978295$ Aluminum Fluoride Oxide, Ion ($OAlF_2^-$) $Al_1F_2O_1^-(g)$

$\Delta_fH°(0\ K) = -1300 \pm 105\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = [284.9 \pm 13]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = [-1309.592]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}
[950](1)	[900](1)
[650](1)	[270](1)
[260](1)	[300](1)

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

Point Group: $[C_{2v}]$

Bond Distances: Al–F = [1.63] Å; Al–O = [1.66] Å

Bond Angles: F–Al–F = [120]°; F–Al–O = [120]°

Product of the Moments of Inertia. $I_AI_BI_C = [3.468404 \times 10^{-114}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

We adopt $\Delta_fH°(298.15\ K) = -313 \pm 25\ kcal{\cdot}mol^{-1}$ which corresponds to $EA(AlF_2O) = 46 \pm 25\ kcal{\cdot}mol^{-1}$ (2.0 ± 1.1 eV) and the fluoride–ion affinity IA(AlFO) = 112 $kcal{\cdot}mol^{-1}$. $\Delta_fH°$ is derived from Kp for reaction A (see below) observed by Faraber *et al.*[1] with a mass spectrometer operating in both positive– and negative–ion modes. Farber *et al.*[1] used a molecular–flow–effusion technique to study vapor species in the systems $KF(g)–AlF_3(g)–Al_2O_3(cr)$, $KF(g)–AlF_3(g)–Al_2O_3(cr)$, and $KCl(g)–AlF_3(g)–Al_2O_3(cr)$. They considered the results to be limiting values; we presume this is due to very low intensities of AlF_2O^-.

The three reactions reported by Farber *et al.* are analyzed below using JANAF auxiliary data.[2] We give inequalities consistent with the authors' limiting values. Reactions B and C yield less stringent limits are are not used. Reaction A involves AlF_2^- which depends on our possibly biased value[2] of $\Delta_fH°(AlF_2)$. Use of the alternative $\Delta_fH°$ [2] based on mass spectrometry[1,3] reduces the discrepancy between reactions A and C form 35 to 21 $kcal{\cdot}mol^{-1}$. This may mot be significant if B and C yield only limiting values. The alternative result from A would yield $EA(AlF_2O) = 61$ and IA(AlFO) = 127 $kcal{\cdot}mol^{-1}$.

Reaction	Data Points	T/K	$\Delta_rH°(298.15\ K)$ $kcal{\cdot}mol^{-1}$	$\Delta_fH°(298.15\ K)$ $kcal{\cdot}mol^{-1}$
A) $AlFO(g) + AlF_2^-(g) = AlF_2O^-(g) + AlF(g)$	1	1793	≥−21.1	≥−313.6[a] or ≥ − 327.8[a]
B) $AlF_2O(g) + F^-(g) = AlF_2O^-(g) + F(g)$	1	1753	>0.1	>−344.8
C) $AlF_2O(g) + Cl^-(g) = AlF_2O(g) + Cl(g)$	2	1653–1793	>0.8	>−349.1

[a] Assuming $\Delta_fH°(AlF_2^-, g, 298.15\ K) = -217$ or $-231.2\ kcal{\cdot}mol^{-1}$ depending on choice of $\Delta_fH°(AlF_2)$.[2]

Heat Capacity and Entropy

All molecular parameters are estimated via data for BF_2O^+ (or BF_2O) as discussed on the table for $AlF_2O(g)$.[2] We assume a C_{2v} structure with equal bond angles. Formation of the negative ion is assumed to decrease the Al–O bond distance by 0.06 Å but leave the Al–F distance unchanged. By analogy with AlF_3^2 we assume a singlet electronic ground state and neglect excited states. Formation of the negative ion is assumed to cause a significant increase in ν_1, ν_5, and ν_6. The principal moments of inertia are $I_A = 11.4723 \times 10^{-39}$, $I_B = 12.5732 \times 10^{-39}$, and $I_C = 24.0455 \times 10^{-39}\ g{\cdot}cm^2$.

References

[1] M. Farber, R. D. Srivastava and O. M. Uy, AD–731303, 50 pp. (1971).

[2] JANAF Thermochemical Tables: $AlF_2^-(g)$, $AlF_2(g)$ and $AlF_2O(g)$, 6–30–76; AlFO(g), 12–31–75, AlF(g), 6–30–75, $AlF_3(g)$, 6–30–70; Cl(g), 6–30–72; Cl (g), 6–30–65; $F^-(g)$, 12–31–71, F(g), 9–30–65.

[3] O. M. Uy, T. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972).

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

T/K	$C_p°$ ($J{\cdot}K^{-1}mol^{-1}$)	$S°$ ($J{\cdot}K^{-1}mol^{-1}$)	$-[G°-H°(T_r)]/T$ ($J{\cdot}K^{-1}mol^{-1}$)	$H°-H°(T_r)$ ($kJ{\cdot}mol^{-1}$)	$\Delta_fH°$ ($kJ{\cdot}mol^{-1}$)	$\Delta_fG°$ ($kJ{\cdot}mol^{-1}$)	log K_f
0	0.	0.	INFINITE	−14.077	−1299.765		
100	41.036	228.775	334.358	−10.558			
200	54.051	261.603	290.340	−5.747			
250	58.755	274.184	285.880	−2.924			
298.15	62.592	284.870	284 870	0.	−1309.592	−1288.797	225.792
300	62.726	285.258	284.871	0.116	−1309.644	−1288.668	224.377
350	66.024	295.183	285.648	3.337	−1311.024	−1285.062	191.785
400	68.721	304.181	287.411	6.708	−1312.344	−1281.262	167.316
450	70.912	312.407	289.738	10.201	−1313.619	−1277.300	148.265
500	72.691	319.973	292.388	13.793	−1314.866	−1273.197	133.010
600	75.329	333.475	298.138	21.202	−1317.323	−1264.632	110.096
700	77.127	345.231	304.044	28.831	−1319.800	−1255.656	93.698
800	78.390	355.617	309.854	36.610	−1322.358	−1246.319	81.376
900	79.304	364.905	315.464	44.497	−1325.048	−1236.654	71 774
1000	79.983	373.298	320.835	52.463	−1338.497	−1225.921	64 036
1100	80.500	380.946	325.957	60.488	−1341.199	−1214.532	57.673
1200	80.902	387.969	330.836	68.559	−1343.903	−1202.898	52.361
1300	81.220	394.457	335.484	76.666	−1346.610	−1191.038	47.856
1400	81.475	400.486	339.914	84.801	−1349.326	−1178.969	43.988
1500	81.684	406.115	344.142	92.959	−1352.053	−1166.706	40.628
1600	81.856	411.392	348.182	101.137	−1354.791	−1154.260	37.683
1700	81.999	416.359	352.047	109.330	−1357.543	−1141.642	35.078
1800	82.120	421.049	355.752	117.536	−1360.309	−1128.863	32.759
1900	82.223	425.492	359.306	125.753	−1363.087	−1115.929	30.679
2000	82.311	429.712	362.722	133.980	−1365.876	−1102.848	28.803
2100	82.387	433.730	366.009	142.215	−1368.674	−1089.628	27.103
2200	82.454	437.564	369.175	150.457	−1371.479	−1076.274	25.554
2300	82.511	441.231	372.228	158.705	−1374.288	−1062.793	24.137
2400	82.562	444.743	375.177	166.959	−1377.098	−1049.190	22.835
2500	82.608	448.115	378.028	175.218	−1379.905	−1035.469	21.635
2600	82.648	451.355	380.786	183.480	−1382.707	−1021.637	20.525
2700	82.683	454 475	383.458	191.747	−1385.499	−1007.696	19 495
2800	82.715	457.483	386.048	200.017	−1682.180	−992.685	18.519
2900	82.744	460.386	388.562	208.290	−1683.849	−968.030	17 436
3000	82.770	463.192	391.003	216.566	−1685.502	−943.319	16.425
3100	82.794	465.906	393.376	224.844	−1687.134	−918.552	15.477
3200	82.815	468.535	395.684	233.124	−1688.746	−893.734	14.589
3300	82.835	471.084	397.930	241.407	−1690.334	−868.865	13.753
3400	82.852	473.557	400.118	249.691	−1691.897	−843.948	12.966
3500	82.869	475.959	402.251	257.977	−1693.435	−818.986	12.223
3600	82.884	478.293	404.331	266.265	−1694.947	−793.980	11.520
3700	82.898	480.564	406.361	274.554	−1696.432	−768.933	10.855
3800	82.910	482.775	408.343	282.844	−1697.891	−743.846	10.225
3900	82.922	484.929	410.279	291.136	−1699.322	−718.720	9.626
4000	82.933	487.029	412.171	299.429	−1700.727	−693.559	9.057
4100	82.943	489.077	414.022	307.723	−1702.106	−668.363	8.515
4200	82.953	491.075	415.833	316.017	−1703.460	−643.133	7.999
4300	82.961	493.027	417.606	324.313	−1704.789	−617.872	7.506
4400	82.970	494.935	419.342	332.610	−1706.096	−592.579	7.035
4500	82.977	496.799	421.042	340.907	−1707.377	−567.258	6.585
4600	82.984	498.623	422.709	349.205	−1708.639	−541.908	6.154
4700	82.991	500.408	424.343	357.504	−1709.882	−516.531	5.741
4800	82.997	502.155	425.946	365.803	−1711.107	−491.127	5.345
4900	83.003	503.867	427.519	374.103	−1712.314	−465.698	4 964
5000	83.009	505.544	429.063	382.404	−1713.508	−440.245	4.599
5100	83.014	507.188	430.579	390.705	−1714.690	−414.768	4.248
5200	83.019	508.800	432.068	399.007	−1715.861	−389.268	3.910
5300	83.024	510.381	433.530	407.309	−1717.023	−363.745	3.585
5400	83.028	511.933	434.968	415.611	−1718.180	−338.201	3.271
5500	83.032	513.456	436.381	423.914	−1719.332	−312.636	2.969
5600	83.036	514.953	437.771	432.218	−1720.483	−287.049	2.677
5700	83.040	516.422	439.138	440.522	−1721.634	−261.442	2.396
5800	83.043	517.867	440.483	448.826	−1722.785	−235.814	2.124
5900	83.047	519.286	441.806	457.130	−1723.945	−210.167	1.861
6000	83.050	520.682	443.109	465.435	−1725.089	−184.502	1.606

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

Aluminum Fluoride Oxide, Ion ($OAlF_2^-$) $Al_1F_2O_1^-(g)$

Aluminum Fluoride (AlF_3) CRYSTAL M_r = 83.976749 Aluminum Fluoride (AlF_3) $Al_1F_3(cr)$

$\Delta_fH°(0\ K) = -1504.3 \pm 1.3\ kJ\cdot mol^{-1}$
$\Delta_fH°(298.15\ K) = -1510.4 \pm 1.3\ kJ\cdot mol^{-1}$
$\Delta_{trs}H° = 0.5632 \pm 0.042\ kJ\cdot mol^{-1}$
$\Delta_{fus}H° = [98.3 \pm 12]\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = 66.48 \pm 0.42\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{trs} = 728 \pm 1\ K$
$T_{fus} = [2523 \pm 100]\ K$

Enthalpy of Formation

The adopted value is that recommended by CODATA.[1] It is based on separate calorimetric studies of the combustion in fluorine of aluminum[2] and aluminum–Teflon mixtures.[3] More extensive auxiliary data[3] for Teflon bring the aluminum–Teflon study into exact agreement with the aluminum study.[2] Calorimetric data relating AlF_3 to PbF_2[2,4] tend to confirm this value, but PbF_2 is probably less certain than is AlF_3.

Values for the $\Delta_fH°(298.15\ K)$ derived indirectly from equilibrium studies[5] and emf of solid galvanic cells[6,7,8,9] are tabulated below. The original data are reanalyzed with the use of the most recent auxiliary data.[4]

Source	Method	Reaction	T/K	$\Delta_rH°(298.15\ K)$, $kcal\cdot mol^{-1}$ 2nd law	3rd law	Drift $cal\cdot K^{-1}\cdot mol^{-1}$	$\Delta_fH°(298.15\ K)$* $kcal\cdot mol^{-1}$
5	equilibria	A	849–1312	33.3 ± 0.20	33.11 ± 0.2	−0.2 ± 0.2	−358.6
6	emf	B	873	—	−43.01	—	−360.0
7	emf	B	873	—	−42.73	—	−360.3
8	emf	B	720–860	−40.26 ± 0.01	−41.47 ± 0.2	−1.5 ± 0.01	−361.6
9	emf	B	748–903	−42.1 ± 0.01	−40.58 ± 0.2	−1.8 ± 0.02	−362.5

*Derived from the third law enthalpy of reaction and is per mole of $AlF_3(cr)$.
A. $2/3\ AlF_3(cr) + H_2O(g) = 1/3\ Al_2O_3(\alpha,cr) + 2\ HF(g)$ B. $AlF_3(cr) + 1.5\ Mg(cr) = Al(cr) + 1.5\ MgF_2(cr)$

With the exception of the equilibrium study of Mashovets and Yudin,[5] the results are in reasonable agreement with the directly measured calorimetric value. It has been suggested[2] that interaction of the condensed phases (activities1) caused the equilibria to deviate from the standard–state reaction assumed above. An alternative may be that the reaction with water vapor produced Al_2O_3 in a metastable form; such forms require ignition temperatures greater than 1400 K for complete conversion to α– Al_2O_3.[10]

Heat Capacity and Entropy

$C_p°$ and $S°(298.15\ K)$ are taken from Douglas and Ditmars,[11] whose tables are based on heat capacity measurements from 54 to 298 K[12] and relative enthalpy measurements from 323 to 1173 K.[11] The enthalpy data confirm earlier data (401–1401 K) of O'Brien and Kelley[13] rather than the adjusted values proposed by Frank.[14] Douglas and Ditmars[11] gave a detailed comparison with other data. The entropy is derived from $C_p°$ using the extrapolation $S°(50\ K) = 2.22 \pm 0.25\ J\cdot K^{-1}\cdot mol^{-1}$.

Transition Data

T_{trs} and $\Delta_{trs}H°$ for this crystalline first order transition are from Douglas and Ditmars.[11] The values were obtained from extensive enthalpy data for the transition region assuming the presence of a very small amount of impurity in solid solution.

Sublimation Data

$T_{sub} = 1549\ K$ is the temperature at which the calculated total pressure (monomer plus dimer) reaches one atm; the mole fraction of dimer is calculated as 0.109 at T_{sub}. Sublimation temperatures of 1533 and 1566 K were obtained in two sublimation– pressure studies[15,16] at the Techische Hochschule, Breslau. The selected enthalpies of sublimation to $AlF_3(g)$ and $Al_2F_6(g)$ reproduce closely the entrainment data of Krause and Douglas.[17] Selection of these values of $\Delta_{sub}H°$ and comparisons with other vapor–pressure data are discussed on the gas–phase tables.

Fusion Data

Refer to the liquid table for details.

References

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

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−11.625	−1504.272	−1504.272	INFINITE
100	24.932	12.058	119.836	−10.778	−1508.269	−1483.221	774.755
200	56.877	39.991	72.814	−6.565	−1510.252	−1457.225	380.588
298.15	75.132	66.484	66.484	0.	−1510.424	−1431.123	250.727
300	75.400	66.949	66.485	0.139	−1510.416	−1430.631	249.095
400	86.287	90.293	69.594	8.280	−1509.613	−1404.138	183.362
500	92.274	110.245	75.781	17.232	−1508.342	−1377.911	143.949
600	97.311	127.494	82.993	26.700	−1506.819	−1351.963	117.699
700	105.357	143.032	90.474	36.791	−1504.904	−1326.297	98.970
728.000	108.692	147.228	92.577	39.786	ALPHA <––> BETA TRANSITION		
728.000	97.579	148.001	92.577	40.349			
800	98.516	157.248	97.987	47.409	−1502.681	−1300.966	84.944
900	99.717	168.922	105.231	57.322	−1501.390	−1275.830	74.047
1000	100.830	179.487	112.137	67.350	−1510.813	−1250.072	65.297
1100	101.893	189 147	118.705	77.486	−1509.431	−1224.064	58.126
1200	102.918	198.057	124.951	87.727	−1507.984	−1198.185	52.156
1300	103.918	206.334	130.897	98.069	−1506.471	−1172.429	47.109
1400	104.897	214.071	136.564	108.510	−1504.892	−1146.793	42.787
1500	105.864	221.341	141.976	119.048	−1503.244	−1121.271	39.046
1600	106.822	228.204	147.153	129.682	−1501.528	−1095.862	35.776
1700	107.771	234.709	152.114	140.412	−1499.741	−1070.562	32.894
1800	108.717	240.896	156.876	151.236	−1497.882	−1045.369	30.336
1900	109.663	246.799	161.454	162.155	−1495.946	−1020.283	28.050
2000	110.604	252.448	165.864	173.169	−1493.929	−995.299	25.995
2100	111.545	257.867	170.117	184.276	−1491.827	−970.419	24.138
2200	112.487	263.078	174.225	195.478	−1489.635	−945.641	22.452
2300	113.428	268.099	178.198	206.773	−1487.347	−920.965	20.916
2400	114.370	272.946	182.045	218.163	−1484.957	−896.391	19.509
2500	115.311	277.634	185.775	229.647	−1482.460	−871.918	18.218
2523.000	115.529	278.691	186.618	232.302	---- BETA <––> LIQUID ----		
2600	116.252	282.175	189.396	241.225	−1479.850	−847.547	17.027
2700	117.194	286.580	192.914	252.898	−1477.122	−823.279	15.927
2800	118.135	290.859	196.336	264.664	−1768.173	−798.147	14.890
2900	119.077	295.021	199.668	276.525	−1764.101	−763.575	13.753
3000	120.018	299.074	202.914	288.480	−1759.898	−729.145	12.696

PREVIOUS: June 1970 CURRENT: September 1979

Aluminum Fluoride (AlF_3) LIQUID, p ~ 4340 bars $M_r = 83.976749$

$S°(298.15\ K) = [95.379]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = [2523 \pm 100]\ K$

$\Delta_f H°(298.15\ K) = [-1422.760]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 98.3 \pm 12\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(AlF_3, l, 298.15\ K)$ is calculated from $\Delta_f H°(AlF_3, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(2523\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

There are no heat capacity or enthalpy measurements covering the liquid region of AlF_3. The pure solid does not melt at ordinary pressures. This $AlF_3(l)$ table, therefore, is a non-standard state table for P = −4400 atm. By analogy[1] with $AlCl_3(l)$, $AlBr_3(l)$, and $AlI_3(l)$, we estimate $C_p°(l) = 30\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$; Holm[2,3] also assumed the same value. We assume a glass transition at 1850 K, below which we adopt the heat capacity data of $AlF_3(cr)$; the transition at 728 K for $AlF_3(cr)$ is not included.

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

Fusion Data

The pure solid sublimes before melting at ordinary pressures. From studies on CaF_2–AlF_3 and NaCl–AlF_3 binary systems, Millet *et al.*[4] estimated a triple point temperature for AlF_3 of 2523 K at 30000 atm. Our adopted values lead to a pressure for $AlF_3(l) = AlF_3(g)$ of −2200 atm. The calculated dimer pressure at this temperature is also −2200 atm.

Holm,[3] attempted to relate his drop-calorimetric data on the melting of a Li_3AlF_6–AlF_3 system to the enthalpy of fusion of AlF_3. Based on the assumption that the enthalpy of mixing of $Li_3AlF_6(l)$ with $AlF_3(l)$ to form the eutectic mixture is small and positive, he obtained $\Delta_{fus}H° = 11.4\ kcal{\cdot}mol^{-1}$ for AlF_3 at 1298 K. This result was challenged by Hong and Kleppa[4,5] who measured the enthalpy of mixing of $AlF_3(cr)$ with a series of liquid alkali fluorides and derived $\Delta_{fus}H° = 26.5 \pm 2\ kcal{\cdot}mol^{-1}$ at this temperature. These results suggest that Holm's assumed enthalpy of mixing is in error, both as to sign and magnitude. We adopt the $\Delta_{fus}H°$ value of Hong and Kleppa[5,6] but adjust the value to the adopted triple point of 2523 K (from 1298 K).

References

[1] JANAF Thermochemical Tables: $AlBr_3(l)$, $AlCl_3(l)$, $AlI_3(l)$, and $AlF_3(cr)$, 9–30–79.
[2] K. Grjotheim, J. L. Holm, and B. J. Welch, Acta Chem. Scand. **25**, 2370 (1971).
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[4] J. P. Millet, H. Pham and M. Rolin, Rev. Int. Hautes Temp. Refract. **11**, 277 (1974).
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[6] K. C. Hong and O. J. Kleppa, J. Phys. Chem. **82**, 176 (1978).

Aluminum Fluoride (AlF_3) $Al_1F_3(l)$

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
0							
100							
200							
298.15	97.475	95.379	95.379	0.	−1422.760	−1352.074	236.878
300	97.479	95.982	95.381	0.180	−1422.711	−1351.636	235.341
400	97.763	124.065	99.208	9.943	−1420.286	−1328.320	173.461
500	98.014	145.908	106.444	19.732	−1418.178	−1305.578	136.393
600	98.224	163.797	114.556	29.544	−1416.311	−1283.237	111.716
700	98.391	178.951	122.701	39.375	−1414.655	−1261.191	94.111
800	98.516	192.086	130.571	49.212	−1413.214	−1239.369	80.922
900	99.717	203.759	138.066	59.124	−1411.923	−1217.717	70.674
1000	100.830	214.324	145.172	69.152	−1421.346	−1195.442	62.444
1100	101.893	223.984	151.904	79.289	−1419.964	−1172.918	55.697
1200	102.918	232.894	158.286	89.529	−1418.518	−1150.523	50.081
1300	103.918	241.172	164.348	99.871	−1417.005	−1128.251	45.334
1400	104.897	248.909	170.114	110.312	−1415.425	−1106.098	41.269
1500	105.864	256.179	175.612	120.850	−1413.777	−1084.060	37.750
1600	106.822	263.042	180.864	131.485	−1412.061	−1062.135	34.675
1700	107.771	269.546	185.891	142.214	−1410.275	−1040.319	31.965
1800	108.717	275.733	190.712	153.039	−1408.415	−1018.610	29.559
1850.000	109.190	278.718	193.050	158.486	____ GLASS <--> LIQUID ____		
1850.000	125.520	278.718	193.050	158.486		TRANSITION	
1900	125.520	282.066	195.349	164.762	−1405.674	−997.017	27.410
2000	125.520	288.504	199.847	177.314	−1402.119	−975.601	25.480
2100	125.520	294.628	204.216	189.866	−1398.573	−954.363	23.738
2200	125.520	300.467	208.459	202.418	−1395.030	−933.293	22.159
2300	125.520	306.047	212.582	214.970	−1391.485	−912.384	20.721
2400	125.520	311.389	216.588	227.522	−1387.933	−891.629	19.406
2500	125.520	316.513	220.483	240.074	−1384.368	−871.023	18.199
2523.000	125.520	317.662	221.364	242.961	---- BETA <--> LIQUID ----		
2600	125.520	321.436	224.272	252.626	−1380.785	−850.560	17.088
2700	125.520	326.173	227.959	265.178	−1377.177	−830.235	16.062
2800	125.520	330.738	231.549	277.730	−1667.443	−809.077	15.094
2900	125.520	335.143	235.045	290.282	−1662.679	−778.505	14.022
3000	125.520	339.398	238.453	302.834	−1657.878	−748.098	13.026
3100	125.520	343.514	241.776	315.386	−1653.038	−717.852	12.096
3200	125.520	347.499	245.018	327.938	−1648.155	−687.762	11.227
3300	125.520	351.361	248.182	340.490	−1643.228	−657.826	10.413
3400	125.520	355.108	251.272	353.042	−1638.253	−628.040	9.649
3500	125.520	358.747	254.291	365.594	−1633.231	−598.401	8.931
3600	125.520	362.283	257.242	378.146	−1628.159	−568.905	8.255
3700	125.520	365.722	260.128	390.698	−1623.038	−539.552	7.617
3800	125.520	369.069	262.951	403.250	−1617.867	−510.338	7.015
3900	125.520	372.330	265.714	415.802	−1612.647	−481.260	6.446
4000	125.520	375.508	268.419	428.354	−1607.378	−452.317	5.907

PREVIOUS: CURRENT: September 1979

Aluminum Fluoride (AlF_3) $Al_1F_3(l)$

CRYSTAL–LIQUID

0 to 2523 K crystal
above 2523 K liquid*, p = ~4340 bars

*The liquid does not exist at 1 bar.

Refer to the individual tables for details.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−11.625	−1504.272	−1504.272	INFINITE
100	24.932	12.058	119.836	−10.778	−1508.269	−1483.221	774.755
200	56.877	39.991	72.814	−6.565	−1510.252	−1457.225	380.588
298.15	75.132	66.484	66.484	0.	−1510.424	−1431.123	250.727
300	75.400	66.949	66.485	0.139	−1510.416	−1430.631	249.095
400	86.287	90.293	69.594	8.280	−1509.613	−1404.138	183.362
500	92.274	110.245	75.781	17.232	−1508.342	−1377.911	143.949
600	97.311	127.494	82.993	26.700	−1506.819	−1351.963	117.699
700	105.357	143.032	90.474	36.791	−1504.904	−1326.297	98.970
728.000	108.692	147.228	92.577	39.786	ALPHA <--> BETA TRANSITION		
728.000	97.579	148.001	92.577	40.349			
800	98.516	157.248	97.987	47.409	−1502.681	−1300.966	84.944
900	99.717	168.922	105.231	57.322	−1501.390	−1275.830	74.047
1000	100.830	179.487	112.137	67.350	−1510.813	−1250.072	65.297
1100	101.893	189.147	118.705	77.486	−1509.431	−1224.064	58.126
1200	102 918	198.057	124.951	87.727	−1507.984	−1198.185	52.156
1300	103.918	206.334	130.897	98.069	−1506.471	−1172.429	47.109
1400	104.897	214.071	136.564	108.510	−1504.892	−1146.793	42.787
1500	105.864	221.341	141.976	119.048	−1503.244	−1121.271	39.046
1600	106.822	228.204	147.153	129.682	−1501.528	−1095.862	35.776
1700	107.771	234.709	152.114	140.412	−1499.741	−1070.562	32.894
1800	108 717	240.896	156.876	151.236	−1497.882	−1045.369	30.336
1900	109.663	246.799	161.454	162.155	−1495.946	−1020.283	28.050
2000	110.604	252.448	165.864	173.169	−1493.929	−995.299	25.995
2100	111.545	257.867	170.117	184.276	−1491.827	−970.419	24 138
2200	112.487	263.078	174.225	195.478	−1489.635	−945.641	22.452
2300	113.428	268.099	178.198	206.773	−1487.347	−920.965	20.916
2400	114.368	272.946	182.045	218.163	−1484.957	−896.391	19.509
2500	115.311	277.634	185.775	229.647	−1482.460	−871.918	18.218
2523.000	115.529	278.691	186.618	232.302	BETA <--> LIQUID TRANSITION		
2523.000	125.520	317.662	186.618	330.626			
2600	125.520	321.436	190.555	340.291	−1380.785	−850.560	17.088
2700	125.520	326.173	195.490	352.843	−1377.177	−830.235	16.062
2800	125.520	330.738	200.240	365.395	−1667.443	−809.076	15.094
2900	125.520	335.142	204.816	377.947	−1662.679	−778.504	14.022
3000	125.520	339.398	209.231	390.499	−1657.878	−748.097	13.026
3100	125.520	343.513	213.497	403.051	−1653.038	−717.851	12.096
3200	125.520	347.499	217.623	415.603	−1648.155	−687.761	11.227
3300	125.520	351.361	221.617	428.155	−1643.228	−657.825	10.413
3400	125.520	355.108	225.489	440.707	−1638.253	−628.039	9.649
3500	125.520	358.747	229.244	453.259	−1633.231	−598.400	8.931
3600	125.520	362.283	232.891	465.811	−1628.159	−568.904	8.255
3700	125.520	365.722	236.435	478.363	−1623.038	−539.551	7.617
3800	125.520	369.069	239.881	490.915	−1617.867	−510.337	7.015
3900	125.520	372.330	243.236	503.467	−1612.647	−481.259	6.446
4000	125.520	375.508	246.503	516.019	−1607.378	−452.316	5.907

PREVIOUS: CURRENT September 1979

$\Delta_f H°(0\ K) = -1205.60 \pm 2.5\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 276.69 \pm 0.8\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = -1209.32 \pm 2.5\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
[650](1)	[935](2)
297 (1)	263 (2)

Ground State Quantum Weight: [1] $\sigma = 6$

Point Group: D_{3h}

Bond Distance: Al–F = 1.63 ± 0.01 Å

Bond Angle: F–Al–F = 120°

Product of the Moments of Inertia: $I_A I_B I_C = 3.975102 \times 10^{-114}\ g^3{\cdot}cm^6$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by use of $\Delta_{sub}H°(298.15\ K) = 71.965 \pm 0.5\ kcal{\cdot}mol^{-1}$. Sublimation studies by mass–spectrometric and entrainment techniques suggest the presence of a small amount of dimer in the saturated vapor. These studies are reviewed on the table for $Al_2F_6(g)$. The heats of sublimation for the monomer and dimer are selected by adopting the JANAF entropies for crystal, monomer and dimer, the mass spectrometric value of $2\ \Delta_{sub}H°(\text{monomer}) - \Delta_{sub}H°(\text{dimer}) = -49\ kcal{\cdot}mol^{-1}$ at 1000 K, and the entrainment data of Krause and Douglas.[1] The resulting calculated pressures deviate by <0.5% from the entrainment data,[1] by <10% from the mass–spectrometric equation[3] and by <3% from the mass–effusion equation.[4]

Further comparisons with experimental data are given below. The adopted values favor the later[11] of two sublimation–point studies;[11, 12] both show considerable scatter and similar deviations from the calculated dP/dT. Torsion–effusion data suggest the possibility of more serious discrepancy. Although data of Witt and Barrow[9] are consistent with the JANAF pressures, Hildenbrand *et al.*[7, 8, 19] noted a trend toward increasing pressure with decreasing orifice area. The most recent study by Hildenbrand and Laughlin[19] yielded equilibrium pressures that are reasonably consistent with the adopted values, unlike the earlier study.[7] The 1981 communication[19] yielded a heat of sublimation value which is within 0 25 kcal·mol of our adopted value In contrast, the JANAF predictions agree closely with mass–effusion data of Ko *et al.*,[4] who reported no significant effect from a twelvefold variation in orifice area.

Comparison of Calculated and Observed Total Pressures Over $AlF_3(cr)$

Source	Method	T/K	Mole Fraction Dimer Calc. Range	P_{calc}/P_{obs} Range	Difference[a] in dP/dT
1	Entrainment	1194–1258	0.019–0.029	1.004–0.996	Very small (−)
2	Entrainment	1108–1273	0.010–0.032	0.73–2.22	Uncertain (?)
3	Mass Spec[b]	983–1165	0.003–0.016	1.09–0.91	Small (−)
4	Mass Effusion	1027–1184	0.005–0.018	0.994–0.972	Very small (−)
5	Mass Effusion	889–1006	0.001–0.004	1.42–1.66	Uncertain (+)
6	Mass Effusion	980–1123	0.003–0.012	1.64–0.88	Large (−)
19	Torsion Effusion	902–1098	0.001–0.010	0.88	Small
8	Torsion Effusion				
	Cell Gr−7	992–1101	0.004–0.010	0.89–1.01	Small (+)
	Cell Gr−9	938–1080	0.002–0.008	0.94–1.34	Medium (+)
9	Torsion Effusion	955–1063	0.003–0.007	1.11–1.07	Small (−)
10	Dynamic B.P.	1335–1453	0.044–0.076	0.84–1.64	Large (+)
11	Dynamic B.P.	1367–1524	0.052–0.100	1.33–0.79	Large (−)
12	Dynamic B.P.	1371–1567	0.053–0.116	2.70–1.28	Large (−)

[a] Magnitude and sign of the difference, calculated minus observed, in dP/dT

[b] Absolute pressures of monomer were obtained by integration of the ion intensity during total sublimation.

Heat Capacity and Entropy

The molecular structure is that derived from electron–diffraction data by Akishin *et al.*[13] Observed vibrational frequencies are those reported by Buchler *et al.*[14] from infrared spectra of the vapor at 1000–1200 K. These frequencies are confirmed by infrared spectra of AlF_3 isolated in matricies of neon, argon and krypton.[15, 16] Drake and Rosenblatt[17] have estimated the Raman-active fundamentals based on a correlation of vibrational frequencies and internuclear distances for the Group IIIA trihalides. They estimated $\nu_1 = 685\ cm^{-1}$ which would decrease $S°(298\ 15\ K)$ by $0.05\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ from our adopted value. We adopt $\nu_1 = 650 \pm 50\ cm^{-1}$ as derived from three other methods: (a) calculation of the force constant k_1 from ν_3 and ν_4; (b) comparison of $k_1(XY_3)/k(XY)$ for X = B, Al and Y = F, Cl, and Br; and (c) extrapolation of $\nu_1(BY_3)/\nu_1(AY_3)$ to Y=F from Y=Cl, Br and I, using recent gas–phase Raman data[18] for AlY_3. The principal moments of inertia are: $I_A = I_B = 12.5730 \times 10^{-39}$ and $I_C = 25.1460 \times 10^{-39}\ g{\cdot}cm^2$.

Continued on page 172

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	−14.049	−1205.595	−1205.595	INFINITE
100	41.148	220.719	325.981	−10.526	−1206.916	−1202.734	628.244
200	53.850	253.541	282.132	−5.718	−1208.303	−1197.987	312.882
250	58.444	266.064	277.695	−2.908	−1208.861	−1195.342	249.753
298.15	62.239	276.691	276.691	0.	−1209.322	−1192.695	208.955
300	62.373	277.076	276.692	0.115	−1209.339	−1192.592	207.649
350	65.670	286.947	277.464	3.319	−1209.754	−1189.767	177.563
400	68.387	295.899	279.218	6.673	−1210.119	−1186.887	154.991
450	70.606	304.086	281.533	10.149	−1210.446	−1183.963	137.431
500	72.415	311.622	284.170	13.726	−1210.746	−1181.004	123.379
600	75.107	325.079	289.894	21.111	−1211.307	−1175.002	102.293
700	76.949	336.804	295.776	28.720	−1211.873	−1168.907	87.225
800	78.245	347.169	301.565	36.483	−1212.505	−1162.727	75.918
900	79.185	356.442	307.156	44.357	−1213.254	−1156.461	67.119
1000	79.884	364.822	312.511	52.312	−1224.749	−1149.344	60.036
1100	80.416	372.462	317.619	60.328	−1225.488	−1141.768	54.218
1200	80.830	379.478	322.485	68.391	−1226.218	−1134.124	49.367
1300	81.158	385.961	327.122	76.491	−1226.947	−1126.420	45.260
1400	81.421	391.986	331.542	84.621	−1227.679	−1118.660	41.738
1500	81.636	397.611	335.761	92.774	−1228.416	−1110.847	38.683
1600	81.814	402.885	339.794	100.947	−1229.162	−1102.985	36.009
1700	81.962	407.850	343.652	109.136	−1229.916	−1095.076	33.648
1800	82.087	412.538	347.350	117.338	−1230.678	−1087.122	31.547
1900	82.193	416.979	350.899	125.552	−1231.447	−1079.126	29.667
2000	82.284	421.198	354.309	133.776	−1232.220	−1071.089	27.974
2100	82.362	425.214	357.591	142.009	−1232.993	−1063.014	26.441
2200	82.431	429.047	360.752	150.248	−1233.763	−1054.901	25.047
2300	82.491	432.713	363.802	158.495	−1234.524	−1046.754	23.773
2400	82.543	436.225	366.747	166.746	−1235.272	−1038.574	22.604
2500	82.590	439.595	369.594	175.003	−1236.002	−1030.363	21.528
2600	82.631	442.835	372.349	183.264	−1236.710	−1022.124	20.535
2700	82.668	445.955	375.018	191.529	−1237.389	−1013.857	19.614
2800	82.701	448.962	377.605	199.798	−1531.938	−1004.599	18.741
2900	82.731	451.864	380.116	208.069	−1531.455	−985.773	17.756
3000	82.758	454.669	382.555	216.344	−1530.932	−966.966	16.836
3100	82.782	457.383	384.925	224.621	−1530.367	−948.176	15.977
3200	82.804	460.012	387.231	232.900	−1529.756	−929.405	15.171
3300	82.824	462.560	389.475	241.182	−1529.099	−910.654	14.414
3400	82.843	465.033	391.661	249.465	−1528.393	−891.924	13.703
3500	82.860	467.435	393.792	257.750	−1527.638	−873.215	13.032
3600	82.875	469.769	395.870	266.037	−1526.832	−854.528	12.399
3700	82.889	472.040	397.898	274.325	−1525.974	−835.865	11.800
3800	82.903	474.251	399.879	282.615	−1525.066	−817.226	11.234
3900	82.915	476.404	401.813	290.906	−1524.107	−798.611	10.696
4000	82.926	478.504	403.704	299.198	−1523.097	−780 021	10.186
4100	82.936	480.552	405.554	307.491	−1522.038	−761 457	9.701
4200	82.946	482.550	407.363	315.785	−1520.931	−742.919	9.240
4300	82.955	484.502	409.135	324.080	−1519.776	−724.409	8.800
4400	82.964	486.409	410.869	332.376	−1518.576	−705.926	8.380
4500	82.972	488.274	412.569	340.673	−1517.328	−687.471	7.980
4600	82.979	490.098	414.234	348.970	−1516.040	−669.044	7.597
4700	82.986	491.882	415.868	357.268	−1514.710	−650 645	7.231
4800	82.992	493.629	417.470	365.567	−1513.341	−632.275	6.881
4900	82.999	495.341	419.041	373.867	−1511.935	−613.934	6.545
5000	83.004	497.018	420.584	382.167	−1510.493	−595.622	6.222
5100	83.010	498.661	422.099	390.468	−1509.018	−577.339	5.913
5200	83.015	500.273	423.587	398.769	−1507.513	−559.085	5.616
5300	83.020	501.855	425.049	407.071	−1505.978	−540.861	5.331
5400	83.024	503.406	426.486	415.373	−1504.417	−522.666	5.056
5500	83.028	504.930	427.898	423.676	−1502.831	−504.500	4.791
5600	83.033	506.426	429.287	431.979	−1501.223	−486.363	4.537
5700	83.036	507.896	430.653	440.282	−1499.595	−468.255	4.291
5800	83.040	509.340	431.997	448.586	−1497.947	−450.176	4.054
5900	83.044	510.759	433.320	456.890	−1496.285	−432.125	3.826
6000	83.047	512.155	434.623	465.195	−1494.588	−414.105	3.605

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

Tetrafluoroaluminate, Ion (AlF_4^-) IDEAL GAS $M_r = 102.975701$ Tetrafluoroaluminate, Ion (AlF_4^-) $Al_1F_4^-(g)$

$\Delta_fH°(0\ K) = -1980 \pm 105\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 294.75 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = [-1991.584]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
622(1)	760(3)
210(2)	322(3)

Ground State Quantum Weight: [1] $\sigma = 12$

Point Group: T_d

Bond Distance: Al–F = 1.69 Å

Bond Angle: F–Al–F = 109.4712°

Product of the Moments of Inertia. $I_AI_BI_C = 1.387252 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

We adopt $\Delta_fH°(298.15\ K) = -476 \pm 25\ kcal \cdot mol^{-1}$ which corresponds to the fluoride–ion affinity $IA(AlF_3) = 125 \pm 25\ kcal \cdot mol^{-1}$ for $AlF_4^-(g) = AlF_3(g) + F^-(g)$. $\Delta_rH°$ is a compromise based mainly on K_p data (7 points, 1130–1485 K) for the reaction $2\ AlF_2(g) + AlF_2^-(g) = 2\ AlF(g) + AlF_4^-(g)$. K_p data were measured by Srivastava *et al.*[1] with a mass spectrometer operating in both positive– and negative–ion modes. The authors used a molecular–flow–effusion technique to react vapors from AlF_3 and K_3AlF_6 or KF with Al(l). Analysis with JANAF auxiliary data[2] yields $\Delta_rH°(298.15\ K)(3rd\ law) = -38.2 \pm 2.7$ and $\Delta_rH°(298.15\ K)(2nd\ law) = -33.9 \pm 6.3\ kcal \cdot mol^{-1}$ with $[\Delta_rS°(2nd\ law) - \Delta_rS°(3rd\ law)] = -3.3 \pm 4.8\ cal \cdot K^{-1} \cdot mol^{-1}$. The 3rd law $\Delta_rH°$ yields $\Delta_fH°(AlF_4^-, g, 298.15\ K) = -460.4 \pm 14\ kcal \cdot mol^{-1}$ or $-502.4 \pm 14\ kcal \cdot mol^{-1}$, depending on the choice of $\Delta_fH°(AlF_2, g, 298.15\ K) = -166 \pm 10^2$ or $-180 \pm 5\ kcal \cdot mol^{-1}$.[2,3]

The difference of $14\ kcal \cdot mol^{-1}$ in $\Delta_fH°(AlF_2)$ causes a three–fold change ($42\ kcal \cdot mol^{-1}$) in $\Delta_fH°(AlF_4^-)$ and increases the fluoride–ion affinity $IA(AlF_3)$ from 109 ± 25 to $151 \pm 15\ kcal \cdot mol^{-1}$. The latter value seems rather large in comparison to related species:[2,1] ≤112 or ≤127(OAlF), 92 or 106 (AlF), ≤101 (BF_3), ≤92 (OBF) and 98 or 103 (BF).

By combining published data for $NaAlF_4(g)$ with a coulomb–energy calculation, Holm[4] estimated $IA(AlF_3) = 131\ kcal \cdot mol^{-1}$. This result has an unknown bias due to limitations of the calculational model and auxiliary data. Refined lattice energy calculations[5] yield halide–ion affinities $IA = 87 \pm 7$ ($AlCl_3$) and ($AlBr_3$) $kcal \cdot mol^{-1}$. $\Delta_fH°(BF_4^-) = -421\ kcal \cdot mol^{-1}$ [6] derived from lattice energy yields $IA(BF_3) = 90$ compared to ≤101 $kcal \cdot mol^{-1}$ from mass spectrometry. Comparison of stretching force constants[2,7,8] with average bond energies in AlX_3 and AlX_4^- suggests a slight, but not definitive, preference for $IA(AlF_3) = 109\ kcal \cdot mol^{-1}$. As a compromise, we adopt $IA(AlF_3) = 125 \pm 25$ and $\Delta_fH°(AlF_4^-, g, 298.15\ K) = -476 \pm 25\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Vibrational frequencies are from Raman spectra of AlF_4^- observed in molten salt mixtures of AlF_3 with NaF or KF.[8] Similar spectra were observed in mixtures of AlF_3 with LiF.[9] The spectra[8] are consistent with T_d symmetry except for some asymmetry in ν_3 which was attributed to influence of the metal ion. By analogy with SiF_4,[2] we assume a singlet electronic ground state and neglect excited states. The bond distance is that derived from high–temperature electron diffraction[10] of $NaAlF_4(g)$. Within experimental uncertainty, the AlF_4 grouping was found to be tetrahedral.[2,10] The principal moments of inertia are $I_A = I_B = I_C = 24.0280 \times 10^{-39}\ g\ cm^2$.

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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⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_fH°$ (kJ·mol⁻¹)	$\Delta_fG°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−16.981	−1980.178		
100	46.882	225.025	357.855	−13.283			
200	68.417	264.662	301.864	−7.440			
250	76.195	280.796	296.068	−3.818			
298.15	82.157	294.747	294.747	0.	−1991.584	−1943.855	340.555
300	82.359	295.256	294.749	0.152	−1991.631	−1943.558	338.404
350	87.157	308.328	295.770	4.395	−1992.840	−1935.449	288.850
400	90.872	320.219	298.094	8.850	−1993.959	−1927.173	251.663
450	93.760	331.096	301.166	13.469	−1995.016	−1918.761	222.724
500	96.025	341.097	304.666	18.216	−1996.036	−1910.233	199.561
600	99.261	358.912	312.259	27.992	−1998.020	−1892.886	164.790
700	101.387	374.383	320.053	38.031	−2000.010	−1875.206	139.930
800	102.844	388.022	327.714	48.247	−2002.073	−1857.238	121.265
900	103.881	400.199	335.103	58.586	−2004.262	−1839.003	106.733
1000	104.643	411.185	342.171	69 014	−2017.208	−1819.757	95.054
1100	105.218	421.187	348.907	79.508	−2019.407	−1799.905	85.470
1200	105.661	430.362	355.318	90.053	−2021.607	−1779.853	77.475
1300	106.010	438.834	361.420	100.637	−2023.815	−1759.618	70.702
1400	106.289	446.700	367.234	111.253	−2026.035	−1739.212	64.891
1500	106.516	454.042	372.779	121.893	−2028.269	−1718.646	59.849
1600	106.702	460.922	378.075	132.555	−2030.519	−1697.932	55.432
1700	106.858	467.396	383.141	143.233	−2032.785	−1677.075	51.530
1800	106.989	473.507	387.993	153.925	−2035.066	−1656.086	48.058
1900	107.100	479.295	392.648	164.630	−2037.359	−1634.969	44.948
2000	107.195	484.791	397.119	175.345	−2039.660	−1613.731	42.146
2100	107.277	490.023	401.419	186.069	−2041.964	−1592.378	39.608
2200	107.348	495.015	405.561	196.800	−2044.265	−1570.915	37.298
2300	107.411	499.789	409.555	207.538	−2046.557	−1549.347	35.187
2400	107.465	504.361	413.410	218.282	−2048.834	−1527.681	33.249
2500	107.514	508.749	417.137	229.031	−2051.088	−1505.920	31.464
2600	107.557	512.967	420.742	239.784	−2053.312	−1484.069	29.815
2700	107.595	517.027	424.233	250.542	−2055.501	−1462.133	28.287
2800	107.629	520.940	427.618	261.303	−2351.550	−1439.150	26.848
2900	107.660	524.718	430.901	272.068	−2352.555	−1406.546	25.335
3000	107.688	528.368	434.090	282.835	−2353.508	−1373.909	23.922
3100	107.713	531.899	437.188	293.605	−2354.406	−1341.241	22.600
3200	107.736	535.320	440.201	304.378	−2355.244	−1308.544	21.360
3300	107.757	538.635	443.134	315.152	−2356.020	−1275.823	20.195
3400	107.776	541.852	445.991	325.929	−2356.732	−1243.079	19.098
3500	107.794	544.977	448.774	336.708	−2357.377	−1210.314	18.063
3600	107.810	548.014	451.489	347.488	−2357.955	−1177.533	17.086
3700	107.824	550.968	454.138	358.269	−2358.465	−1144.736	16.161
3800	107.838	553.843	456.724	369.053	−2358.907	−1111.927	15.285
3900	107.851	556.645	459.250	379.837	−2359.282	−1079.106	14.453
4000	107.862	559.375	461.720	390.623	−2359.588	−1046.277	13.663
4100	107.873	562.039	464.134	401.409	−2359.828	−1013.441	12.911
4200	107.883	564.638	466.496	412.197	−2360.003	−980.600	12.196
4300	107.892	567.177	468.808	422.986	−2360.114	−947.756	11.513
4400	107.901	569.658	471.072	433.776	−2360.163	−914.910	10.861
4500	107.909	572.082	473.290	444.566	−2360.148	−882.063	10.239
4600	107.917	574.454	475.464	455.358	−2360.077	−849.218	9.643
4700	107.924	576.775	477.594	466.150	−2359.950	−816.374	9.073
4800	107.931	579.047	479.684	476.942	−2359.768	−783.534	8.527
4900	107.937	581.273	481.735	487.736	−2359.533	−750.698	8.003
5000	107.943	583.454	483.748	498.530	−2359.249	−717.868	7.500
5100	107.949	585.591	485.724	509.324	−2358.918	−685.043	7.016
5200	107.954	587.688	487.665	520.120	−2358.543	−652.225	6.552
5300	107.959	589.744	489.571	530.915	−2358.126	−619.415	6.105
5400	107.964	591.762	491.445	541.711	−2357.669	−586.614	5.674
5500	107.968	593.743	493.287	552.508	−2357.175	−553.822	5.260
5600	107.972	595.688	495.098	563.305	−2356.647	−521.037	4.860
5700	107.976	597.600	496.880	574.102	−2356.087	−488.265	4.474
5800	107.980	599.477	498.633	584.900	−2355.495	−455.501	4.102
5900	107.984	601.323	500.358	595.698	−2354.880	−422.747	3.743
6000	107.987	603.138	502.055	606.497	−2354.218	−390.007	3.395

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

Lithium Tetrafluoroaluminate (LiAlF$_4$) IDEAL GAS M_r = 109.916152

$S°$(298.15 K) = [326.5 ± 8] J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = −1846 ± 12 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = −1854 ± 12 kJ·mol^{-1}

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
817(1)	560 (1)	220 (1)	911 (1)	[157](1)	450(1)
608(1)	[361](1)	[269](1)	316 (1)	644(1)	270(1)

Ground State Quantum Weight: [1] σ = [2]
Point Group: [C$_{2v}$]
Bond Distances: Al–F$_{br}$ = Al–F$_{ter}$ = [1.69 ± 0.02] Å; Li–F$_{br}$ = [1.68] Å
Bond Angles. F$_{br}$–Al–F$_{br}$ = [110]°; F$_{ter}$–Al–F$_{ter}$ = [109.47]°; F$_{br}$–Li–F$_{br}$ = [110.98]°
Product of the Moments of Inertia: $I_A I_B I_C$ = 1.887733 x 10^{-113} g^3·cm^6

Enthalpy of Formation

Mass spectrometric studies[1 2 3] indicate that the vapor above the LiF–AlF$_3$ system is composed mainly of LiAlF$_4$, (LiAlF$_4$)$_2$, and Li$_3$AlF$_5$ with LiAlF$_4$ being the major component, 90% according to[1] or 77% according to.[3] For (LiAlF$_4$)$_2$(g) = 2 LiAlF$_4$(g), ln K_p = −48500/RT + 33.5/R at 946 K.[3] This is in agreement with the equilibrium constant for the dimer–monomer equilibrium of the sodium analog[4 5] which has been determined over a wider temperature range. As a first approximation, we ignore any gaseous species other than LiAlF$_4$(g) and (LiAlF$_4$)2 (g) and adjust the total pressure measurements over the LiF–AlF$_3$ system to the partial pressure of LiAlF$_4$(g) by assuming that ln K_p = −43900/RT + 28.50/R for the (NaAlF$_4$)$_2$(g) = 2 NaAlF$_4$(g) equilibrium[5] also represents the equilibrium of the lithium analog. Rao[6] has made a similar assumption.

$\Delta_f H°$(298.15 K) results from our 3rd law analysis of pressure measurements and equilibrium constants of the following:

[1] Li$_2$F$_2$(g) + AlF$_3$(g) = LiF(g) + LiAlF$_4$(g)
[2] Li$_3$AlF$_6$(cr) = 2 LiF(cr) + LiAlF$_4$(g)
[3] 1/3 Li$_3$AlF$_4$(cr) = 2/3 AlF$_3$(cr) + LiAlF$_4$(g)
[4] LiAlF$_4$(g) = LiF(g) + AlF$_3$(g)
[5] LiF(l) + AlF$_3$(cr) = LiAlF$_4$(g)

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)[a] kcal·mol^{-1}
Porter and Zeller[7]	Mass Spec	1	1000–1100	−0.86	−6.036	−4.9	−438.95
Hildenbrand *et al.*[8]	Torsion–Effusion	2	987–1058	101.93	68.86	−32.3	−444.94
		3(cell 7)	899–980	71.10	66.97	−4.4	−443.27
		3(cell 9)	873–976	67.28	67.10	−0.2	−443.13
		3(cell 15x)	854–980	67.53	67.23	−0.3	−443.00
Rao[6]	Effusion	3	872–979	68.59	67.27	−1.4	−442.97
Shol'ts and Sidorov[3]	Mass Spec	3	946		68.28		−441.95
Sidorov *et al.*[9]	Mass Spec	4	946		72.02		−442.51
Dewing[10]	b	5	1293		59.155		−444.93

a. From third low heat of reaction plus auxiliary data.[11]

b. Dewing has determined activities of LiF and AlF$_3$ in LiF–AlF$_3$ melts and combined them with the vapor pressure measurement over the melts of Kuxmann and Tillessen[12] and Chin[13] to obtain an equilibrium constant for Reaction 5.

We give more weight to the results which lead to reasonable agreement in 2nd and 3rd law enthalpies of reaction and adopt $\Delta_f H°$(LiAlF$_4$, g, 298.15 K) = −443 ± 3 kcal·mol^{-1}.

Heat Capacity and Entropy

We adopt the structural and vibrational frequency assignments given by Huglen *et al.*[14] While the C$_{2v}$ structure has not been conclusively established, it is strongly supported by the interpolation of the infra–red spectroscopic studies,[14] by an electron diffraction study of NaAlF$_4$,[15] and by ab initio molecular orbital calculations.[16] The C$_{2v}$ structure consists of an irregular AlF$_4$ tetrahedron combined with Li to form a planar ring, AlF$_2$Li, through coordination with two fluorines. Thus luminum forms two types of bonds, Al–F$_{bridge}$ and Al–F$_{terminal}$, considered by Huglen *et al.*[14] to be the same length. A C$_s$ structure and two C$_{3v}$ structures have also been considered.

The AlF$_4$ tetrahedral angles and the Al–F$_{br}$ and Al–F$_{ter}$ bond distances are those from an electron diffraction study of NaAlF$_4$.[15] These are assumed to be the same for LiAlF$_4$. The Li–F$_{br}$ bond length is estimated.[17] The F$_{br}$–Al–F$_{br}$ and the F$_{ter}$–Al–F$_{ter}$ angles are from the sodium analog;[17] the F$_{br}$–Li–F$_{br}$ angle results from the adopted dimensions. The slightly different dimensions for the LiAlF$_4$ C$_{2v}$ structures used by Cyvin[17] lead to a $S°$(298.15 K) value 0.12 cal·K·mol^{-1} less than the adopted values. The dimensions derived by Curtiss[16] in his ab initio study are quite different, but $S°$(298.15 K) is only 0.20 cal·K·mol^{-1} greater.

Nine vibrational frequencies were assigned by Huglen *et al.*[14] from infra–red matrix–isolation studies; the remaining three were calculated by force field analysis.[14]

The principal moments of inertia are I_A = 24.1060 × 10^{-39}, I_B = 27.9447 × 10^{-39} and I_C = 28.0231 × 10^{-39} g·cm^2.

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Lithium Tetrafluoroaluminate (LiAlF$_4$) Al$_1$F$_4$Li$_1$(g)

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0	0.	0.	INFINITE	−19.620	−1846.320	−1846.320	INFINITE
90	52.024	244.477	401.931	−15.745	−1849.239	−1838.179	960.167
200	81.507	290.240	335.102	−8.972	−1851.967	−1825.960	476.892
250	91.971	309.600	328.099	−4.625	−1852.866	−1819.349	380.132
298.15	99.790	326.497	326.497	0.	−1853.512	−1812.832	317.601
300	100.052	327.116	326.499	0.185	−1853.533	−1812.579	315.598
350	106.249	343.025	327.742	5.349	−1854.045	−1805.712	269.488
400	111.011	357.537	330.573	10.786	−1854.480	−1798.777	234.896
450	114.701	370.835	334.318	16.433	−1854.894	−1791.789	207.985
500	117.591	383.075	338.590	22.243	−1858.320	−1784.448	186.420
600	121.719	404.907	347.868	34.223	−1859.005	−1769.606	154.058
700	124.434	423.888	357.402	46.540	−1859.564	−1754 661	130.934
800	126.299	440.633	366.780	59.082	−1860.118	−1739.638	113.587
900	127.627	455.589	375.832	71.782	−1860.759	−1724.541	100.090
1000	128.603	469.089	384.493	84.596	−1872.126	−1708.605	89.248
1100	129.340	481.383	392.751	97.495	−1872.723	−1692.224	80.357
1200	129.909	492.662	400.614	110.458	−1873.303	−1675.789	72.945
1300	130.357	503.079	408.100	123.472	−1873.874	−1659.306	66.672
1400	130.716	512.753	415.234	136.527	−1874.442	−1642.780	61.293
1500	131.008	521.782	422.039	149.613	−1875.010	−1626.213	56.630
1600	131.248	530.244	428.540	162.726	−1875.578	−1609.608	52.548
1700	131.448	538.207	434.760	175.862	−2021.386	−1585.791	48.725
1800	131.616	545.726	440.717	189.015	−2021.208	−1560.173	45.275
1900	131.759	552.846	446.433	202.184	−2021.040	−1534.565	42.188
2000	131.881	559.607	451.924	215.366	−2020.878	−1508.965	39.410
2100	131.987	566.044	457.207	228.560	−2020.721	−1483.373	36.897
2200	132.079	572.187	462.294	241.763	−2020.561	−1457.789	34.612
2300	132.159	578.060	467.201	254.975	−2020.396	−1432.212	32.527
2400	132.229	583.686	471.938	268.194	−2020.220	−1406.642	30.615
2500	132.292	589.085	476.517	281.421	−2020.027	−1381.081	28.856
2600	132.347	594.275	480.947	294.653	−2019.812	−1355.527	27.233
2700	132.396	599.270	485.237	307.890	−2019.572	−1329.982	25.730
2800	132.441	604.086	489.396	321.132	−2313.202	−1303.479	24.317
2900	132.480	608.734	493.432	334.378	−2311.802	−1267.442	22.829
3000	132.516	613.226	497.350	347.628	−2310.365	−1231.454	21.442
3100	132.549	617.572	501.159	360.881	−2308.890	−1195.515	20.144
3200	132.578	621.781	504.863	374.137	−2307.373	−1159.623	18.929
3300	132.605	625.861	508.468	387.396	−2305.814	−1123.780	17.788
3400	132.630	629.820	511.979	400.658	−2304.212	−1087.985	16.715
3500	132.652	633.665	515.401	413.922	−2302.568	−1052.237	15.704
3600	132.673	637.402	518.738	427.188	−2300.881	−1016.537	14.750
3700	132.692	641.037	521.995	440.457	−2299.153	−980.884	13.848
3800	132.709	644.576	525.174	453.727	−2297.385	−945.280	12.994
3900	132.725	648.024	528.280	466.998	−2295.578	−909.721	12.184
4000	132.740	651.384	531.316	480.272	−2293.734	−874.209	11.416
4100	132.754	654.662	534.285	493.547	−2291.857	−838.745	10.686
4200	132.767	657.861	537.189	506.823	−2289.948	−803.326	9.991
4300	132.779	660.985	540.032	520.100	−2288.011	−767.953	9.329
4400	132.791	664.038	542.816	533.378	−2286.027	−732.627	8.697
4500	132.801	667.022	545.543	546.658	−2284.030	−697.345	8.095
4600	132.811	669.941	548.215	559.939	−2282.018	−662.108	7.518
4700	132.820	672.798	550.836	573.220	−2279.989	−626.914	6.967
4800	132.829	675.594	553.406	586.503	−2277.947	−591.764	6.440
4900	132.837	678.333	555.928	599.786	−2275.895	−556.656	5.934
5000	132.845	681.017	558.403	613.070	−2273.839	−521.591	5.449
5100	132.852	683.647	560.833	626.355	−2271.776	−486.567	4.983
5200	132.859	686.227	563.219	639.640	−2269.721	−451.582	4.536
5300	132.865	688.758	565.564	652.927	−2267.673	−416.638	4.106
5400	132.871	691.242	567.869	666.214	−2265.636	−381.732	3.693
5500	132.877	693.680	570.134	679.501	−2263.614	−346.864	3.294
5600	132.882	696.074	572.362	692.789	−2261.612	−312.031	2.911
5700	132.887	698.426	574.553	706.077	−2259.634	−277.236	2.541
5800	132.892	700.737	576.709	719.366	−2257.681	−242.474	2.184
5900	132.897	703.009	578.830	732.656	−2255.763	−207.745	1.839
6000	132.901	705.243	580.918	745.946	−2253 859	−173.051	1.507

PREVIOUS. December 1979 (1 atm) CURRENT December 1979 (1 bar)

Lithium Tetrafluoroaluminate (LiAlF$_4$) Al$_1$F$_4$Li$_1$(g)

Sodium Tetrafluoroaluminate ($NaAlF_4$) IDEAL GAS M_r = 125.964922 Sodium Tetrafluoroaluminate ($NaAlF_4$) $Al_1F_4Na_1(g)$

$S°(298.15\ K) = 344.9 \pm 8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1834 \pm 12\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1841 \pm 12\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
808(1)	[291](1)	893(1)	669(1)
613(1)	[180](1)	304(1)	339(1)
378(1)	[269](1)	[102](1)	[200](1)

Ground State Quantum Weight: [1] σ = [2]
Point Group: [C_{2v}]
Bond Distances: $Al–F_{br} = Al–F_{ter} = 1.69 \pm 0.02$ Å; $Na–F_{br} = 2.11 \pm 0.02$ Å
Bond Angles: $F_{br}–Al–F_{br} = 110°$; $F_{ter}–Al–F_{ter}$ 109.47°; $F_{br}–Na–F_{br} = 82°$
Product of the Moments of Inertia: $I_AI_BI_C = 4.775246 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is based on our 3rd law analysis of pressure measurements of the NaF–AlF_3 system for the equilibria:

[1] $Na_3AlF_6(cr, \beta) = 2\ NaF(cr) + NaAlF_4(g)$
[2] $Na_3AlF_6(l) = 02\ NaF(l) + NaAlF_4(g)$
[3] $0.2\ Na_5Al_3F_{14}(cr) + 0.4\ AlF_3(cr) = NaAlF_4(g)$
[4] $0.5\ Na_5Al_3F_{14}(cr) = 0.5\ Na_3AlF_6(cr, \beta) + NaAlF4(g)$

The mass–spectrometric measurements of Sidorov *et al.*[1] showed that the most important species over solid phases in the NaF–AlF_3 system are $NaAlF_4(g)$ and the dimer $[NaAlF_4]_2(g)$. We ignore any other gaseous species in our data treatment. The enthalpy and entropy for the $[NaAlF_4]_2(g) = 2\ NaAlF_4(g)$ dissociation have been determined.

Investigator	T/K	$\Delta_{dso}H°$, cal·mol^{-1}	$\Delta_{dso}S°$, cal·K^{-1}·mol^{-1}
Sidorov and Kolosov[2]	910	42600	27.14
Shol'ts and Sidorov[3]	910	45000	33.6
Grjotheim, Kvande, and Motzfeldt[4]	1190–1420	43900	28.50

A plot of ln K_p vs 1/T shows Sidorov and Kolosov[2] and Grjotheim *et al.*[4] to be in excellent agreement. We use $\ln K_p = -43900/RT + 28.50/R$ to calculate the mole fraction $NaAlF_4$ monomer in the gas in order to correct the total pressure over the NaF–AlF_3 system to the partial pressure of monomer for the 3rd law analysis. The use of the total pressure rather than partial pressure leads to a heat of formation which is more negative by less than one kcal·mol^{-1}.

Source	Method	Reaction	T/K	$\Delta_r H°(298.15\ K)$ 2nd law	kcal·mol^{-1} 3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Sidorov and Kolosov[2]*	Mass Spec	1	900–1050	63.27	62.27	−1.5	−449.16
Shol'ts and Sidorov[3]	Mass Spec	1	1100		67.76		−443.68
Kolosov *et al.*[5]	Mass Spec	1	910		65.78		−445.66
Grjotheim *et al.*[6]	Effusion	3	840–960	65.14	65.49	0.4	−440.03
Shol'ts and Sidorov[3]	Mass Spec	3	910		65.98		−439.54
Kolosov *et al.*[5]	Mass Spec	3	910		66.90		−439.43
Grjotheim *et al.*[6]	Effusion	4	840–960	66.41	70.21	4.3	−439.35
Kolosov *et al.*[5]	Mass Spec	4	910		71.62		−437.94

*Partial pressures by the investigator.

The total vapor pressure over molten cryolite, reaction [2], measured by effusion by Grjotheim *et al.*,[4] corrected to monomer partial pressure, leads to $\Delta_f H°(NaAlF_4, g, 298.15\ K) = -447.70$ kcal·mol^{-1}. Unit activity of NaF in molten cryolite was used in this calculation so that −447.70 kcal·mol^{-1} is a lower limit. There is no evident explanation for the more negative grouping of heats of formation from reactions [1] and [2] compared with the grouping from reactions [3] and [4].

In view of the difficulties and uncertainties in working with the NaF–AlF_3 system, we adopt $\Delta_f H°(NaAlF_4, g, 298.15\ K) = -440 \pm 3$ kcal·mol^{-1}.

Heat Capacity and Entropy

The adopted structure, C_{2v}, consists of an irregular AlF_4 tetrahedron combined with Na to form the planar ring, AlF_2Na, through coordination with two fluorines. The Al atom forms two types of bonds, $Al–F_{bridge}$ and $Al–F_{terminal}$, which are of the same length.[8] Other structures have been considered, a C_s symmetry in which the ring is not planar and two C_{3v} structures where the Na is coordinated with one or three fluorines, but interpretation of the infra–red spectra supports the C_{2v} model.[9]

The bond distances and bond angles are from the electron diffraction study of Spiridonov and Erokin.[8] Seven vibrational frequencies were assigned from infrared matrix–isolation studies by Huglen *et al.*,[9] the remaining five were calculated by force field analysis.[9] The principal moments of inertia are $I_A = 24.1060 \times 10^{-39}$, $I_B = 44.4685 \times 10^{-39}$, and $I_C = 44.5470 \times 10^{-39}\ g \cdot cm^2$.

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

T/K	$C_p°$ (J·K^{-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	−21.223	−1833.547	−1833.547	INFINITE
100	59.284	255.634	425.562	−16.993	−1836.954	−1825.364	953.472
200	87.953	306.516	353.949	−9.487	−1839.564	−1812.638	473.412
250	97.151	327.177	346.571	−4.849	−1840.369	−1805.808	377.303
298.15	103.954	344.896	344.896	0.	−1840.960	−1799.096	315.194
300	104.182	345.539	344.898	0.193	−1840.980	−1798.836	313.205
350	109.570	362.022	346.187	5.542	−1841.496	−1791 771	267.407
400	113.718	376.936	349.113	11.129	−1844.612	−1784.428	233.022
450	116.938	390.523	352.971	16.899	−1845.043	−1776.878	206.255
500	119.464	402.980	357.358	22.811	−1845.395	−1769.285	184.836
600	123.080	425.105	366.852	34.952	−1845.954	−1754.008	152.700
700	125.464	444.269	376.573	47.387	−1846.421	−1738.646	129.739
800	127.102	461.135	386.111	60.020	−1846.897	−1723.218	112.515
900	128.270	476.177	395.298	72.791	−1847.462	−1707.725	99.114
1000	129.129	489.738	404 075	85.663	−1858.773	−1691.402	88.350
1100	129 778	502.077	412.432	98.610	−1859.349	−1674 637	79.522
1200	130.279	513.392	420.380	111.614	−1956.723	−1655.378	72.057
1300	130.674	523.836	427.942	124.663	−1956.466	−1630.277	65.505
1400	130.990	533.532	435.142	137.746	−1956.218	−1605.195	59.891
1500	131.247	542.578	442.006	150.859	−1955.980	−1580.130	55.025
1600	131.459	551.056	448.559	163.994	−1955 756	−1555.081	50.768
1700	131.635	559.031	454.826	177.149	−1955.545	−1530.045	47.013
1800	131.783	566.559	460.826	190.320	−1955.348	−1505.021	43.675
1900	131.909	573.688	466.580	203.505	−1955.161	−1480.009	40.688
2000	132.017	580.457	472.106	216.701	−1954.982	−1455.005	38.001
2100	132.110	586.900	477.420	229.908	−1954.806	−1430.011	35.570
2200	132.191	593.048	482.537	243.123	−1954.627	−1405.025	33.360
2300	132.262	598.926	487.471	256.346	−1954.440	−1380.047	31.342
2400	132.324	604.556	492.233	269.575	−1954.240	−1355.077	29.492
2500	132.379	609.959	496.835	282.810	−1954.019	−1330.117	27.791
2600	132.428	615.152	501.286	296.051	−1953.773	−1305.165	26.221
2700	132.471	620.150	505.596	309.296	−1953.496	−1280.224	24.767
2800	132.510	624.969	509.774	322.545	−2247.085	−1254.326	23 400
2900	132.545	629.619	513.827	335 798	−2245.638	−1218.895	21.955
3000	132.577	634.113	517.762	349.054	−2244.148	−1183.516	20.607
3100	132.605	638.461	521.586	362.313	−2242.612	−1148.187	19.347
3200	132.631	642.672	525.304	375.575	−2241.029	−1112.908	18.166
3300	132.655	646.753	528.923	388.839	−2239.397	−1077.679	17.058
3400	132.677	650.714	532.447	402.106	−2237.716	−1042.501	16.016
3500	132.697	654.560	535.882	415.374	−2235.986	−1007.372	15.034
3600	132.715	658.298	539.230	428.645	−2234.208	−972.294	14.108
3700	132.732	661.935	542.498	441.917	−2232.384	−937.266	13.232
3800	132.747	665.475	545.688	455.191	−2230.515	−902.288	12.403
3900	132.761	668.923	548.803	468.467	−2228.604	−867.359	11.617
4000	132.775	672.285	551.849	481.744	−2226.653	−832.480	10.871
4100	132.787	675.563	554.826	495.022	−2224.667	−797.651	10.162
4200	132.798	678.763	557.739	508.301	−2222.647	−762.869	9.488
4300	132.809	681.888	560.590	521.581	−2220.601	−728.138	8.845
4400	132.819	684.941	563.382	534.863	−2218.489	−693.456	8.232
4500	132.828	687 926	566.116	548.145	−2216.375	−658.821	7.647
4600	132.837	690.846	568.796	561.428	−2214.254	−624.232	7.088
4700	132.845	693.703	571.424	574.712	−2212.120	−589.689	6.554
4800	132.853	696.500	574.000	587.997	−2209.979	−555.192	6.042
4900	132.860	699.239	576.528	601.283	−2207.834	−520.740	5.551
5000	132.867	701.923	579.010	614.569	−2205.686	−486.332	5.081
5100	132.873	704.555	581.445	627.856	−2203.550	−451.966	4.629
5200	132.879	707.135	583.838	641.144	−2201.428	−417.641	4.195
5300	132.885	709.666	586.188	654.432	−2199.323	−383.358	3.778
5400	132.890	712.150	588.498	667.721	−2197.242	−349.114	3.377
5500	132.895	714.588	590.768	681.010	−2195.189	−314.909	2.991
5600	132.900	716.983	593.001	694.300	−2193.169	−280.740	2.619
5700	132.904	719.335	595.197	707.590	−2191.187	−246.608	2.260
5800	132.909	721.647	597.357	720.881	−2189.246	−212.510	1.914
5900	132.913	723.919	599.483	734.172	−2187.354	−178.443	1.580
6000	132.917	726.153	601.575	747.463	−2185.335	−144.431	1.257

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

Sodium Tetrafluoroaluminate ($NaAlF_4$) $Al_1F_4Na_1(g)$

Potassium Hexafluoroaluminate (K_3AlF_6) CRYSTAL $M_r = 258.266858$

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = [284.5 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-3326 \pm 21]\ kJ \cdot mol^{-1}$

$T_{fus} = 1293\ K$ $\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

$\Delta_f H°(K_3AlF_6$, cr, 298.15 K) is calculated from $\Delta_r H° = -30.2\ kcal \cdot mol^{-1}$ for the reaction, $AlF_3(cr) + 3\ KF(cr) = K_3AlF_6(cr)$, which was estimated by comparison with the values of $\Delta_r H°$ of the similar reactions for $Na_3AlF_6(cr)$, $Na_3AlCl_6(cr)$ and $K_3AlCl_6(cr)$.

Heat Capacity and Entropy

Heat capacities are estimated by the addition of a correction term $3(M_{KI}-M_{NaI})$ to the corresponding values for $Na_3AlF_6(cr)$ where M denotes heat capacity. In a similar manner, $S°(298.15\ K)$ is calculated to be $68 \pm 1\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

T_{fus} was determined from Hall and Insley.[1]

Reference

[1] F. P. Hall and H. Insley, J. Am. Ceram. Soc. 21, 113 (1938).

Potassium Hexafluoraluminate (K_3AlF_6) $Al_1F_6K_3(cr)$

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	222.798	284.512	284.512	0.	−3326.280	−3163.447	554.223
300	223.384	285.892	284.516	0.413	−3326.250	−3162.437	550.629
400	241.082	352.662	293.500	23.665	−3331.598	−3106.741	405.699
500	255.308	408.026	311.022	48.502	−3328.814	−3050.825	318.718
600	267.399	455.652	331.248	74.642	−3324.948	−2995.574	260.788
700	278.905	497.740	352.082	101.960	−3320.120	−2941.047	219.464
800	290.077	535.740	372.702	130.431	−3314.390	−2887.274	188.520
900	298.738	570.425	392.772	159.888	−3307.984	−2834.264	164.496
1000	305.432	602.254	412.151	190.103	−3311.793	−2781.230	145.277
1100	311.290	631.646	430.786	220.946	−3541.341	−2714.695	128.910
1200	316.310	658.953	448.676	252.333	−3530.603	−2640.016	114.917
1300	320.390	684.437	465.842	284.173	−3519.481	−2566.249	103.113
1400	323.842	708.311	482.318	316.390	−3508.049	−2493.351	93.028
1500	326.509	730.746	498.139	348.910	−3496.374	−2421.279	84.316
1600	328.862	751.895	513.345	381.681	−3484.506	−2349.992	76.719
1700	330.954	771.898	527.971	414.676	−3472.470	−2279.452	70.039
1800	332.628	790.864	542.053	447.858	−3460.298	−2209.625	64.122
1900	333.883	808.883	555.627	481.187	−3448.026	−2140.478	58.846
2000	334.720	826.033	568.722	514.621	−3435.694	−2071.978	54.115

PREVIOUS: September 1963 CURRENT: December 1963

Potassium Hexafluoraluminate (K_3AlF_6) $Al_1F_6K_3(cr)$

Lithium Hexafluoroaluminate (Li_3AlF_6) CRYSTAL(β–γ–δ–ε) $M_r = 161.794958$ Lithium Hexafluoroaluminate (Li_3AlF_6) $Al_1F_6Li_3(cr)$

$\Delta_fH°(0\ K) = -3370.9 \pm 4.6\ kJ\cdot mol^{-1}$
$\Delta_fH°(298.15\ K) = -3383.6 \pm 4.6\ kJ\cdot mol^{-1}$
$\Delta_{trs1}H° = [2.092]\ kJ\cdot mol^{-1}$
$\Delta_{trs2}H° = [1.255]\ kJ\cdot mol^{-1}$
$\Delta_{trs3}H° = [0.418]\ kJ\cdot mol^{-1}$
$\Delta_{fus}H° = 86.19 \pm 4.2\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = 187.89 \pm 0.21\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{trs1}\ (\beta \rightarrow \gamma) = 748\ K$
$T_{trs2}\ (\gamma \rightarrow \delta) = 848\ K$
$T_{trs3}\ (\delta \rightarrow \epsilon) = 978\ K$
$T_{fus} = 1058 \pm 3\ K$

Enthalpy of Formation

$\Delta_fH°$ is derived from $\Delta_fH°(298.15\ K) = -5.4 \pm 0.5\ kcal\cdot mol^{-1}$ for the reaction $3\ LiF(cr) + AlF_3(cr) \rightarrow Li_3AlF_6(\alpha,\ \beta\ mixture)$. Greene *et al.*[1] obtained this result by heating the fluorides under standardized conditions in a small electrical furnace contained in their calorimeter at 25°C. $\Delta_fH°$ includes a small endothermic effect observed during heating of the reaction product. The authors suggest that the enthalpy of conversion between the α– and β– forms is small and thus their result should apply to both forms.

Heat Capacity and Entropy

Furukawa *et al.*[2] measured $C_p°$ (15–370 K) using a sample prepared by stoichiometric proportions of LiF and AlF_3 in graphite. X-ray diffraction and petrographic examination of separate portions of the sample indicated a single phase identified as β–Li_3AlF_6. The authors tabulated values of $C_p°$ and $S°$ based on their data and the extrapolation $S°(15\ K) = 0.042\ cal\cdot K^{-1}\cdot mol^{-1}$. These values are adopted.

Douglas and Neufer[3] reported relative enthalpy data (323–973 K) for part of the same sample used in measurement of $C_p°$.[2] Their study was made prior to discovery of the five crystalline phases, and their drop-calorimetric data reveal only the transition near 748 K. Reinterpretation of the data above 748 K is complicated by the proximity of the furnace temperatures to the transition temperatures and by the tendency of high– temperature forms to revert to both α– and β– forms under different conditions of cooling. Bjorge and and Jenssen[4] and Rolin *et al.*[5] also reported crystalline enthalpy data, but these are relatively imprecise and include similar uncertainties in the final state after the drop. These difficulties preclude the derivation of accurate heat capacities for the high-temperature forms.

$C_p°$ for the β– form is adopted from,[2, 3] since the two methods are in good agreement. The curve is extrapolated linearly above 748 K to obtain $C_p°$ for the high-temperature forms. Obvious differences in $C_p°$ are not apparent in the observed data for the different forms, so this should be an adequate approximation.

Transition Data

Existence of five polymorphic forms was shown by high– temperature X-ray diffraction[1, 6, 7] and differential thermal analysis.[6, 7] Both α– and β– forms persisted at room temperature, but the α– form appeared only on quenching of high-temperature forms.[1] The α– form transformed to β near 490 K,[1, 6] but the reverse transformation was not observed. Single-crystal X-ray diffraction showed the α– form to be orthorhombic.[8]

The adopted values of T_{trs} are the lowest temperatures at which the high-temperature form was observed growing at the expense of the low-temperature form.[1] DTA data[6, 7] were higher by roughly 30 K for T_{trs1} and 25 K for T_{trs2}. Combination of the observed enthalpies[3] with the adopted $C_p°$ yields $\Delta_{trs1}H° = 0.76$ and $\Delta_{trs2}H° = 0.03$ or $0.15\ kcal\cdot mol^{-1}$; we prefer to adopt $\Delta_{trs}H°$ values (0.5 and 0.3 $kcal\ mol^{-1}$) which are more consistent with the areas of peaks in the DTA curve.[7] Evidence suggests that $\Delta_{trs3}H°$ is small, so we estimate $0.1\ kcal\cdot mol^{-1}$.

Fusion Data

Refer to the liquid table for details.

References

[1] P. D. Greene, P. Gross and C. Hayman, Trans. Faraday Soc. 64, 633 (1968).
[2] G. T. Furukawa, W. G. Saba and J. C. Ford, U. S. Nat. Bur. Stand. Report 10074, 47, (July 1, 1969).
[3] T. B. Douglas and J. E. Neufer, U. S. Nat. Bur Stand. Report 8186, p. 68, (January 1, 1964).
[4] B. Bjorge and B. Jenssen, Acta Chem. Scand. 22, 1347 (1968).
[5] M. Rolin, H. Latreille and H. Pham, Bull Soc Chim. Fr. 1969 (7), 2271.
[6] G. Garton and B. M. Wanklyn, J. Inorg Nucl. Chem. 27, 2466 (1965).
[7] J. L. Holm, Acta Chem. Scand. 20, 1167 (1966).
[8] J. H. Burns, A. C. Tennissen and G D. Brunton, Acta Cryst. B24, 225 (1968).

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−32.146	−3370.866	−3370.866	INFINITE
100	70.982	38.225	333.657	−29.543	−3378.953	−3328.763	1738.767
200	156.222	115.960	205.121	−17.832	−3383.356	−3276.431	855.716
298.15	202.506	187.891	187.891	0.	−3383.601	−3223.790	564.795
300	203.133	189.145	187.895	0.375	−3383.581	−3222.799	561.139
400	229.869	251.549	196.222	22.131	−3381.793	−3169.443	413.887
500	248.111	304.904	212.753	46.075	−3388.377	−3115.708	325.496
600	262.295	351.440	232.072	71.621	−3384.937	−3061.477	266.525
700	274.052	392.779	252.131	98.453	−3380.383	−3007.913	224.453
748.000	279.073	411.132	261.751	111.737	BETA <––> GAMMA		
748 000	279.073	413.929	261.751	113.829	TRANSITION		
800	284.512	432.865	272.262	128.482	−3372.851	−2955.211	192.956
848.000	289.533	449.589	281.830	142.259	GAMMA <––> DELTA		
848.000	289.533	451.069	281.830	143.515	TRANSITION		
900	294.972	468.460	292.114	158.712	−3365.399	−2903.447	168.512
978.000	303.131	493.311	307.178	182.038	DELTA <––> EPSILON		
978.000	303.131	493.739	307.178	182.456	TRANSITION		
1000	305.432	500.508	311.357	189.150	−3368.604	−2851.735	148.959
1058.000	311 499	517.898	322.206	207.041	––– EPSILON <––> LIQUID –––		
1100	315.892	530.109	329.912	220.217	−3360.516	−2800.432	132.981
1200	326.352	558.044	347.770	252.329	−3351.444	−2749.908	119.700
1300	336.812	584.579	364.974	285.487	−3341.386	−2700.181	108.495
1400	347.272	609.922	381.571	319.691	−3330.327	−2651.266	98.920
1500	357.732	634.238	397.611	354.941	−3318.256	−2603.177	90.651
1600	368.192	657.660	413.136	391.238	−3305.169	−2555.926	83.442

PREVIOUS: December 1963 CURRENT: June 1970

Lithium Hexafluoroaluminate (Li_3AlF_6) LIQUID $M_r = 61.794958$

$S°(298.15\ K) = [245.847]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$T_{fus} = 1058 \pm 3\ K$

$\Delta_f H°(298.15\ K) = [-3317.640]\ kJ{\cdot}mol^{-1}$

$\Delta_{fus}H° = 86.190 \pm 4.2\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Li_3AlF_6,\ l,\ 298.15\ K)$ is calculated from $\Delta_f H°(Li_3AlF_6,\ l,\ 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1058\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Relative enthalpy data were measured by Bjorge and Jenssen[1] from 1065 to 1088 K and by Rolin *et al.*[2] from about 1075 to 1145 K. The data are consistent with liquid heat capacities in the range from roughly 82 to 92 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ We adopt the me,uccirclan value of 86 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ ($359.824\ J{\cdot}K^{-1}{\cdot}mol^{-1}$) and extrapolate this to higher and lower temperatures. A glass transition is assumed at 750 K and $C_p°$ at lower temperatures is taken to be the same as that of β–Li_3AlF_6.

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

Fusion Data

T_{fus} was observed at 780°C,[3] 782°C,[2,4] 783°C[5,8] and 785°C.[1] The last and highest value is adopted for this table. Combination of the observed liquid enthalpies with the adopted crystal enthalpies yields values for $\Delta_{fus}H°$ of 19.7 $kcal{\cdot}mol^{-1}$ [1] (authors gave 20.2 ± 1.0) and 21.5 ± 0.3 $kcal{\cdot}mol^{-1}$ [2] (authors gave 21.5) *We adopt the mean value of* 20.6 kcal mol^{-1}(86.190 $kJ{\cdot}mol^{-1}$) which is confirmed by values of 20.7,[8] 20.8,[4] 22.2,[4] 20.1,[4] and 22.0[2] derived from crystal–liquid phase data for binary systems. The agreement among values for $\Delta_{fus}H°$ seemingly excludes the possibility of large discrepancies in the enthalpies due to formation of the α–phase instead of β during drop–calorimetry from high temperatures.

Vaporization Data

Li_3AlF_6 vaporizes mainly to $LiAlF_4(g)$ with small contributions from species such as $Li_2AlF_5(g)$, $Li_2F_2(g)$ and $LiF(g)$.[6,7]

References

[1] B. Bjorge and B. Jenssen, Acta Chem. Scand. **22**, 1347 (1968).
[2] R. Rolin, H. Latreille and H. Pham, Bull. Soc. Chim. Fr. **1969** (7), 2271.
[3] J. L. Holm, Acta Chem. Scand. **20**, 1167 (1967).
[4] M. Malinovsky, Chem. Zvesti **21**, 783 (1967); ibid. **21**, 794 (1967).
[5] G. Garton and B. Wanklyn, J. Inorg. Nucl. Chem. **27**, 2466 (1965).
[6] A. Buchler and J. Berkowitz-Mattuck, AD 653163, pp. 41–3, (June, 1967).
[7] R F. Porter and E. E. Zeller, J Chem. Phys. **33**, 858 (1960).
[8] T. Matsushima, Denki Kagaku Oyobi Kogyo Butsuri Kagaku (Electrochemistry and Industrial Physical Chemistry) **37**, 778 (1969).

Lithium Hexafluoroaluminate (Li_3AlF_6) $Al_1F_6Li_3(l)$

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
0							
100							
200							
298.15	202.506	245.847	245.847	0.	−3317.640	−3175.109	556.266
300	203.133	247.101	245.851	0.375	−3317.620	−3174.224	552.682
400	229.869	309.505	254.178	22.131	−3315.832	−3126.664	408.301
500	248.111	362.860	270.709	46.075	−3322.416	−3078.725	321.632
600	262.295	409.396	290.028	71.621	−3318.976	−3030.290	263.810
700	274.052	450.736	310.087	98.454	−3314.421	−2982.521	222.558
700.000	274.052	450.736	310.087	98.454	——— GLASS <−−> LIQUID ———		
700.000	359.824	450 736	310.087	98.454	TRANSITION		
800	359.824	498.783	330.738	134.436	−3300.936	−2936.031	191.703
900	359.824	541.165	351.811	170.419	−3287.731	−2891.213	167.802
1000	359.824	579.076	372.675	206.401	−3285.392	−2847.092	148.717
1058.000	359.824	599.363	384.551	227.271	−−− EPSILON <−−> LIQUID −−−		
1100	359.824	613.371	393.022	242.383	−3272.388	−2803.892	133.146
1200	359.824	644 680	412.708	278.366	−3259.446	−2761.873	120.221
1300	359.824	673.481	431.675	314.348	−3246.563	−2720.931	109.328
1400	359.824	700.147	449.911	350.331	−3233.726	−2680.980	100.029
1500	359.824	724.972	467.430	386.313	−3220.923	−2641.945	92.001
1600	359.824	748.194	484.260	422.295	−3208.150	−2603.763	85.004
1700	359.824	770.009	500.433	458.278	−3631.111	−2544.851	78.194
1800	359.824	790.576	515.987	494.260	−3616.124	−2481.386	72.008
1900	359.824	810.030	530.955	530.243	−3601.178	−2418.753	66.496
2000	359.824	828.487	545.374	566.225	−3586.265	−2356.906	61.556
2100	359.824	846.043	559.277	602.207	−3571.378	−2295.804	57.105
2200	359.824	862.782	572.696	638.190	−3556.510	−2235.411	53.075
2300	359.824	878.777	585.658	674.172	−3541.653	−2175 693	49.412
2400	359.824	894 091	598.193	710.155	−3526.799	−2116.622	46.067
2500	359.824	908.779	610.324	746.137	−3511.942	−2058.170	43.003
2600	359.824	922.892	622.077	782.119	−3497.076	−2000.313	40.187
2700	359.824	936.472	633.471	818.102	−3482.194	−1943.028	37.590
2800	359.824	949.558	644.528	854.084	−3761.194	−1885.326	35.171
2900	359.824	962.184	655.265	890.067	−3745.173	−1818.614	32.757
3000	359.824	974.383	665.700	926.049	−3729.127	−1752.454	30.513

PREVIOUS: CURRENT· June 1970

Lithium Hexafluoroaluminate (Li_3AlF_6) $Al_1F_6Li_3(l)$

Lithium Hexafluoroaluminate (Li_3AlF_6) CRYSTAL(β–γ–δ–ε)–LIQUID

M_r = 161.794958 Lithium Hexafluoroaluminate (Li_3AlF_6) $Al_1F_6Li_3(cr,l)$

0	to	748 K	crystal, beta
748	to	848 K	crystal, gamma
848	to	978 K	crystal, delta
978	to	1058 K	crystal, epsilon
above		1058 K	liquid

Refer to the individual tables for details.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−32.146	−3370.866	−3370.866	INFINITE
100	70.982	38.225	333.657	−29.543	−3378.953	−3328.763	1738.767
200	156.222	115.960	205.121	−17.832	−3383.356	−3276.431	855.716
298.15	202.506	187.891	187.891	0.	−3383.601	−3223.790	564.795
300	203.133	189.145	187.895	0.375	−3383.581	−3222.799	561.139
400	229.869	251.549	196.222	22.131	−3381.793	−3169.443	413.887
500	248.111	304.904	212.753	46.075	−3388.377	−3115.708	325.496
600	262.295	351.440	232.072	71.621	−3384.937	−3061.477	266.525
700	274.052	392.779	252.131	98.453	−3380.383	−3007.913	224.453
748.000	279.073	411.132	261.751	111.737	BETA <--> GAMMA		
748.000	279.073	413.929	261.751	113.829	TRANSITION		
800	284.512	432.865	272.262	128.482	−3372.851	−2955.211	192.956
848.000	289.533	449.589	281.830	142.259	GAMMA <--> DELTA		
848.000	289.533	451.069	281.830	143.515	TRANSITION		
900	294.972	468.460	292.114	158.712	−3365.399	−2903.447	168.512
978.000	303.131	493.311	307.178	182.038	DELTA <--> EPSILON		
978.000	303.131	493.739	307.178	182.456	TRANSITION		
1000	305.432	500.508	311.357	189.150	−3368.604	−2851.735	148.959
1058.000	311.499	517.898	322.206	207.041	EPSILON <--> LIQUID		
1058.000	359.824	599.363	322.206	293.232	TRANSITION		
1100	359.824	613.371	333.058	308.344	−3272.388	−2803.892	133.146
1200	359.824	644.680	357.741	344.327	−3259.446	−2761.873	120.221
1300	359.824	673.481	380.935	380.309	−3246.563	−2720.931	109.328
1400	359.824	700.147	402.796	416.292	−3233.726	−2680.980	100.029
1500	359.824	724.972	423.456	452.274	−3220.923	−2641.945	92.001
1600	359.824	748.195	443.034	488.256	−3208.150	−2603.763	85.004
1700	359.824	770.009	461.633	524.239	−3631.111	−2544.851	78.194
1800	359.824	790.576	479.342	560.221	−3616.125	−2481.386	72.008
1900	359.824	810.030	496.239	596.204	−3601.178	−2418.753	66.496
2000	359.824	828.487	512.394	632.186	−3586.265	−2356.906	61.556
2100	359.824	846.043	527.867	668.168	−3571.378	−2295.805	57.105
2200	359.824	862.782	542.713	704.151	−3556.510	−2235.412	53.075
2300	359.824	878.777	556.980	740.133	−3541.653	−2175.694	49.412
2400	359.824	894.091	570.709	776.116	−3526.799	−2116.623	46.067
2500	359.824	908.779	583.940	812.098	−3511.942	−2058.171	43.003
2600	359.824	922.892	596.707	848.080	−3497.076	−2000.313	40.187
2700	359.824	936.472	609.041	884.063	−3482.194	−1943.028	37.590
2800	359.824	949.558	620.970	920.045	−3761.194	−1885.327	35.171
2900	359.824	962.184	632.520	956.028	−3745.173	−1818.614	32.757
3000	359.824	974.383	643.713	992.010	−3729 127	−1752.455	30.513

PREVIOUS: CURRENT June 1970

Lithium Hexafluoroaluminate (Li_3AlF_6) $Al_1F_6Li_3(cr,l)$

Cryolite, Alpha (α–Na_3AlF_6) CRYSTAL (α) $M_r = 209.941268$ Cryolite, Alpha (Na_3AlF_6) $Al_1F_6Na_3(cr)$

$\Delta_fH°(0\ K) = -3304.65 \pm 3.3\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 238.47 \pm 1.7\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = -3316.91 \pm 3.3\ kJ{\cdot}mol^{-1}$

$T_{trs}(\alpha \to \beta) = 836 \pm 2\ K$ $\Delta_{trs}H°(\alpha \to \beta) = 9.456 \pm 1.7\ kJ{\cdot}mol^{-1}$

$T_{fus} = 1285 \pm 3\ K$ $\Delta_{fus}H° = 110.039 \pm 5.0\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The heats of solution of Al(cr), NaCl(cr), and Na_3AlF_6(cr) in 4.36 m HCl acid solution were determined at 303.15 K by Coughlin.[1] The enthalpy change for the reaction Al(cr) + 2.96 NaCl(cr) + 2.96($HF{\cdot}5\ 716\ H_2O$) + 3.617 H_2O(l) = $Na_{2.96}AlF_{5\ 96}$(cr) + 2.96($HCl{\cdot}12.731\ H_2O$) + 3/2 H_2(g) was derived as $\Delta_rH°(298.15\ K) = -153.22 \pm 0.14$ kcal·mol. Using auxiliary $\Delta_fH°(298.15\ K)$ data from,[2, 3] we obtain $\Delta_fH°$(($Na_{2.96}AlF_{5\ 96}$, cr, 298.15 K) = −787.25 ± 0.34 kcal mol^{-1}. Assuming $\Delta_rH°(298.15\ K) = 0$ for the reaction $Na_{2.96}AlF_{5\ 96}$ + 0.04 NaF = Na_3AlF_6, we obtain $\Delta_fH°$(Na_3AlF_6, cr, 298.15 K) = −792.76 ± 0.4 kcal·mol^{-1}).

Gross *et al.*[4] measured the heat of the reaction 3/2 PbF_2(cr) + Al(cr) + 3 NaF(cr) = 3/2 Pb(cr) + Na_3AlF_6(cr) directly in a bomb calorimeter. The average heat of the reaction was found to be $\Delta_rH°(298.15\ K) = -138.3$ kcal mol^{-1} Using auxiliary data [2], we obtain $\Delta_fH°$(Na_3AlF_6, cr, 298.15 K) = −794.40 ± 1.5 kcal·mol^{-1}. Gross *et al.* [4] also measured the heat of reaction for 3/2 PbF_2(cr) + Al(cr) = 3/2 Pb(cr) + AlF_3(cr) as $\Delta_rH°$(AlF_3, cr, 298.15 K) = −360.99 ± 0.31 kcal·mol^{-1}), we obtain $\Delta_fH°$(Na_3AlF_6, cr, 298.15 K) = −794 19 ± 1.0 kcal·mol^{-1}.

Baud[6] reported $\Delta_rH° = -40.7$ kcal mol^{-1} for the reaction 2 AlF_3(cr) + 6 NaF(cr) = 2 Na_3AlF_6(cr). Using auxiliary data from 2, as above, we obtain $\Delta_fH°$(Na_3AlF_6, cr, 298.15 K) = −792.8 ± 2.0 kcal·mol^{-1}.

Grjotheim *et al.*[7] measured the enthalpy of mixing of 3/4 NaF(cr) + 1/4 Na_3AlF_6(cr) as $\Delta_rH°(910\ K) = -3.8 \pm 0.8$ kcal·mol^{-1}. When this result is combined with JANAF auxiliary data for the enthalpies and $\Delta_fH°(298.15\ K)$ values from[2] we obtain $\Delta_fH°$(Na_3AlF_6, cr, 298.15 K) = −792.8 ± 2.0 kcal·mol^{-1}.

The amounts of sodium over mixtures of cryolite and aluminum have been measured by Ono *et al.*,[8] Dewing,[9] and by Stokes and Frank.[10] The data have been corrected for the formation of sodium dimer by using JANAF functions for Na_2(g) and Na(g) to determine the equilibrium constants for the reaction Na_2(g) = 2 Na(g). Our evaluation of this data is presented below. We were unable to evaluate the data of Stokes and Frank[10] due to lack of appropriate data on the activities of Na_3AlF_6(l) Also shown in the table are the emf work of Dewing,[11] and the equilibrium study of Mashovets and Yudin.[12]

Our adopted value for the heat of formation of cryolite, $\Delta_fH°$(Na_3AlF_6, cr, 298.15 K) = −792.76 ± 0.8 kcal·mol^{-1}(−3316.91 kJ·mol^{-1}) is based on the study by Coughlin[1] and discussions with Dewing.[23]

Source	Method	Reaction[a]	T/K	Data	δS cal·K^{-1}·mol^{-1}	$\Delta_rH°$(298.15 K), kcal·mol^{-1} 2nd Law	3rd Law	$\Delta_fH°$(298.15 K) kcal·mol^{-1}
Mashovets[12] (1962)	transpiration	A	1101−1239	5	1.32 ± 1.3	48.11 ± 0.8	46.57 ± 0.2	−792.78 ± 1.0
Mashovets[12] (1962)	transpiration	B	1274	1	−	−	60.54	−792.81 ± 1.0
Ono[8] (1965)	DTA	C	1063−1153	eqn	4.98	115.86	110.38 ± 2.0	−793.22 ± 3.0
Dewing[8] (1969)	transpiration	C	949−1089	11	−3.71 ± 1.0	104.21 ± 1.0	108.03 ± 0.50	−795.57 ± 2.0
Dewing[9] (1969)	transpiration	D	908−913	2	−12.0	99.3	110.20 ± 0.1	−793.40 ± 1.5
Dewing[11] (1970)	emf	E	839−943	9	1.02 ± 0.2	−18.20 ± 0.2	−19.115 ± 0.09	−793.52 ± 0.6

[a] Reactions:

A) 2/3 Na_3AlF_6(cr) + H_2O(g) = 1/3 Al_2O_3(cr) + 2 HF(g) + 2 NaF(cr)

B) 2/3 Na_3AlF_6(cr) + H_2O(g) = 1/3 Al_2O_3(cr) + 2 HF(g) + 2 NaF(l)

C) 6 NaF(cr) + Al(l) = 3 Na(g) + Na_3AlF_6(cr)

D) 6 NaF(cr) + Al(cr) = 3 Na(g) + Na_3AlF_6(cr)

E) 3 NaF(cr) + AlF_3(cr) = Na_3AlF_6(cr)

Heat Capacity and Entropy

The low temperature heat capacities, 53.66–296.00 K, were measured by King.[13] The values of $C_p°$ below 53.66 K are extrapolated using the $C_p°$ equation (combination of Debye and Einstein functions) given by King. $S°$(298 15 K) is derived based on the low temperature heat capacities $S°(50\ K) = 3.953$ cal·K^{-1}·mol^{-1} and $H°(50\ K) = 0.140$ kcal·mol^{-1}.

High temperature enthalpies have been determined by drop calorimetry by O'Brien and Kelley[14] (401.3–809.7 K), and by Albright[15] (349.99–812.70 K). The enthalpies reported by Albright are 7% higher than those reported by O'Brien and Kelley. Enthalpy data from these two calorimeters have been compared previously (see MoO_3(cr) table) indicating that the CRT calorimeter[15] results were 2% higher than the Bureau of Mines calorimeter.[14] Frank[16] commented that the enthalpies reported by O'Brien and Kelley were incorrect due to an apparent error in temperature measurement but Douglas and Ditmars[17] have questioned this correction (see NaF(cr) table for details). Our analysis indicates that the enthalpies of O'Brien and Kelley join smoothly with the low temperature $C_p°$ s of King. This is not true of Albright's enthalpy data. We adopt heat capacities for the α–phase derived from the original enthalpy data reported by O'Brien and Kelley.[14]

The high temperature enthalpies have also been measured by the following investigators: Joly[18] (284.5–373.3 K), Baud[19] (289–328 K), Roth and Bertram[20] (369–802 K), Krestovnikov and Karetnikov[21] (288–1173 K), and by Lyshenko[22] (293–838 K). Their data are not used for evaluation due to inconsistencies among the reported values.

Transition Data and Fusion Data

Refer to the β–crystal table for details.

Continued on page 172

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	−38.095	−3304.649	−3304.649	INFINITE
100	100.039	62.287	402.572	−34.028	−3313.806	−3261.080	1703.414
200	179.033	159.302	257.165	−19.573	−3317.306	−3206.528	837 459
298.15	215.727	238.467	238.467	0.	−3316.908	−3152.168	552.247
300	216.212	239.803	238.471	0.400	−3316.883	−3151.146	548.663
400	236.379	305.007	247.223	23.114	−3323.200	−3095.511	404.232
500	248.634	358.934	264.326	47.304	−3321.044	−3038.816	317.463
600	262.793	405.519	284.058	72.876	−3317.675	−2982.666	259.664
700	276.822	447.083	304.429	99.858	−3313.053	−2927 179	218.429
800	290.780	484.959	324.661	128.238	−3307.209	−2872.439	187.551
836.000	295.809	497.868	331.843	138.797	---- ALPHA <--> BETA ----		
900	304.691	520.012	344.443	158.013	−3300.200	−2818.502	163.582
1000	318.582	552.834	363.657	189.176	−3302.683	−2764.645	144 410
1100	332.461	583.849	382.277	221.729	−3293.191	−2711.290	128.748
1200	346.310	613.371	400.315	255.668	−3572.796	−2651.533	115.418

PREVIOUS: December 1968 CURRENT December 1979

Cryolite, Beta (β–Na_3AlF_6) CRYSTAL (β) $M_r = 209.941268$

$S°(298.15\ K) = [284.881]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta) = 836 \pm 2\ K$
$T_{fus}(\beta \rightarrow l) = 1285 \pm 3\ K$

$\Delta_f H°(298.15\ K) = [-3288.781]\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°(\alpha \rightarrow \beta) = 9.456 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°(\beta \rightarrow l) = 110.039 \pm 5.0\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Na_3AlF_6$, cr, β, 298.15 K) is calculated from $\Delta_f H°(Na_3AlF_6$, cr, α, 298 15 K) by adding the enthalpy of transition, $\Delta_{trs}H°$, and the difference in enthalpy, $H°(836\ K)–H°(298\ 15\ K)$, between the α– and β–phases.

Heat Capacity and Entropy

High–temperature enthalpies of the β–phase have been determined by drop calorimetry by O'Brien and Kelley[1] (846.7–1263.5 K), Albright[2] (824.21–1267.17 K), and by Holm and Gronvold[3] (1070–1175 K). The data of Holm and Gronvold is in very good agreement with the data of Albright but the data of O'Brien and Kelley are systematically lower by 2%. We have already discussed the discrepancy between the data of O'Brien and Kelley and that of Albright (see the discussion on the Na_3AlF_6(cr, α) table). Our experience with the enthalpies reported by Holm, which are primarily aimed at determining heats of fusion, is that the enthalpies show a positive bias (see the $Na_5Al_3F_{14}$(cr) table) of 2–4%. For these reasons, we adopt the enthalpies from the work of O'Brien and Kelley.[1] Heat capacities derived from these enthalpies have been extended smoothly below 836 K and above 1285 K.

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

Transition Data

The α–phase is the low temperature monoclinic modification of cryolite (sodium hexafluoroaluminate), space group $P2_1/n$.[4, 10] The transition to the cubic high–temperature β–phase (space group Fm3m) occurs at 836 ± 2 K. Reported values for $T_{trs}(\alpha \rightarrow \beta)$ are 823 K,[2] 832 K,[6] 833 K,[7] 833.5 K,[6] 834 K,[8] 834.5 K,[9] 837 K,[9] 838 K,[10, 11, 12] and 845 K.[1] The value of $\Delta H_{trs}H°(\alpha \rightarrow \beta)$ is calculated as the difference between the adopted enthalpies for the α– and β–phases at 836 K. Reported values of $\Delta H_{trs}H°(\alpha \rightarrow \beta)$ are (in $kJ \cdot mol^{-1}$) = 5.19,[12] 9.04,[1] 9.37 ± 1.7,[9] 9.87,[9] and 9.96.[2] The cause of the discrepancies among the reported values for T_{trs}, $\Delta_{trs}H°$ and the high temperature enthalpies may be due to differences in the sample composition. The samples used have normally been hand–picked naturally occurring crystals.

Fusion Data

Our adopted value for the melting point of cryolite is 1285 ± 3 K. Reported values include (all in K): 1273,[12] 1279,[2] 1281,[7] 1282,[13, 14] 1284,[3, 15] 1285,[10] 1293,[8] and 1300.[1] The value of $\Delta_{fus}H°$ is calculated as the difference between the adopted enthalpies of the β–crystal and liquid at 1285 K. Other reported values of $\Delta_{fus}H°$ are (in $kJ \cdot mol^{-1}$) 69.62,[12] 106.7 ± 10.5,[15] 111.3 ± 0.8,[16] 111.75,[6] 113.4 ± 2.1,[3] 115.65,[1] and 116.77.[2]

References

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Cryolite, Beta (Na_3AlF_6) $Al_1F_6Na_3(cr)$

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

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	194.723	284.881	284.881	0.	−3288.781	−3137 880	549.744
300	194.744	286.086	284.885	0.360	−3288.796	−3136.943	546.190
400	200.916	342.763	292.572	20.077	−3298.111	−3085.524	402.928
500	212.464	388.778	307.340	40.719	−3299.502	−3032.196	316.771
600	226.103	428.705	324.306	62.639	−3299.786	−2978.688	259.318
700	240.747	464.652	341.827	85.977	−3298.807	−2925.231	218.283
800	255.977	497.791	359.276	110.812	−3296.509	−2872.005	187.523
836.000	261.500	509.179	363.999	121.370	---- ALPHA <--> BETA ----		
900	271.458	528.831	376.408	137.181	−3292.905	−2819.145	163.619
1000	287.148	558.243	393.133	165 109	−3298.624	−2765.994	144.481
1100	302.963	586.352	409.430	194.615	−3292.178	−2713.032	128.831
1200	318.863	613.395	425.307	225.706	−3574.631	−2653.397	115.499
1285.000	332.461	635.677	438.489	253.387	---- BETA <--> LIQUID ----		
1300	334.846	639.549	440.786	258.392	−3562.664	−2577.103	103.549
1400	350.870	664.950	455.895	292.678	−3549.161	−2501.787	93.343
1500	366.895	689.704	470.661	328.566	−3534 115	−2427.490	84.533

PREVIOUS: CURRENT: December 1979

Cryolite (Na_3AlF_6) **LIQUID** **$M_r = 209.941268$** **Cryolite (Na_3AlF_6)** **$Al_1F_6Na_3(l)$**

$S°(298.15\ K) = [286.058]\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{fus}(\beta \rightarrow l) = 1285 \pm 3\ K$

$\Delta_f H°(298.15\ K) = [-3246.472]\ kJ\cdot mol^{-1}$
$\Delta_{fus}H°(\beta \rightarrow l) = 110.039 \pm 5.0\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Na_3AlF_6, l\ 298.15\ K)$ is calculated from $\Delta_f H°(Na_3AlF_6, cr, \beta, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1285\ K)-H°(298\ 15\ K)$, between the β–crystal and liquid.[1]

Hong and Kleppa,[2] using a twin micro calorimeter, have determined the enthalpy of mixing for the reaction 3 NaF(l) + AlF_3(cr) = $NaAlF_6$(l) as $\Delta_r H°(1298\ K) = -10.595 \pm 0.05\ kcal\cdot mol^{-1}$ When this result is combined with JANAF auxiliary data and heats of formation from 3, we obtain $\Delta_f H°(Na_3AlF_6, l, 298.15\ K) = -775.1 \pm 1.0\ kcal\cdot mol^{-1}$.

Yudin and Mashovets[5] studied the equilibrium reaction between water vapor and cryolite (reaction B below). Results of our analysis of these studies are given below. The average of the three experimental values, $\Delta_f H°(Na_3AlF_6, l, 298.15\ K) = -776.2 \pm 1.5\ kcal\cdot mol^{-1}$, is in good agreement with our adopted value.

Source	Reaction[a]	T/K	Data Points	δS cal·K⁻¹·mol⁻¹	$\Delta_r H°(298.15\ K)$, kcal·mol⁻¹ 2nd law	3rd law	$\Delta_f H°(Na_3AlF_6, l, 298.15\ K)$ kcal·mol⁻¹
Yudin[1] (1963)	A	1300	1	–	–	24.30 ± 2.0	−777.76 ± 2.0
Mashovets[2] (1962)	B	1286–1315	3	−6.15 ± 0.1	41.10 ± 0.1	49.12 ± 0.2	−775.67 ± 2.0

[a] Reactions:
A $Na_3AlF_6(l) = 3\ NaF(l) + AlF_3(cr)$
B $2/3\ Na_3AlF_6(l) + H_2O(g) = 1/3\ Al_2O_3(cr) + 2\ HF(g) + 2\ NaF(l)$

Heat Capacity and Entropy

The high temperature enthalpies, 1285.5–1370.5 K, were measured by O'Brien and Kelley[6] Using their data and smoothing, we derive a constant $C_p° = 94.53\ cal\cdot K^{-1}\cdot mol^{-1}$ ($395.514\ J\cdot K^{-1}\cdot mol^{-1}$) for Na_3AlF_6(l). A hypothetical glass transition is assumed at 790 K. The $C_p°$ values above 1370.5 K are obtained by linear extrapolation. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Albright[7] meaured the high temperature enthalpies of Na_3AlF_6(l) in the temperature range 1298.1–1311.8 K. His data are systematically higher (5%) than the values determined by O'Brien and Kelley. Holm and Gronvold[8] also measured enthalpies of Na_3AlF_6(l) by drop calorimetry (1290.3–1333.1 K). Their data are intermediate between that of Albright and that of O'Brien and Kelley. For reasons discussed previously (see the Na_3AlF_6(cr, β) table), we believe both sets[7,8] are biased and have not used the data in this evaluation.

Fusion Data

Refer to the β–crystal table for details.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	215.727	286.058	286.058	0.	−3246.472	−3095.921	542.393
300	216.212	287.394	286.062	0.400	−3246.447	−3094 987	538.885
400	236.379	352.597	294.813	23.114	−3252.764	−3044.111	397.520
500	248.634	406.524	311.917	47.304	−3250.608	−2992.175	312.590
600	262.793	453.110	331.649	72.876	−3247.240	−2940.784	256.018
700	276.822	494.674	352.020	99.858	−3246.799	−2894.239	215.971
790 000	289.366	528.901	370.246	125.337	——— GLASS <––> LIQUID ———		
790.000	395.514	528.901	370.246	125.337	TRANSITION		
800	395.514	533.876	372.260	129.292	−3235 719	−2840.082	185.438
836.000	395.514	551.285	379.597	143.531	– – – – ALPHA <––> BETA – – – –		
900	395.514	580.461	392.856	168.844	−3218 933	−2791.638	162.022
1000	395.514	622.132	413.737	208.395	−3213.029	−2744.289	143.347
1100	395.514	659.829	434.423	247.946	−3196.537	−2698.214	128.128
1200	395.514	694.243	454.661	287.498	−3470.530	−2646.313	115.191
1285.000	395.514	721.311	471 415	321.116	– – – – BETA <––> LIQUID – – – –		
1300	395.514	725.901	474.324	327.049	−3451.697	−2578.393	103.601
1400	395.514	755.211	493.354	366.600	−3432.929	−2511.920	93.721
1500	395.514	782.499	511.731	406.152	−3414.220	−2446.787	85.205
1600	395.514	808.025	529.460	445.703	−3395.566	−2382.900	77.794
1700	395.514	832.003	546.559	485.254	−3376.962	−2320.178	71.290
1800	395.514	854.610	563.051	524.806	−3358.402	−2258.550	65.541
1900	395.514	875.994	578.964	564.357	−3339.880	−2197.953	60.426
2000	395.514	896.281	594.327	603.909	−3321.387	−2138.329	55.847
2100	395.514	915.578	609.169	643.460	−3302.915	−2079.631	51.728
2200	395.514	933.978	623.518	683.011	−3284 455	−2021.812	48.004
2300	395.514	951.559	637.401	722.563	−3265.996	−1964.832	44 623
2400	395.514	968.392	650.844	762.114	−3247.531	−1908.656	41.541
2500	395.514	984.537	663.871	801.665	−3229.049	−1853.249	38 722
2600	395.514	1000 050	676.505	841.217	−3210.544	−1798.582	36 134
2700	395.514	1014.977	688.766	880.768	−3192.008	−1744.628	33 752
2800	395.514	1029.360	700 675	920.319	−3467.335	−1690.393	31.535
2900	395.514	1043.240	712.250	959.871	−3447.624	−1627.279	29.310
3000	395.514	1056 648	723.507	999.422	−3427.867	−1564.845	27.246

PREVIOUS: December 1968   CURRENT: December 1979

Cryolite (Na_3AlF_6) **$Al_1F_6Na_3(l)$**

Cryolite (Na_3AlF_6) CRYSTAL(α-β)–LIQUID M_r = 209.941268 Cryolite (Na_3AlF_6) $Al_1F_6Na_3(cr,l)$

0 to 836 K	crystal, alpha
836 to 1285 K	crystal, beta
above 100285 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°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	0.	0.	INFINITE	−38.095	−3304.649	−3304.649	INFINITE
100	100.039	62.287	402.572	−34.028	−3313.806	−3261.080	1703.414
200	179.033	159.302	257.165	−19.573	−3317.306	−3206.528	837.459
298.15	215.727	238.467	238.467	0.	−3316.908	−3152.168	552.247
300	216.212	239.803	238.471	0.400	−3316.883	−3151.146	548.663
400	236.379	305.007	247.223	23.114	−3323.200	−3095.511	404.232
500	248.634	358.934	264.326	47.304	−3321.044	−3038.816	317.463
600	262.793	405.519	284.058	72.876	−3317.675	−2982.666	259.664
700	276.822	447.083	304.429	99.858	−3313.053	−2927.179	218.429
800	290.780	484.959	324.661	128.238	−3307.209	−2872.439	187.551
836.000	295.809	497.868	331.843	138.797	ALPHA <−−> BETA TRANSITION		
836.000	261.500	509.179	331.843	148.253			
900	271.458	528.831	345.157	165.307	−3292.905	−2819.145	163.619
1000	287.148	558.243	365.007	193.236	−3298.624	−2765.994	144.481
1100	302.963	586.352	383.860	222.741	−3292.178	−2713.032	128.831
1200	318.863	613.395	401.868	253.832	−3574.631	−2653.397	115.499
1285.000	332.461	635.677	416.601	281.513	BETA <−−> LIQUID TRANSITION		
1285.000	395.514	721.311	416.601	391.552			
1300	395.514	725.901	420.143	397.485	−3451.697	−2578.392	103.601
1400	395.514	755.211	443.043	437.036	−3432.929	−2511.920	93.721
1500	395.514	782.499	464.774	476.588	−3414.220	−2446.787	85.205
1600	395.514	808.025	485.438	516.139	−3395.566	−2382.900	77.794
1700	395.514	832.003	505.126	555.690	−3376.962	−2320.178	71.290
1800	395.514	854.610	523.920	595.242	−3358.402	−2258.550	65.541
1900	395.514	875.994	541.892	634.793	−3339.880	−2197.953	60.426
2000	395.514	896.281	559.109	674.345	−3321.387	−2138.329	55.847
2100	395.514	915.578	575.628	713.896	−3302.915	−2079.631	51.728
2200	395.514	933.978	591.502	753.447	−3284.454	−2021.812	48.004
2300	395.514	951.559	606.777	792.999	−3265.996	−1964.832	44.623
2400	395.514	968.392	621.496	832.550	−3247.531	−1908.656	41.541
2500	395.514	984.537	635.697	872.101	−3229.049	−1853.249	38.722
2600	395.514	1000.050	649.414	911.653	−3210.544	−1798.582	36.134
2700	395.514	1014.977	662.679	951.204	−3192.008	−1744.628	33.752
2800	395.514	1029.360	675.519	990.755	−3467.335	−1690.393	31.535
2900	395.514	1043.240	687.961	1030.307	−3447.624	−1627.278	29.310
3000	395.514	1056.648	700.029	1069.858	−3427.867	−1564.845	27.246

PREVIOUS: CURRENT. December 1979

$\Delta_fH°(0\ K) = 259.5 \pm 20\ kJ\cdot mol^{-1}$
$S°(298.15\ K) = 187.86 \pm 0.5\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = 259.4 \pm 20\ kJ\cdot mol^{-1}$

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

$\omega_e = 1682.56\ cm^{-1}$ $\omega_ex_e = 29.09\ cm^{-1}$ $\sigma = 1$
$B_e = 6.3907\ cm^{-1}$ $\alpha_e = 0.1858\ cm^{-1}$ $r_e = 1.6477$ Å

Enthalpy of Formation

Gaydon[1] extrapolated the available $X^1\Sigma$ vibrational levels, also considered predissociation in the A^1 state and concluded that the best value of D_0° was 2.9 ± 0.2 ev. The linear Birge–Sponer extrapolation gave a value of 3.05 ev while the predissociation limit was 3.07 ev. The value recommended by Gaydon[1] is adopted here and leads to a value of $\Delta_fH°$(AlH, g, 298.15 K) = 62.16 ± 0 5.0 kcal·mol^{-1}, using JANAF auxiliary data.

Heat Capacity and Entropy

Zeeman and Ritter[2] examined the UV band system of AlH under high resolution and reported the molecular constants adopted above.

References

[1] A. G. Gaydon, 'Dissociation Energies', 2nd ed., Chapman and Hall, Ltd., London, 261 pp. (1953).
[2] P. B. Zeeman and E. G. Ritter, Can. J. Phys. 32, 555 (1954).

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−8.669	259.512	259.512	INFINITE
100	29.124	156 000	213.828	−5.783	260.415	250.550	−130.874
200	29.154	176.194	190.540	−2.869	260.180	240.711	−62.867
250	29.220	182.705	188.346	−1.410	259.827	235.882	−49.285
298.15	29.373	187.864	187.864	0	259.408	231.308	−40.524
300	29.381	188.045	187.864	0.054	259.391	231.133	−40.244
350	29.658	192.594	188.223	1.530	258.907	226.462	−33.798
400	30.041	196.578	189.023	3.022	258.397	221.861	−28.972
450	30.498	200.142	190.064	4.535	257.877	217.325	−25.226
500	30.996	203.381	191.236	6.072	257.354	212.848	−22.236
600	32.008	209.122	193.751	9.223	256.304	204.045	−17.764
700	32.942	214.128	196.312	12.471	255.236	195.419	−14.582
800	33 754	218.581	198.822	15.807	254.115	186.949	−12.207
900	34.441	222.597	201.244	19.218	252.897	178.626	−10.367
1000	35.018	226.257	203.565	22.692	240.954	171.204	−8.943
1100	35.505	229.618	205.783	26.218	239.786	164.286	−7.801
1200	35.917	232.725	207.900	29.790	238.643	157.473	−6.855
1300	36.271	235.615	209.922	33.400	237.518	150.755	−6.057
1400	36.577	238.314	211.855	37.043	236.403	144.123	−5.377
1500	36.844	240.847	213.704	40.714	235.296	137.570	−4.791
1600	37.081	243.232	215.476	44.410	234.191	131.091	−4.280
1700	37.293	245.487	217.176	48.129	233.089	124.681	−3.831
1800	37.484	247.624	218.808	51.868	231.985	118.336	−3.434
1900	37.658	249.655	220.379	55.626	230.881	112.052	−3.081
2000	37.818	251.591	221.891	59.399	229.775	105.826	−2.764
2100	37.966	253.440	223.350	63.189	228.667	99.656	−2.479
2200	38.104	255.209	224.758	66.992	227.556	93.539	−2.221
2300	38.234	256.906	226.119	70.809	226.442	87.472	−1.987
2400	38.356	258.536	227.436	74.639	225.326	81.454	−1.773
2500	38.473	260.104	228.712	78.480	224.207	75.482	−1.577
2600	38.584	261 615	229.948	82.333	223.086	69.555	−1.397
2700	38.691	263.073	231.148	86.197	221.963	63.671	−1.232
2800	38.793	264.482	232.314	90.071	−73.064	58 797	−1.097
2900	38.893	265 845	233.447	93.955	−73.096	63.507	−1.144
3000	38.989	267.165	234.549	97.850	−73.130	68.218	−1.188
3100	39.082	268.445	235.622	101.753	−73.166	72.930	−1.229
3200	39.174	269.688	236.667	105.666	−73.205	77.644	−1.267
3300	39.263	270 894	237.686	109.588	−73.245	82.358	−1.304
3400	39.350	272.068	238.680	113.518	−73.288	87 074	−1.338
3500	39.435	273.210	239.650	117.458	−73.333	91.791	−1.370
3600	39.520	274.322	240.598	121.406	−73.380	96.510	−1.400
3700	39.602	275.406	241.524	125.362	−73.430	101.230	−1.429
3800	39.684	276.463	242.430	129.326	−73.483	105.951	−1.456
3900	39.764	277.495	243.316	133.298	−73.540	110 674	−1.482
4000	39.844	278.503	244.183	137.279	−73.600	115.398	−1.507
4100	39.922	279.487	245.032	141.267	−73.664	120.124	−1.530
4200	40.000	280.450	245 864	145.263	−73.732	124.851	−1.553
4300	40.077	281.393	246.679	149.267	−73.805	129.580	−1.574
4400	40.154	282.315	247.479	153.279	−73.883	134.311	−1.594
4500	40.229	283.218	248.263	157.298	−73.965	139.043	−1.614
4600	40.305	284.103	249.032	161.324	−74.055	143.778	−1.633
4700	40.379	284.971	249.788	165.359	−74.152	148.514	−1.651
4800	40.454	285.821	250.530	169.400	−74.256	153.253	−1.668
4900	40.527	286.656	251.259	173.449	−74.367	157.994	−1.684
5000	40 601	287.476	251.975	177.506	−74.488	162.737	−1.700
5100	40.674	288.281	252.679	181.570	−74.618	167.483	−1.715
5200	40.746	289.071	253.371	185.641	−74.758	172.231	−1.730
5300	40.819	289.848	254.052	189.719	−74.909	176.982	−1.744
5400	40.891	290.612	254.722	193.804	−75.071	181.737	−1.758
5500	40.963	291.363	255.381	197.897	−75.246	186.494	−1.771
5600	41.034	292 101	256.030	201.997	−75.433	191.254	−1.784
5700	41.106	292.828	256.670	206.104	−75.634	196.018	−1.796
5800	41.177	293.544	257.299	210.218	−75.846	200.786	−1.808
5900	41.247	294.248	257.920	214.339	−76.076	205.557	−1.820
6000	41.318	294.942	258.531	218.467	−76.300	210.331	−1.831

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

Aluminum Hydride Oxide (OAlH) IDEAL GAS $M_r = 43.98888$ Aluminum Hydride Oxide (OAlH) $Al_1H_1O_1(g)$

$\Delta_f H°(0\ K) = [37.6 \pm 84]\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 215.3 \pm 2.4\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [33.5 \pm 84]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[900] (1)
[1000] (2)
[1600] (1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: [$C_{\infty v}$]
Bond Distances: Al–O = [1.62] Å; A–H = [1.64] Å
Bond Angle: H–Al–O = [180]°
B_0 = [0.538347] cm^{-1}

Enthalpy of Formation

The enthalpy of formation is estimated by summing the constituent bond energies. The Al=O was taken as that in AlO(g) and the Al–H bond was taken as that in AlH(g); this gave a heat of atomization of 182 kcal·mol^{-1}.

Heat Capacity and Entropy

Vibrational frequencies, bond lengths and angles and point group are taken from NBS.[1]

References

[1] U. S. Nat. Bur. Stand. Report 6297, 148 pp. (January 1, 1959).

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.018	37.569	37.569	INFINITE
100	29.106	182.067	243.166	−6.110	37.041	33.235	−17.360
200	30.298	202.437	218.263	−3.165	35.382	30.013	−7.839
250	32.196	209.387	215.811	−1.606	34.400	28.784	−6.014
298.15	34.569	215.256	215.256	0	33.472	27.787	−4.868
300	34.666	215.470	215.257	0.064	33.437	27.752	−4.832
350	37.323	221.013	215.688	1.864	32.539	26.876	−4.011
400	39.919	226.168	216.680	3.795	31.722	26.124	−3.411
450	42.325	231.011	218.006	5.852	30.987	25.469	−2.956
500	44.491	235.584	219.537	8.024	30.327	24.892	−2.600
600	48.094	244.029	222.927	12.661	29.184	23.916	−2.082
700	50.851	251.659	226.496	17.614	28.194	23.118	−1.725
800	52.953	258.593	230.081	22.809	27.263	22.457	−1.466
900	54.567	264.927	233.606	28.189	26.312	21.912	−1.272
1000	55.822	270.744	237.033	33.711	14.685	22.238	−1.162
1100	56.810	276.112	240.345	39.344	13.870	23.033	−1.094
1200	57.598	281.091	243.536	45.066	13.103	23.901	−1.040
1300	58.235	285 727	246.605	50.859	12.369	24.830	−0.998
1400	58.755	290.062	249.556	56.709	11.655	25.816	−0.963
1500	59.186	294.131	252.393	62.607	10.953	26.852	−0.935
1600	59.545	297.963	255.123	68.544	10.256	27.934	−0.912
1700	59.847	301.582	257.750	74.514	9.558	29.061	−0.893
1800	60.105	305.010	260.281	80.512	8.856	30.228	−0.877
1900	60.325	308.266	262.722	86.534	8.147	31.434	−0.864
2000	60.514	311.365	265.077	92.576	7.428	32.679	−0.853
2100	60.679	314.322	267.352	98.636	6.697	33.959	−0.845
2200	60.823	317.148	269.552	104.711	5.954	35.275	−0.838
2300	60.949	319.854	271.681	110.800	5.197	36.625	−0.832
2400	61.061	322.451	273.742	116.900	4.425	38.007	−0.827
2500	61.160	324.945	275.741	123.011	3.639	39.423	−0.824
2600	61.248	327.346	277.680	129.132	2.837	40.870	−0.821
2700	61.327	329.659	279.562	135.261	2.020	42.348	−0.819
2800	61.397	331.891	281.392	141.397	−292.713	44.825	−0.836
2900	61.461	334.046	283.170	147.540	−292.466	56.875	−1.024
3000	61.519	336.131	284.901	153.689	−292.233	68.918	−1.200
3100	61.571	338.149	286.586	159.844	−292.017	80.953	−1.364
3200	61.619	340.104	288.229	166.003	−291.815	92.980	−1.518
3300	61.662	342.001	289.829	172.167	−291.629	105.002	−1.662
3400	61.702	343.843	291.391	178.335	−291.458	117.019	−1.798
3500	61.738	345.632	292.915	184.507	−291.302	129.030	−1.926
3600	61.772	347.371	294.404	190.683	−291.161	141.038	−2.046
3700	61.803	349.064	295.859	196.862	−291.036	153.041	−2.161
3800	61.831	350.713	297.280	203.043	−290.926	165.042	−2.269
3900	61.858	352.319	298.671	209.228	−290.831	177.041	−2.371
4000	61.882	353.886	300.032	215.415	−290.752	189.036	−2.469
4100	61.905	355.414	301.364	221.604	−290.689	201.030	−2.561
4200	61.926	356.906	302.669	227.796	−290.643	213.022	−2.649
4300	61.945	358.363	303.947	233.989	−290.613	225.014	−2.733
4400	61.964	359.788	305.200	240.185	−290.600	237.005	−2.814
4500	61.981	361.181	306.429	246.382	−290.603	248.996	−2.890
4600	61.997	362.543	307.634	252.581	−290.626	260.987	−2.964
4700	62.012	363.876	308.817	258.781	−290.668	272.979	−3.034
4800	62.026	365.182	309.977	264.983	−290.729	284.972	−3.101
4900	62.040	366.461	311.117	271.187	−290.810	296.967	−3.166
5000	62.052	367.715	312.236	277.391	−290.913	308.964	−3.228
5100	62.064	368.944	313.336	283.597	−291.038	320.962	−3.287
5200	62.075	370.149	314.417	289.804	−291.186	332.963	−3.345
5300	62.086	371.331	315.480	296.012	−291.359	344.968	−3.400
5400	62.096	372.492	316.525	302.221	−291.557	356.976	−3.453
5500	62.105	373.632	317.553	308.431	−291.781	368.987	−3.504
5600	62.114	374.751	318.565	314.642	−292.033	381.004	−3.554
5700	62.122	375.850	319.560	320.854	−292.314	393.025	−3.602
5800	62.130	376.931	320.540	327.067	−292.621	405.051	−3.648
5900	62.138	377.993	321.505	333.280	−292.962	417.082	−3.693
6000	62.145	379.037	322.455	339.494	−293.314	429.118	−3.736

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

Aluminum Hydride Oxide (OAlH) $Al_1H_1O_1(g)$

Aluminum Hydroxide (AlOH) **IDEAL GAS** **M_r = 43.98888** **Aluminum Hydroxide (AlOH)** **$Al_1H_1O_1(g)$**

$S°(298.15\ K) = [216.4 \pm 2]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [-175.6 \pm 13]\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [-179.9 \pm 13]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[1000](1)
[1300](2)
[3600](1)

Ground State Quantum Weight: [1]
Point Group: [$C_{\infty v}$]
Bond Distances: Al–O = [1.87] Å; O–H = [0.96] Å
Bond Angle. Al–O–H = [180]°
Rotational Constant: B_0 = [0.425629] cm^{-1}

$\sigma = 1$

Enthalpy of Formation

From a mass-spectrometric investigation of the equilibrium 1/3 $Al_2O_3(cr)$ + 1/3 Al(g) + 1/2 $D_2(g)$ = AlOD(g), Farber *et al.*[1] report second law heats of reaction of 56.7 + 0.6 kcal·mol^{-1} at 1980 K, 57.1 ± 2.8 kcal·mol^{-1} at 2060 K and 62.7 ± 1.4 kcal·mol^{-1} at 2000 K. Using JANAF auxiliary data, assuming AlOD to be AlOH, we obtain $\Delta_fH°$(AlOD, g, 298.15 K) = −44.6 ± 1, −44 0 ± 3.2 and −38.6 ± 1.8 kcal·mol^{-1}. A second equilibrium in the same investigation was $Al_2O(g) + D_2O(g)$ = 2 AlOD(g). for which second law heats of reaction of 6.3 ± 2.1 kcal mol^{-1} at 2060 K and 5.7 ± 0.8 kcal·mol^{-1} at 2000 K were reported. Farber *et al.*[1] also measured the heat of reaction 1/3 $Al_2O_3(cr)$ + 4/3 Al(g) = $Al_2O(g)$ at the same temperatures as −10.7 ± 2.8 kcal·mol^{-1} at 2060° and −10.3 ± 10 2 kcal·mol^{-1} at 2000 K. Combining these reactions and eliminating $Al_2O(g)$ yields $\Delta_rH°$(2060 K) = −4.4 ± 5 0 kcal·mol^{-1} and $\Delta H°$(2000 K) = −5 ± 11 kcal·mol^{-1} for the reaction 1/3 $Al_2O_3(cr)$ + 4/3 Al(g) + 2 AlOD(g).

Using auxiliary JANAF values for $Al_2O_3(cr)$ and Al(g), $\Delta_fH°(D_2O$, g, 298.15 K) = −59.56 kcal·mol^{-1} [2] and functions for $D_2O(g)$ from Friedman and Haar,[3] we obtain $\Delta_fH°$(AlOD, g, 298.15 K) = −43.9 ± 6 kcal·mol^{-1} and −43.4 ± 3 kcal·mol^{-1}. From all the above results we adopt a value of $\Delta_fH°$(AlOD, g, 298.15 K) = −44 ± 3 kcal·mol^{-1}, assuming that AlOH is less stable than AlOD by 1 kcal·mol^{-1} as is the case for H_2O, HDO and D_2O, we obtain $\Delta_fH°$(AlOH, g, 298.15 K) = −43 ± 3 kcal·mol^{-1}.

Farber *et al.*[1] also performed weight loss experiments under molecular flow conditions by allowing hydrogen to flow over $Al_2O_3(cr)$. The products assumed were AlOH(g), Al(g), $Al_2O(g)$, H(g) and $H_2O(g)$ and the equilibrium amounts of H(g), Al(g) and $Al_2O(g)$ were assumed to be those predicted by the free energies from the JANAF tables. A 3rd law analysis of the equilibrium constants given by Farber for the reaction 2 $H_2(g)$ + $Al_2O_3(cr)$ = 2 AlOH(g) + $H_2O(g)$ yields $\Delta_rH°$(298.15 K) = 238 ± 12 kcal mol^{-1} and $\Delta_fH°$(AlOH, g, 298.15 K) = −52 ± 6 kcal·mol^{-1}. However, the assumed equilibria involving $Al_2O(g)$ and Al(g) may be significantly in error and thus the $\Delta_fH°$(298 15 K) should be considered as simply confirming the magnitude determined mass-spectrometrically.

Heat Capacity and Entropy

The vibrational frequencies are estimated by using the AlO(g) fundamental as approximately the Al–O stretch; the O–H stretch is that in $H_2O(g)$, and the bending frequency is approximately the OH bend in $CD_3OH(g)$ reported by Shimanouchi.[4]

The AlO bond length was taken from NBS,[5] and the OH bond length is assumed to be that in $H_2O(g)$. The bond angle is assumed to be 180° using the prediction of Walsh[6] for "HAB" molecules with less than 11 valence electrons. Confirmation of this prediction is scanty for molecules having A more electronegative than B; however, Kuczkowski *et al.*[7] confirmed the linearity of KOH and CsOH which have B valence electrons.

References

[1] M. Farber, M. A Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Final Report, USAF contract FO4611–67–C–0010, AFRPL–TR–67–244, November (1967).
[2] U. S. Nat. Bur. Stand. Tech. Note 270–1, 124 pp. (1965).
[3] A. S. Friedman and L. Haar, J. Chem. Phys. 22, 2051 (1954).
[4] T. Shimanouchi, NSRDS–NBS 6, 56 pp (1967).
[5] U. S. Nat. Bur. Stand. Report 6297, 148 pp. (January 1, 1959).
[6] A. D. Walsh, J. Chem. Soc. 1953, 2288.
[7] R. L. Kuczkowski, D. R. Lide, Jr., and L. C. Krishner, J. Chem. Phys. 44, 3131 (1966).

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−8.830	−175.627	−175.627	INFINITE
100	29.101	184.020	243.238	−5.922	−176.155	−180.156	94.104
200	29.550	204.257	219.257	−3 000	−177.837	−183.570	47.944
250	30.503	210.942	216.947	−1.501	−178.879	−184.884	38.629
298 15	31.918	216 430	216.430	0.	−179.912	−185.947	32.577
300	31.979	216.628	216.431	0.059	−179.952	−185.984	32.383
350	33.772	221.689	216.826	1.702	−181.006	−186.906	27.894
400	35.672	226.323	217.728	3.438	−182.019	−187.679	24.508
450	37.532	230.633	218.925	5.269	−182 981	−188.328	21.861
500	39.273	234.678	220.300	7.189	−183.892	−188.873	19.731
600	42.302	242.116	223.327	11.273	−185.588	−189.708	16.516
700	44.763	248.828	226.499	15.631	−187 174	−190.268	14.198
800	46.782	254.941	229.678	20.211	−188.719	−190.604	12.445
900	48.471	260.552	232.801	24.976	−190.285	−190.747	11.071
1000	49.912	265.735	235.838	29.897	−202.512	−189.951	9.922
1100	51.158	270.552	238.778	34.952	−203.907	−188.626	8.957
1200	52.245	275.051	241.615	40.123	−205.224	−187 179	8.148
1300	53.200	279.271	244.351	45.397	−206 477	−185.624	7.458
1400	54 041	283.245	246.989	50.759	−207.679	−183.974	6.864
1500	54.784	287.000	249.532	56.201	−208.836	−182.241	6.346
1600	55.442	290.557	251.986	61.713	−209 959	−180.431	5 890
1700	56 026	293.936	254.355	67.287	−211 052	−178.552	5.486
1800	56.546	297 153	256.644	72.916	−212.123	−176.609	5.125
1900	57.010	300.223	258.857	78.595	−213 176	−174.607	4.800
2000	57.424	303.158	261.000	84.317	−214.215	−172.550	4.507
2100	57.796	305.969	263.075	90.078	−215.245	−170 441	4.239
2200	58.130	308.665	265.086	95.875	−216.267	−168.284	3.996
2300	58.430	311.256	267.037	101.703	−217.284	−166.080	3.772
2400	58.702	313.749	268.932	107.560	−218.300	−163.832	3.566
2500	58.948	316.150	270.773	113.442	−219.314	−161.542	3.375
2600	59.171	318.466	272.563	119.348	−220.330	−159.211	3.199
2700	59.373	320 703	274.305	125.276	−221.349	−156.841	3 034
2800	59.558	322.866	276.001	131.223	−516.272	−153.465	2.863
2900	59.727	324.959	277.653	137.187	−516.203	−140.509	2.531
3000	59.882	326.987	279.264	143.167	−516.139	−127.555	2.221
3100	60.023	328.952	280.835	149.163	−516.081	−114 603	1.931
3200	60.154	330.860	282.369	155.172	−516 030	−101.653	1.659
3300	60.274	332.713	283.867	161.193	−515.987	−88 705	1.404
3400	60.385	334.514	285.330	167.226	−515.951	−75.757	1.164
3500	60.487	336.266	286.760	173.270	−515.923	−62.811	0.937
3600	60.582	337.971	288.159	179.323	−515.905	−49.865	0.724
3700	60 670	339.632	289.528	185.386	−515.895	−36.920	0.521
3800	60.752	341.251	290.868	191 457	−515.896	−23.974	0.330
3900	60.828	342.831	292.180	197.536	−515.907	−11.029	0.148
4000	60.899	344.371	293 466	203.623	−515.928	1.917	−0.025
4100	60.965	345.876	294.726	209.716	−515.962	14.863	−0.189
4200	61.027	347.346	295.961	215.815	−516 007	27.811	−0.346
4300	61.085	348.783	297.173	221.921	−516.065	40.760	−0.495
4400	61.139	350.188	298.362	228.032	−516.137	53 710	−0.638
4500	61.190	351.562	299.529	234.149	−516.220	66.661	−0.774
4600	61.238	352.908	300.675	240.270	−516.320	79.615	−0.904
4700	61.283	354.225	301.800	246.396	−516 437	92.572	−1.029
4800	61.325	355.516	302.906	252.527	−516.570	105.531	−1.148
4900	61.365	356.781	303.993	258.661	−516 719	118.493	−1.263
5000	61.403	358.021	305.061	264.800	−516.888	131.458	−1.373
5100	61.439	359.237	306.111	270.942	−517.077	144.427	−1.479
5200	61 472	360.430	307.144	277.087	−517.287	157.399	−1.581
5300	61.504	361.602	308.161	283.236	−517.519	170.377	−1.679
5400	61.535	362.752	309.161	289.388	−517.774	183.358	−1.774
5500	61.563	363.881	310.146	295.543	−518.053	196.344	−1.865
5600	61.591	364.990	311.115	301.701	−518.358	209.336	−1.953
5700	61.616	366.081	312.070	307.861	−518.690	222.334	−2.037
5800	61.641	367.153	313.011	314.024	−519.048	235.337	−2.119
5900	61.664	368.207	313.937	320.189	−519.437	248.346	−2.199
6000	61.687	369.243	314 850	326.357	−519.835	261.361	−2.275

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

Aluminum Hydroxide (AlOH) **$Al_1H_1O_1(g)$**

Aluminum Hydroxide, Ion ($AlOH^+$) IDEAL GAS $M_r = 43.98833$ Aluminum Hydroxide, Ion ($AlOH^+$) $Al_1H_1O_1^+(g)$

$S°(298.15\ K) = [228.7 \pm 2]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [541.9 \pm 109]\ kJ{\cdot}mol^{-1}$

$\Delta_fH°(298.15\ K) = [543.920]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[900](1)
[1100](2)
[3600](1)

Ground State Quantum Weight: [4]

Point Group: $[C_{\infty v}]$ $\sigma = 1$

Bond Distances: Al–O = [1.90] Å; O–H = [0.96] Å

Bond Angle: Al–O–H = [180]°

Rotational Constant: $B_0 = [0.412959]\ cm^{-1}$

Enthalpy of Formation

The enthalpy of formation is obtained from $\Delta_fH°$(AlOH, g, 298.15 K) and its ionization potential, which is estimated to be 7.5 ± 1 eV (173 ± 23 kcal·mol^{-1}). The ionization potential is estimated from a reported value of 7.5 eV for the appearance potential of $AlOD^+$, presumably from the parent AlOD, by Farber *et al.*[1]

Heat Capacity and Entropy

According to the correlation diagram given by Walsh[2] for "HAB" molecules, a compound with 9 valence electrons would have the three outermost electrons is an unfilled Π orbital. Thus, it would be a $^2\Pi$ state since the molecule ought to be linear if it has less than 11 valence electrons. The outermost orbital is a bonding orbital and thus the loss of an electron from it would weaken the bonding. The vibrational frequencies are estimated from those for AlOH(g) with somewhat lower frequencies due to the weaker bonding. Similarly, the Al–O bond length is slightly increased over that in AlOH(g).

References

[1] M Farber, M. A. Frisch, G. Grenier, and H. C. Ko, Space Sciences, Inc., Final Report, USAF contract F04611–67–C–0010, AFRPL–TR–67–144, (November 1967).

[2] A. D. Walsh, J. Chem. Soc. 1953, 2288.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−8.947	541.890		
100	29.104	195.798	256.187	−6.039			
200	30.021	216.119	231.632	−3.103			
250	31.562	222.970	229.234	−1.566			
298.15	33.535	228.693	228.693	0.	543.920	527.974	−92.499
300	33.616	228.901	228.694	0.062	543.922	527.875	−91.911
350	35.837	234.250	229.111	1.798	544.000	525.195	−78.381
400	37.986	239.177	230.066	3.645	544.136	522.500	−68.232
450	39.947	243.766	231.336	5.594	544.333	519.784	−60.335
500	41.684	248.067	232.796	7.636	544.582	517.044	−54.015
600	44.529	255.930	236.009	11.953	545.198	511.480	−44.528
700	46.724	262.966	239.367	16.520	545.900	505.806	−37.744
800	48.476	269.324	242.720	21.283	546.616	500.029	−32.649
900	49.928	275.119	246.003	26.205	547.286	494.165	−28.681
1000	51.167	280.446	249.184	31.261	537.272	488.990	−25.542
1100	52.245	285.374	252.253	36.433	538.074	484.124	−22.989
1200	53.191	289.961	255.207	41.706	538.936	479.182	−20.858
1300	54.029	294.253	258.047	47.068	539.850	474.166	−19.052
1400	54.771	298.284	260.778	52.508	540.805	469.077	−17.501
1500	55.432	302.086	263.407	58.019	541.795	463.920	−16.155
1600	56.020	305.683	265.938	63.592	542.813	458.695	−14.975
1700	56.544	309.095	268.377	69.221	543.852	453.406	−13.931
1800	57.013	312.341	270.730	74.899	544.909	448.055	−13.002
1900	57.432	315.434	273.002	80.622	545.979	442.645	−12.169
2000	57.809	318.390	275.198	86.384	547.059	437.178	−11.418
2100	58.147	321.219	277.323	92.182	548.145	431.658	−10.737
2200	58.451	323.931	279.380	98.013	549.235	426.085	−10.117
2300	58.726	326.536	281.374	103.872	550.327	420.463	−9.549
2400	58.975	329.040	283.308	109.757	551.419	414.793	−9.028
2500	59.200	331.452	285.186	115.666	552.509	409.078	−8.547
2600	59.405	333.778	287.010	121.596	553.596	403.319	−8.103
2700	59.591	336.024	288.784	127.546	554.678	397.519	−7.690
2800	59.761	338.194	290.511	133.514	261.855	392.647	−7.325
2900	59.917	340.294	292.191	139.498	264.022	397.279	−7.156
3000	60.059	342.328	293.829	145.497	266.183	401.838	−6.997
3100	60.190	344.299	295.425	151.509	268.337	406.324	−6.847
3200	60.311	346.212	296.982	157.534	270.482	410.741	−6.705
3300	60.422	348.070	298.503	163.571	272.620	415.091	−6.570
3400	60.524	349.875	299.987	169.618	274.749	419.376	−6.443
3500	60.619	351.631	301.438	175.676	276.868	423.599	−6.322
3600	60.707	353.340	302.856	181.742	278.978	427.761	−6.207
3700	60.788	355.004	304.243	187.817	281.078	431.865	−6.097
3800	60.864	356.626	305.600	193.899	283.168	435.913	−5.992
3900	60.934	358.208	306.929	199.989	285.247	439.905	−5.892
4000	61.000	359.752	308.230	206.086	287.314	443.844	−5.796
4100	61.061	361.259	309.505	212.189	289.369	447.732	−5.704
4200	61.119	362.731	310.755	218.298	291.412	451.570	−5.616
4300	61.173	364.170	311.981	224.413	293.441	455.359	−5.532
4400	61.223	365.576	313.183	230.533	295.457	459.101	−5.450
4500	61.270	366.953	314.362	236.657	297.460	462.798	−5.372
4600	61.315	368.300	315.520	242.787	299.446	466.450	−5.297
4700	61.357	369.619	316.657	248.920	301.416	470.059	−5.224
4800	61.396	370.911	317.774	255.058	303.369	473.627	−5.154
4900	61.433	372.178	318.872	261.199	305.305	477.154	−5.087
5000	61.468	373.419	319.950	267.345	307.221	480.642	−5.021
5100	61.501	374.637	321.011	273.493	309.117	484.091	−4.958
5200	61.533	375.831	322.053	279.645	310.992	487.503	−4.897
5300	61.563	377.004	323.079	285.800	312.845	490.880	−4.838
5400	61.591	378.155	324.088	291.957	314.674	494.222	−4.781
5500	61.617	379.285	325.082	298.118	316.479	497.530	−4.725
5600	61.643	380.395	326.060	304.281	318.258	500.806	−4.671
5700	61.667	381.487	327.023	310.446	320.010	504.050	−4.619
5800	61.690	382.559	327.971	316.614	321.736	507.264	−4.568
5900	61.711	383.614	328.905	322.784	323.430	510.447	−4.519
6000	61.732	384.652	329.825	328.956	325.115	513.601	−4.471

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

Aluminum Hydroxide, Ion ($AlOH^-$) IDEAL GAS $M_r = 43.98943$ Aluminum Hydroxide, Ion ($AlOH^-$) $Al_1H_1O_1^-(g)$

$S^\circ(298.15\ K) = [239.8 \pm 2]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H^\circ(0\ K) = [-221 \pm 95]\ kJ{\cdot}mol^{-1}$
$\Delta_f H^\circ(298.15\ K) = [-230.120]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm $^{-1}$
[900](1)
[1100](1)
[3600](1)

Ground State Quantum Weight: [2] $\sigma = 1$
Point Group: [C_s]
Bond Distances: Al–O = [1.90] Å; O–H = [0.96] Å
Bond Angle: Al–O–H = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [4.487473 \times 10^{-117}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

The enthalpy of formation is obtained from $\Delta_f H^\circ$(AlOH, g, 298 15 K) and its electron affinity, which is estimated to be 0.5 ± 0.9 eV (12 ± 20 kcal·mol^{-1}) The electron affinity is estimated to be small, or even negative, since the additional electron must go into an antibonding orbital, according to the correlation diagram of Walsh.[1]

Heat Capacity and Entropy

Since the molecule now has 11 valence electrons, the Walsh correlation diagram predicts a bent molecule. The extra electron is antibonding thus making the bonds weaker than in AlOH(g). The vibrational frequencies and bond lengths are taken to be the same as in $AlOH^+(g)$, which is also less strongly bound than AlOH(g). The bond angle is arbitrarily chosen as 120°. The principal moments of inertia are $I_A = 0.1049 \times 10^{-39}$, $I_B = 6.4867 \times 10^{-39}$, and $I_C = 6.5917 \times 10^{-39}\ g{\cdot}cm^2$.

Reference

[1] A. D. Walsh, J. Chem. Soc. 1953, 2288.

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	−10.123	−220.931		
100	33.261	202.633	270.605	−6.797			
200	33.987	225.808	243.059	−3.450			
250	35.123	233.506	240.403	−1.724			
298.15	36.521	239.810	239.810	0.	−230.120	−236.871	41.499
300	36.578	240.036	239.810	0.068	−230.190	−236.912	41.250
350	38.106	245.789	240.261	1.935	−232.059	−237.885	35.502
400	39.556	250.973	241.281	3.877	−233.906	−238.591	31.157
450	40.861	255.709	242.625	5.888	−235.726	−239.067	27.750
500	42.009	260.075	244.155	7.960	−237.524	−239.341	25.004
600	43.887	267.908	247.476	12.259	−241.084	−239.370	20.839
700	45.359	274.788	250.896	16.724	−244.641	−238.804	17.820
800	46.572	280.926	254.273	21.322	−248.247	−237.725	15.522
900	47.619	286.473	257.548	26.033	−251.946	−236.188	13.708
1000	48.548	291.539	260.697	30.842	−266.364	−233.474	12.195
1100	49.385	296.206	263.716	35.740	−269.994	−230.008	10.922
1200	50.141	300.536	266.606	40.717	−273.584	−226.214	9.847
1300	50.826	304.577	269.373	45.766	−277.141	−222.123	8.925
1400	51.446	308.367	272.025	50.880	−280.669	−217.758	8.125
1500	52.005	311.936	274.567	56.053	−284.175	−213.142	7.422
1600	52.508	315.309	277.009	61.279	−287.661	−208.292	6 800
1700	52.962	318.506	279.357	66.553	−291.134	−203.225	6.244
1800	53.371	321.545	281.617	71.870	−294.595	−197.955	5.744
1900	53.740	324.440	283.795	77.226	−298.049	−192.491	5.292
2000	54 072	327.206	285.897	82.616	−301.498	−186.846	4.880
2100	54.372	329.851	287.928	88.039	−304.945	−181.029	4.503
2200	54 644	332.387	289.891	93.490	−308.391	−175.047	4.156
2300	54.889	334.821	291.792	98.967	−311.839	−168.909	3.836
2400	55.112	337.162	293.634	104.467	−315.289	−162.621	3.539
2500	55.315	339.416	295.421	109.989	−318.744	−156.189	3.263
2600	55.500	341.589	297.155	115.529	−322.204	−149.618	3.006
2700	55.668	343.687	298.840	121.088	−325.670	−142.915	2.765
2800	55.822	345.714	300.478	126.663	−623.043	−135.115	2.521
2900	55.963	347.676	302.072	132.252	−625.428	−117.647	2.119
3000	56.092	349.575	303.624	137.855	−627.820	−100.096	1.743
3100	56.211	351.416	305.136	143.470	−630.221	−82.466	1.390
3200	56.321	353.203	306 610	149.097	−632.631	−64.758	1.057
3300	56.422	354.938	308.048	154.734	−635.050	−46.975	0.744
3400	56.515	356.623	309.452	160.381	−637.479	−29.118	0.447
3500	56.602	358.263	310.824	166.037	−639.918	−11.189	0.167
3600	56.682	359.858	312.164	171.701	−642.367	6.809	−0.099
3700	56.756	361.413	313.474	177.373	−644.827	24.875	−0.351
3800	56.826	362.927	314.755	183.052	−647.298	43.009	−0.591
3900	56.890	364.404	316.010	188.738	−649.781	61.208	−0.820
4000	56.950	365.845	317.238	194.430	−652.276	79.469	−1.038
4100	57.007	367.252	318 440	200.128	−654.783	97.794	−1.246
4200	57.059	368.626	319.619	205.831	−657.303	116.180	−1.445
4300	57 109	369.970	320.774	211.540	−659.837	134.627	−1.635
4400	57.155	371.283	321.907	217.253	−662.385	153.131	−1.818
4500	57.198	372.568	323.019	222.971	−664.946	171.694	−1.993
4600	57.239	373.826	324.110	228.692	−667.525	190.315	−2.161
4700	57.278	375.057	325.181	234.418	−670.120	208.992	−2.323
4800	57.314	376.263	326.232	240.148	−672.732	227.724	−2.478
4900	57.348	377.445	327.266	245.881	−675.362	246.510	−2.628
5000	57.380	378.604	328.281	251 617	−678.011	265.351	−2.772
5100	57.411	379.741	329.279	257.357	−680.682	284.245	−2.911
5200	57.440	380.856	330.260	263.100	−683.373	303.191	−3.046
5300	57.467	381.950	331.225	268.845	−686.087	322.190	−3.175
5400	57 493	383.025	332.174	274.593	−688.824	341.239	−3.301
5500	57.517	384.080	333.108	280.343	−691.587	360.339	−3.422
5600	57.541	385.117	334 028	286.096	−694.375	379.491	−3.540
5700	57.563	386.135	334.933	291.851	−697.191	398.692	−3.654
5800	57.584	387.136	335.825	297.609	−700.032	417.943	−3.764
5900	57 604	388.121	336.703	303.368	−702.906	437.242	−3.871
6000	57.623	389.089	337.568	309.129	−705.789	456.589	−3.975

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

Aluminum Hydroxide, Ion ($AlOH^-$) $Al_1H_1O_1^-(g)$

$S°(298.15\ K) = 254.4 \pm 6\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = [-455 \pm 63]\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [-460 \pm 63]\ kJ{\cdot}mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}	 ν, cm^{-1}
[3400](1)	[700](1)
[1200](1)	[500](1)
[1100](1)	[400](1)

Ground State Quantum Weight: 1 $\alpha = 1$
Point Group: [C_s]
Bond Distances: Al=O = [1.62] Å; Al–O = [1.87] Å; O–H = [0.94] Å
Bond Angles: O–Al–O = [180]°; Al–O–H = [105]°
Product of the Moments of Inertia: $I_AI_BI_C = [37.497324 \times 10^{-117}]\ gm^3{\cdot}cm^6$

Enthalpy of Formation

The hydroxyl group can often be considered as intermediate between F and Cl as is illustrated by the following examples of bond energies from these tables. $D_0°$(F–H) = 136 kcal·mol^{-1}, $D_0°$(Cl–H) = 103 kcal·mol^{-1} and $D_0°$(HO–H) = 119 kcal·mol^{-1}; also, $D_0°$(F–BO) = 163 kcal·mol^{-1}, $D_0°$(Cl–BO) = 105 kcal·mol^{-1} and $D_0°$(HO–BO) = 143 kcal·mol^{-1}. Thus from $D_0°$(F–AlO) = 181 kcal·mol^{-1} and $D_0°$(Cl–AlO) = 134 kcal·mol^{-1}, we estimate $D_0°$(HO–AlO) = 158 ± 20 kcal·mol^{-1}. This yields $\Delta_fH°$(HOAlO, g, 298.15 K) = −127 ± 20 kcal·mol^{-1}.

Consider also $D_0°$(FB–O) = 175 kcal·mol^{-1} and $D_0°$(ClB–O) = 169 kcal·mol^{-1}; and $D_0°$(FAl–O) = 138 kcal·mol^{-1} and $D_0°$(ClAl–O) = 132 kcal·mol^{-1}; it is evident that the substituent F or Cl has little effect on the B–O and Al–O bonds. Thus, we assume that $D_0°$(HOAl–O) = 135 ± 10 kcal·mol^{-1} which leads to $\Delta_fH°$(HOAlO, g, 298.15 K) = −119 ± 10 kcal·mol^{-1}.

Farber *et al.*[1] found no evidence for the ion DOAlO$^+$ when reacting $D_2O(g) + Al_2O_3(cr)$. Form estimates of the pressure needed to ensure detection of DOAlO and a knowledge of the D_2O pressure, they calculated the most negative value of $\Delta_fH°$(HOAlO, g, 298.15 K) = −104 ± 10 kcal·mol^{-1} The absence of DOAlO$^+$ may be caused by fragmentation by the ionizing electrons and thus the value quoted may not be a real limit.

We adopt $\Delta_fH°$(HOAlO, g, 298.15 K) = −110 ± 15 kcal·mol^{-1} which encompasses all the values.

Heat Capacity and Entropy

Vibrational frequencies, bond distances, bond angles, and the product of the moments of inertia are taken from NBS.[2] The principal moments of inertia are. $I_A = 0.1301 \times 10^{-39}$, $I_B = 16.9121 \times 10^{-39}$, and $I_C = 17.0422 \times 10^{-39}$ g·cm^2.

References

[1] M. Farber, M. A. Frisch, G. Grenier, and H. C. Ko, "Investigation of the Thermodynamic Properties of Rocket Combustion Products", AFRPL–TR–67–244, (November, 1967).

[2] U. S. Nat. Bur. Stand. Report 6297, 148 pp. (January 1, 1959).

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

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$ (kJ·mol^{-1})	$\Delta_fG°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−11.722	−454.505	−454.505	INFINITE
100	34.495	209.798	293.555	−8.376	−456.047	−453.961	237.125
200	42.414	235.968	258.738	−4.554	−458.285	−451.012	117.792
250	46.534	245.881	255.197	−2.329	−459.330	−449.071	93.828
298.15	50.137	254.391	254.391	0.	−460.240	−447.011	78.314
300	50.267	254.702	254.392	0.093	−460.273	−446.929	77.817
350	53.561	262.704	255.017	2.690	−461.111	−444 637	66.358
400	56.415	270 047	256.443	5.442	−461.856	−442.231	57.750
450	58.859	276.837	258.336	8.325	−462.524	−439.738	51.043
500	60.945	283.149	260.506	11.322	−463.130	−437.173	45.671
600	64.267	294.569	265.252	17.590	−464.220	−431.877	37.598
700	66.781	304.673	270.176	24.148	−465.234	−426.406	31.819
800	68.767	313.725	275.063	30.929	−466.247	−420.790	27.475
900	70.398	321.921	279.821	37.890	−467.320	−415.045	24.089
1000	71.774	329 412	284.411	45.000	−479.089	−408.414	21.333
1100	72.954	336.309	288.820	52.238	−480.054	−401.300	19.056
1200	73.978	342.702	293.047	59.586	−480.970	−394.099	17.155
1300	74.871	348.659	297.098	67.029	−481.845	−386.825	15.543
1400	75.653	354.237	300.983	74.556	−482.688	−379.483	14.159
1500	76.341	359.481	304.709	82.157	−483.508	−372.083	12.957
1600	76.948	364.427	308.289	89.822	−484.311	−364.629	11.904
1700	77.484	369.109	311.730	97.544	−485.102	−357.124	10.973
1800	77.959	373.551	315.042	105.317	−485.888	−349.574	10.144
1900	78.382	377.778	318.234	113.134	−486.671	−341.979	9 402
2000	78.758	381.808	321.312	120.991	−487.456	−334.343	8.732
2100	79.094	385.659	324.285	128.884	−488.247	−326.668	8.125
2200	79.396	389.345	327.160	136.809	−489.045	−318.955	7.573
2300	79.667	392.881	329.941	144.762	−489.853	−311.206	7.068
2400	79.911	396.277	332.634	152.742	−490.672	−303.421	6.604
2500	80.131	399.543	335.246	160.744	−491.505	−295.602	6.176
2600	80.330	402.690	337.780	168.767	−492.352	−287.749	5.781
2700	80.512	405.725	340.240	176.809	−493.214	−279.863	5.414
2800	80.676	408.656	342.632	184.869	−787.993	−270.977	5.055
2900	80.827	411.490	344.957	192.944	−787.792	−252.517	4.548
3000	80.964	414.232	347.221	201.034	−787.607	−234.062	4.075
3100	81.090	416.889	349.426	209.137	−787.440	−215.613	3.633
3200	81.206	419.466	351.575	217.251	−787.290	−197.170	3.218
3300	81.313	421.966	353.670	225.377	−787.157	−178.731	2.829
3400	81.411	424.395	355.715	233.514	−787.042	−160.295	2.463
3500	81.501	426.756	357.711	241.659	−786.945	−141.863	2.117
3600	81.585	429.053	359.661	249.814	−786.865	−123.433	1.791
3700	81.663	431.290	361.567	257.976	−786.803	−105.006	1.482
3800	81.735	433.469	363.430	266.146	−786.759	−86.579	1.190
3900	81.802	435.593	365.253	274.323	−786.732	−68.153	0.913
4000	81.865	437.665	367.038	282.506	−786.725	−49.729	0 649
4100	81.923	439.687	368.785	290.696	−786.736	−31.304	0.399
4200	81.978	441.662	370.497	298.891	−786.767	−12.878	0.160
4300	82.029	443.591	372.175	307.091	−786.817	5.549	−0.067
4400	82.077	445.477	373.819	315.297	−786.888	23.976	−0.285
4500	82.121	447.322	375.432	323.507	−786.976	42.405	−0.492
4600	82.164	449.128	377.015	331.721	−787.089	60.837	−0.691
4700	82.203	450.895	378.568	339.939	−787.224	79.272	−0.881
4800	82.240	452.626	380.093	348.161	−787.383	97.710	−1.063
4900	82.276	454.322	381.590	356.387	−787.565	116.151	−1.238
5000	82.309	455.985	383.062	364.616	−787.774	134.597	−1.406
5100	82.340	457.615	384.508	372.849	−788.010	153.047	−1.568
5200	82.370	459.214	385.929	381.084	−788.274	171.500	−1.723
5300	82.398	460.784	387.327	389.323	−788.567	189.961	−1.872
5400	82.424	462.324	388.701	397.564	−788.893	208.426	−2.016
5500	82.449	463.837	390.054	405.808	−789.250	226.898	−2.155
5600	82.473	465.323	391.384	414.054	−789.642	245.378	−2.289
5700	82.496	466.783	392.694	422.302	−790.071	263.864	−2.418
5800	82.517	468.217	393.984	430.553	−790.534	282.358	−2.543
5900	82.538	469 628	395.254	438.806	−791.040	300.859	−2.664
6000	82.557	471.016	396.506	447.060	−791.565	319.369	−2.780

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

Lithium Tetrahydroaluminate ($LiAlH_4$) CRYSTAL $M_r = 37.95414$

$S°(298.15\ K) = [87.86 \pm 0.4]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = \text{Unknown}$

$\Delta_f H°(298.15\ K) = -117.15 \pm 8.4\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The heats of solution of $LiAlH_4(cr)$ in HCl(aq) were measured calorimetrically by Davis *et al.*,[1] Fasolino *et al.*,[2] and Smith and Bass.[3] The results are given in the following table.

Source	Reaction	$\Delta_r H°(298.15\ 1K)$ kcal·mol^{-1}
Davis *et al.*[1]	(1) $LiAlH_4(cr) + 10\ HCl(aq, 50\ H_2O) \rightarrow [LiCl + AlCl_3 + 6\ HCl](aq, 500\ H_2O) + 4\ H_2(g)$	−165.87
	(2) $[AlCl_3 + LiCl + 6\ HCl](aq, 500\ H_2O) + 41020\ H_2O(l) \rightarrow [AlCl_3 + LiCl + 6\ HCl](aq, 41520\ H_2O)$	−4.43
	(3) $[AlCl_3 + LiCl + 6\ HCl](aq, 41520\ H_2O) \rightarrow [AlCl_3 + LiCl + 6\ HCl](aq, 5190\ H_2O)$	0.00(assumed)
	(1) + (2) + (3)	−170.30
Fasolino *et al.*[2]	(4) $Al + 60\ HCl(aq, 14\ H_2O) \rightarrow [AlCl_3 + 57\ HCl](aq, 840\ H_2O) + 3/2\ H_2(g)$	−128.14
	(5) $Li + 60\ HCl(aq, 14\ H_2O) \rightarrow [LiCl + 59\ HCl](aq, 840\ H_2O) + 1/2\ H_2(g)$	−67.05
	(6) $LiAlH_4(cr) + 60\ HCl(aq, 14\ H_2O) \rightarrow [LiCl + AlCl_3 + 56\ HCl](aq, 840\ H_2O) + 4\ H_2(g)$	−170.52
	(4) + (5) − (6)	−24.67
Smith and Bass[3]	(7) $LiAlH_4(cr) + 39.715\ HCl(aq, 11.624\ H_2O) \rightarrow [LiCl + AlCl_3 + 35.715\ HCl](aq, 12.926\ H_2O) + 4\ H_2(g)$	−164.6
	(8) $LiCl(cr) + [AlCl_3 + 35.715\ HCl](aq, 12.926\ H_2O) \rightarrow [LiCl + AlCl_3 + 35.715\ HCl](aq, 12.926\ H_2O)$	−6.75
	(7) − (8)	−157.85

Incorporating appropriate thermal data, the values for $\Delta_f H°(LiAlH_4, cr, 298.15\ K)$ were derived as −28.51 (recalculated value, by Smith and Bass),[3] −24.67 ± 1.31 and −28.4 ± 1.5 kcal·mol^{-1}, respectively. The adopted value, −28.0 ± 2.0 kcal·mol^{-1} (−117.152 ± 8.4 kJ·mol^{-1}), is the weighted average of the above three values.

Heat Capacity and Entropy

Bonnetot *et al.*[4] measured $C_p°$ in the region 15 to 308 K. Our adopted thermal functions at 300 K and below are based on the smoothed values and integration by those authors using $S°(15\ K) = 0.10\ J{\cdot}K^{-1}{\cdot}mol^{-1}$. Above 300 K we have used $C_p°$ values estimated by comparison with those for $LiBH_4(cr)$, $LiBO_2(cr)$ and $LiAlO_2(cr)$.[5]

Decomposition Data

$T_{dcm}(410 \pm 10\ K)$ was reported by Finholt *et al.*[6] The decomposition products are aluminum, hydrogen, and lithium hydride. This reaction is apparently kinetically controlled since the Gibbs free energy for the decomposition is negative even at room temperature.

References

[1] W. D. Davis, L. S. Mason and G. Stegeman, J. Am. Chem. Soc. **71**, 2775 (1949).
[2] L. G. Fasolino *et al.*, "Heat of Formation of Lithium Aluminum Hydride," Special Report, National Research Corporation, (April 26, 1963).
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[5] JANAF Thermochemical Tables: $LiBH_4(cr)$ 12–31–64, $LiBO_2(cr)$ 6–30–71; $LiAlO_2(cr)$ 12–31–79.
[6] A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, J. Am. Chem. Soc. 69, 1199 (1947).

Lithium Tetrahydroaluminate ($LiAlH_4$) $Al_1H_4Li_1(cr)$

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							
250							
298.15	86.400	87.864	87.864	0.	−117.152	−48.323	8.466
300	86.944	88.400	87.866	0.160	−117.189	−47.895	8.339
400	93.722	114.323	91.354	9.187	−119.082	−24.508	3.200
500	101.253	136.080	98.176	18.952	−123.729	−0.360	0.038
600	106.901	155.059	106.109	29.370	−124.888	24.431	−2.127
700	111.294	171.886	114.327	40.292	−125.614	49.379	−3.685
800	114.223	186.947	122.480	51.574	−126.114	74 414	−4.859
900	116.200	200.519	130.409	63.099	−126.571	99.507	−5.775
1000	117.780	212.847	138.046	74.801	−137.678	125.414	−6.551
1100	118.847	224.124	145.366	86.634	−137.979	151.738	−7.205
1200	119.746	234.505	152.368	98.565	−138.256	178.088	−7.752
1300	120.416	244.116	159.060	110.573	−138.536	204.461	−8.215
1400	121.043	253.063	165.459	122.646	−138.832	230.857	−8.613
1500	121.615	261.434	171.581	134.779	−139.148	257.274	−8.959
1600	122.173	269.301	177.445	146.969	−139.485	283 713	−9.262
1700	122.717	276.724	183.069	159.213	−285.080	317.350	−9.751
1800	123.247	283.753	188.469	171.512	−284.705	352.776	−10.237
1900	123.763	290.431	193.661	183.862	−284.357	388 182	−10.672
2000	124.265	296.792	198.660	196.264	−284.034	423.570	−11.063

PREVIOUS: June 1963 CURRENT· March 1964

Aluminum Iodide (AlI) IDEAL GAS $M_r = 153.88604$ Aluminum Iodide (AlI) $Al_1I_1(g)$

$S°(298.15\ K) = 247.830 \pm 0.21\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 69.34 \pm 4.18\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 67.95 \pm 4.18\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
	21899.6	2
$a^3\Pi$	[22290.]	[2]
$A^1\Pi$	31487.	2
$[b^3\Sigma^+]$	[43000.]	3

$\omega_e = 316.16\ cm^{-1}$ $\omega_e x_e = 0.960\ cm^{-1}$ $\sigma = 1$
$B_e = 0.11770\ cm^{-1}$ $\alpha_e = 0.0005586\ cm^{-1}$ $r_e = 2.5371$

Enthalpy of Formation

Gaydon,[1] Rosen[2] and Huber and Herzberg[3] reference the analysis by Barrow[4] for values of the dissociation energy of AlI(g). Barrow[4] reports $D_0^\circ = 364\ 0\ kJ\cdot mol^{-1}$ from an analysis of fluctuation bonds in the AlI spectrum. Martin and Barrow[5] report a value of 365.97 ± 1.92 kJ mol^{-1} for the dissociation energy of AlI based on previous observations of the $A^1 - X^1\Sigma^+$continuum and calculated potentials for these states. Our adopted dissociation energy is the average of these values, 365.01 ± 0.21 kJ·mol^{-1}, and yields $\Delta_f H°$(AlI, g, 298.15 K) = 67.95 ± 4.18 kJ·mol^{-1}.

Heat Capacity and Entropy

Molecular and spectroscopic constants are based on the analysis of electronic spectra published by Martin and Barrow.[5] The constants are in excellent agreement with those from earlier studies.[6 7] The electronic states are taken from Rosen[2] with the exception of the upper $^3\Pi$ state and the $b^3\Sigma^+$ state. The upper $^3\Pi$ state is estimated to be approximately in a linear relationship with the two lower $^1\Pi$ states. The $b^3\Sigma^+$ state is assigned by analogy with AlF, AlCl and AlBr, JANAF Thermochemical Tables, 3rd ed.[8]

References

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[8] JANAF Thermochemical Tables: AlF(g), AlCl(g), and AlBr(g), 9–30–79.

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	−9.749	69.337	69.337	INFINITE
100	31.012	210.863	278.841	−6.798	70.280	52.942	−27.654
200	34.703	233.666	251.098	−3.486	69.323	35.915	−9.380
250	35.586	241.513	248.422	−1.727	68.655	27.638	−5.775
298.15	36.127	247.830	247.830	0.	67.948	19.802	−3.469
300	36.144	248.054	247.831	0.067	67.920	19.503	−3.396
350	36.516	253.655	248.273	1.884	67.096	11.497	−1.716
400	36.778	258.549	249.258	3.717	58.242	3.887	−0.508
450	36.971	262.893	250.536	5.561	56.766	−2.819	0.327
500	37.119	266.796	251.970	7.413	35.208	−7.460	0.779
600	37.333	273.584	255.023	11.136	34.318	−15.912	1.385
700	37 484	279.351	258.097	14.877	33.328	−24.207	1.806
800	37.601	284.364	261.074	18.632	32.212	−32.351	2.112
900	37.697	288.798	263.913	22.397	30.941	−40.347	2.342
1000	37.780	292.774	266.604	26.171	18.899	−47.432	2.478
1100	37.856	296.379	269.149	29.953	17.598	−54.002	2.564
1200	37.925	299.676	271.558	33.742	16.296	−60.454	2.632
1300	37.990	302.714	273.839	37.538	14.988	−66.797	2.684
1400	38.053	305.532	276.003	41.340	13.672	−73.039	2.725
1500	38.113	308.159	278.060	45.148	12.342	−79.186	2.758
1600	38.171	310.621	280.019	48.962	10.992	−85.244	2.783
1700	38.228	312.937	281.888	52.782	9.619	−91.217	2.803
1800	38.284	315.123	283.674	56.608	8.219	−97.108	2.818
1900	38.340	317.195	285.385	60.439	6.790	−102.921	2.829
2000	38.396	319.163	287.025	64.276	5.332	−108.658	2.838
2100	38.451	321.037	288.600	68.118	3.845	−114.321	2.844
2200	38.507	322.827	290.115	71.966	2.333	−119.912	2.847
2300	38.564	324.540	291.575	75.820	0.799	−125.435	2.849
2400	38.623	326.183	292.983	79.679	−0.752	−130.890	2.849
2500	38.685	327.761	294.343	83.544	−2.314	−136.280	2.847
2600	38.750	329.279	295.658	87.416	−3.880	−141.608	2.845
2700	38.819	330.743	296.930	91.295	−5.445	−146.875	2.841
2800	38.893	332.156	298.163	95.180	−300.904	−151 117	2.819
2900	38.974	333.522	299.359	99.073	−301.352	−145 760	2.625
3000	39.063	334.845	300.520	102.975	−301.782	−140.387	2.444
3100	39.159	336.127	301.648	106.886	−302.188	−135.000	2.275
3200	39.266	337.372	302.745	110.807	−302.565	−129.601	2.116
3300	39.383	338.582	303.813	114.740	−302.910	−124.191	1.966
3400	39.512	339.760	304.853	118.684	−303.218	−118.770	1.825
3500	39.653	340.907	305.867	122.643	−303.488	−113.341	1.692
3600	39.808	342.027	306.856	126.616	−303.717	−107.905	1.566
3700	39.977	343.120	307.821	130.605	−303.902	−102.463	1.447
3800	40.160	344.188	308.764	134.611	−304.041	−97.017	1.334
3900	40.359	345.234	309.686	138.637	−304.134	−91.568	1.226
4000	40.572	346.258	310.587	142.684	−304.178	−86.117	1.125
4100	40.802	347.263	311.470	146.752	−304.173	−80.665	1.028
4200	41.047	348.249	312.334	150.844	−304.118	−75.214	0.935
4300	41.307	349.218	313.180	154.962	−304.012	−69.765	0.847
4400	41.583	350.171	314.010	159.106	−303.856	−64.319	0.764
4500	41.875	351.108	314.824	163.279	−303.646	−58.878	0.683
4600	42.180	352.032	315.623	167.482	−303.387	−53.441	0.607
4700	42.500	352.943	316.407	171.716	−303.076	−48.011	0.534
4800	42.834	353.841	317.178	175.982	−302.714	−42.588	0.463
4900	43.181	354.728	317.935	180.283	−302.301	−37.173	0.396
5000	43.540	355.604	318.680	184.619	−301.838	−31.767	0.332
5100	43.910	356.469	319.412	188.991	−301.325	−26.370	0.270
5200	44.291	357.326	320.133	193.401	−300.764	−20.984	0.211
5300	44.681	358.173	320.843	197.850	−300.154	−15.610	0.154
5400	45.080	359.012	321.542	202.338	−299.497	−10.247	0 099
5500	45.486	359.843	322.231	206.866	−298.794	−4.897	0.047
5600	45.899	360.666	322.910	211.435	−298.045	0.440	−0.004
5700	46.318	361.482	323.579	216.046	−297.253	5.763	−0.053
5800	46.740	362.291	324.240	220.699	−296.416	11.072	−0.100
5900	47.167	363.094	324.892	225.394	−295.540	16.366	−0.145
6000	47.595	363.890	325.535	230.132	−294.602	21.642	−0.188

PREVIOUS September 1979 (1 atm) CURRENT September 1979 (1 bar)

Aluminum Iodide (AlI_3) CRYSTAL M_r = 407.69504

$S°(298.15\ K) = [196.10]\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{fus} = 464.15 \pm 0.2\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -302.9 \pm 2.0\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = 15.9 \pm 1.3\ kJ\cdot mol^{-1}$

Enthalpy of Formation

Literature values for the enthalpy of formation of $AlI_3(cr)$ are based on solution calorimetry measurements and differ considerably in magnitude. The heat of solution of the crystal in H_2O at 298.15 K was measured by Dear and Eley[1] and reported as $-91.4 \pm 1.5\ kcal\cdot mol^{-1}$. Adopting CODATA's[2] values for the enthalpies of formation of the aqueous ions, this yields $\Delta_f H°(AlI_3,\ cr,\ 298.15\ K) = -78.0 \pm 2.0\ kcal\cdot mol^{-1}$. This estimate is undoubtedly high because of hydrolysis of the salt.

More reliable measurements have been attempted in aqueous acid and base. Klemm and Tanke[3] measured the heat of solution of $AlI_3(cr)$ at 273 K in aqueous HCl Using auxiliary data including estimated heat capacities, they reported $\Delta_f H°(AlI_3,\ cr,\ 298.15\ K) = -70.6 \pm 0.7\ kcal\cdot mol^{-1}$ Efimov, Kislova and Medvedev[4] measured the heat of solution of $AlI_3(cr)$ in an aqueous HCl solution containing KCl(cr) and the heat of solution of $AlCl_3(cr)$ in an aqueous HCl solution containing KI(cr). From these heats of solution measurements and using the heats of formation of $AlCl_3$,[5] KCl[6,7] and KI[6,8] as auxiliary data, they obtained $\Delta_f H°(AlI_3,\ cr,\ 298.15\ K) = -72.4 \pm 0.5\ kcal\cdot mol^{-1}$. In a similar study, Anthoney *et al.*[9] measured the heat of solution of $AlI_3(cr)$ and $AlCl_3(cr)$ in an aqueous alkaline solution containing dissolved sodium halides. They reported $\Delta_f H°(AlI_3,\ cr,\ 298.15\ K = -67.0 \pm 0.6\ kcal\cdot mol^{-1}$.

Corbett and Gregory[10] investigated the equilibrium $AlI_3(cr) + 3\ HCl(g) \rightarrow AlCl_3(cr) + 3\ HI(g)$ and reported $\Delta_r G°(298.15\ K) = -8.7 \pm 0.2\ kcal\cdot mol^{-1}$. Using auxiliary data, the derived heat of reaction is $-10.7 \pm 0.2\ kcal\cdot mol^{-1}$ and the heat of formation of AlI_3, $\Delta_f H°(AlI_3,\ cr,\ 298.15\ K)$ is evaluated to be $-73.6 \pm 0.8\ kcal\cdot mol^{-1}$. The value reported by Efimov *et al.*[4] is chosen as most reliable and is adopted for the heat of formation.

Heat Capacity and Entropy

The heat capacities, 298.15–464 K, were taken from Kelley,[11] whose values were derived from the enthalpy data measured by Fischer.[12] Above 464 K the $C_p°$ values are obtained by graphical extrapolation. The entropy, $S°(AlI_3,\ cr,\ 298\ 15\ K)$, is calculated from $S°(AlI_3,\ l,\ 298.15\ K)$ by subtracting $\Delta_{fus} S°$ and the difference between $S°(464.15\ K) - S°(298.15\ K)$ for crystal and liquid.

Fusion Data

The temperature and enthalpy of melting were measured by Fischer.[12]

Sublimation Data

The enthalpy of sublimation, $\Delta_{sub} H°(298.15\ K) = 116.3\ kJ\cdot mol^{-1}$ for the process $2\ AlI_3(cr) = 2\ Al_2I_6(g)$, is calculated from vapor pressure data reported by Fischer, Rahlfs and Benze[13] by both the 2nd and 3rd law methods. Refer to the $Al_2I_6(g)$ table for details.

References

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[11] W. Fischer, Z. anorg. allgem. Chem. **200**, 332 (1931).
[12] W. Fischer, O. Rahlfs and B. Benze, Z. anorg. allgem. Chem., **205**, 1 (1932).

Aluminum Iodide (AlI_3) $Al_1I_3(cr)$

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

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	98.910	196.104	196.104	0.	−302.922	−301.018	52.737
300	99.077	196.716	196.106	0.183	−302.934	−301.006	52.410
400	108.533	226.513	200.105	10.563	−327.520	−299.436	39.102
464.150	114.614	243.098	204.919	17.721	--- CRYSTAL <--> LIQUID ---		
500	116.901	251.742	207.972	21.885	−391.126	−286.306	29.910
600	121.986	273.543	217.126	33.850	−387.527	−265.674	23.129
700	125.063	292.599	226.576	46.216	−383.660	−245.669	18.332
800	126.918	309 430	235.902	58.823	−379.703	−226.226	14.771
900	127.901	324 444	244.921	71.571	−375.781	−207.277	12.030
1000	128.449	337.949	253.560	84.390	−382.581	−187.999	9.820
1100	128.875	350.213	261.798	97.257	−378.611	−168.733	8.012
1200	129.160	361.440	269.640	110.160	−374.632	−149.829	6.522
1300	129.319	371.784	277.105	123.084	−370.667	−131.256	5.274
1400	129.501	381.374	284.214	136.024	−366.732	−112.988	4.216
1500	129.704	390.316	290.993	148.984	−362.838	−95.000	3.308

PREVIOUS: June 1964 CURRENT: September 1979

Aluminum Iodide (AlI_3) $Al_1I_3(cr)$

Aluminum Iodide (AlI_3) LIQUID $M_r = 407.69504$ Aluminum Iodide (AlI_3) $Al_1I_3(l)$

$S°(298.15\ K) = [223.648]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 464.15 \pm 0.2\ K$

$\Delta_fH°(298.15\ K) = [-289.444]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 15.9 \pm 1.3\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(AlI_3, l, 298.15\ K)$ is calculated from $\Delta_fH°(AlI_3, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(464.15\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacities, 464–500 K, were taken from Kelley,[1] whose values were derived from the enthalpy data measured by Fischer.[2] The $C_p°$ values above 500 K were assumed to be the same as that at 500 K. $S°(298\ 15\ K)$ is estimated so that the values of $\Delta_{vap}H°$ calculated from vapor pressure data by the 2nd and 3rd law methods are in reasonable agreement. Refer to the $Al_2I_6(g)$ table for details.

Fusion Data

The temperature and enthalpy of melting were reported by Fischer.[2]

References

[1] K. K. Kelley, U. S. Bur. Mines Bull. 584, 232 pp. (1960); refer to p. 13.
[2] W Fischer, Z. anorg. allgem. Chem. 200, 332 (1931).

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	S°	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
250							
298.15	121.336	223.648	223.648	0.	−289.444	−295.752	51.815
300	121.336	224.398	223.650	0.224	−289.415	−295.792	51.502
400	121.336	259.305	228.409	12.358	−312.247	−297.280	38.821
464.150	121.336	277.352	233.957	20.142	--- CRYSTAL <--> LIQUID ---		
500	121.336	286.380	237.397	24.492	−375.041	−287.541	30.039
600	121.336	308.502	247.460	36.625	−371.274	−270.397	23.540
700	121.336	327.206	257.551	48.759	−367.639	−253.873	18.944
800	121.336	343.408	267.293	60.892	−364.155	−237.860	15.531
900	121.336	357.700	276.559	73.026	−360.848	−222.274	12.900
1000	121.336	370.484	285.324	85.160	−368.333	−206.286	10.775
1100	121.336	382.048	293.600	97.293	−365.097	−190.238	9.034
1200	121.336	392.606	301.417	109.427	−361.887	−174.483	7.595
1300	121.336	402.318	308.810	121.560	−358.713	−158.995	6.389
1400	121.336	411.310	315.814	133.694	−355.585	−143.750	5.363
1500	121.336	419.681	322.463	145.828	−352.517	−128.726	4.483
1600	121.336	427.512	328.786	157.961	−349.524	−113.905	3.719
1700	121.336	434.868	334.812	170.095	−346.619	−99 268	3.050
1800	121.336	441.803	340.565	182.228	−343.812	−84.800	2.461
1900	121.336	448.364	346.068	194.362	−341.109	−70.485	1.938
2000	121.336	454.587	351.339	206.496	−338.511	−56.309	1.471

PREVIOUS: June 1964 CURRENT· September 1979

Aluminum Iodide (AlI_3)

CRYSTAL-LIQUID

0 to 464.15 K crystal
above 464.15 K liquid

Refer to the individual tables for details.

$M_r = 407.69504$ **Aluminum Iodide (AlI_3)** **$Al_1I_3(cr,l)$**

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							
90							
200							
250							
298.15	98.910	196.104	196.104	0.	−302.922	−301.018	52.737
300	99.077	196.716	196.106	0.183	−302.934	−301.006	52.410
400	108.533	226.513	200.105	10.563	−327.520	−299.436	39.102
464.150	114.614	243.098	204.919	17.721	____ CRYSTAL <--> LIQUID ____		
464.150	121.336	277.352	204.919	33.620		TRANSITION	
500	121.336	286.380	210.440	37.970	−375.041	−287.540	30.039
600	121.336	308.502	224.996	50.103	−371.274	−270.396	23.540
700	121.336	327.206	238.296	62.237	−367.639	−253.873	18 944
800	121.336	343.408	250.445	74.371	−364.155	−237.860	15.531
900	121.336	357.699	261.584	86.504	−360.848	−222.274	12.900
1000	121.336	370.483	271.846	98.638	−368.332	−206.285	10.775
1100	121.336	382.048	281.347	110.771	−365.097	−190.237	9.034
1200	121.336	392.606	290.185	122.905	−361.887	−174.483	7.595
1300	121.336	402.318	298.442	135.039	−358.712	−158.995	6.388
1400	121.336	411.310	306.187	147.172	−355.584	−143.750	5.363
1500	121.336	419.681	313.477	159.306	−352.517	−128.726	4.483

PREVIOUS.   CURRENT September 1979

Aluminum Iodide (AlI_3)   **$Al_1I_3(cr,l)$**

$S°(298.15\text{ K}) = 373.62 \pm 08\text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_fH°(0\text{ K}) = -187.9 \pm 8.4\text{ kJ·mol}^{-1}$
$\Delta_fH°(298.15\text{ K}) = -193.3 \pm 8.4\text{ kJ·mol}^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}
156 (1)	[450](2)
[140](1)	64 (2)

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: D_{3h}
Bond Distance: Al–I = 2.449 ± 0.013 Å
Bond Angle: I–Al–I = 120 ± 4°
Product of the Moments of Inertia: $I_AI_BI_C = 1.362810 \times 10^{-110}\text{ g}^3\text{·cm}^6$

Enthalpy of Formation

Fischer, Rahlfs and Benze[1] have determined the equilibrium constants for the reaction $Al_2I_6(g) = 2\ AlI_3(g)$ from vapor density measurements. The heats of reaction are calculated from these data using both 2nd and 3rd Law methods. The results are summarized below:

T/K	Data Points	$\Delta_rH°(298.15\text{ K})$, kcal·mol^{-1} Al_2I_6 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_fH°(298.15\text{ K})$ kcal mol^{-1}
656–819	11[a]	24.39 ± 0.5	24.56 ± 0.2	0.2 ± 0.6	−46.2

[a]Points at 614.15, 644.15, 843.15 rejected due to statistical test.

The adopted value, $\Delta_fH°(AlI_3, g, 298\ 15\text{ K}) = -46.2 \pm 2.0\text{ kcal·mol}^{-1}$ ($-193.3 \pm 8.4\text{ kJ·mol}^{-1}$), is based on the 3rd law enthalpy of reaction and $\Delta_fH°(Al_2I_6, g, 298.15\text{ K}) = -489.5 \pm 8.4\text{ kJ·mol}^{-1}$.

Heat Capacity and Entropy

The molecular structure, bond distances and angles were taken from the electron diffraction work reported by Shen.[2] These values are in good agreement with those determined by Akishin, Rambidi and Zasorin.[3] Beattie and Horder[4] studied the gas phase Raman spectra of monomeric AlI_3 and reported $\nu_1 = 156\text{ cm}^{-1}$ and $\nu_4 = 64\text{ cm}^{-1}$. The other vibrational frequencies were adjusted not only for consistency with the frequencies chosen for $AlF_3(g)$, $AlCl_3(g)$ and $AlBr_3(g)$[5] but also for agreement between the 2nd and 3rd Law $\Delta_rH°(298.15\text{ K})$ in the data set tabulated above. The principal moments of inertia are $I_A = 189.5840 \times 10^{-39}$, $I_B = 189.5841 \times 10^{-39}$, and $I_C = 379.1681 \times 10^{-39}\text{ g·cm}^2$.

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[5]JANAF Thermochemical Tables: $AlF_3(g)$, $AlCl_3(g)$ and $AlBr_3(g)$, 9–30–79.

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.	INFINTTE	−18.930	−187.894	−187.894	INFINITE
100	61.385	297.474	438.424	−14.095	−188.118	−208.018	108.658
200	72.150	343.761	380.536	−7.355	−190.578	−227.014	59.290
250	75.138	360.205	374.875	−3.668	−191.946	−235.966	49.302
298.15	77.081	373.616	373.616	0.	−193.301	−244.323	42.804
300	77.142	374.093	373.617	0 143	−193.354	−244.639	42.595
350	78.515	386.094	374.562	4.036	−194.914	−253.067	37.768
400	79 482	396.645	376.676	7.987	−220.475	−260.444	34.010
450	80.184	406 049	379.427	11.980	−223.836	−265.238	30.788
500	80.706	414.526	382.520	16.003	−287.387	−263.960	27.576
600	81.414	429.308	389.122	24.112	−287.645	−259.251	22.570
700	81.856	441.894	395.784	32.277	−287.978	−254.494	18.991
800	82.149	452.844	402.247	40.478	−288.427	−249.681	16.302
900	82.353	462.533	408.417	48.704	−289.027	−244.803	14.208
1000	82.501	471.217	414.271	56.947	−300.403	−239.089	12.489
1100	82.611	479.086	419.811	65.203	−301.045	−232.927	11.061
1200	82.695	486.278	425 054	73.468	−301.703	−226.706	9.868
1300	82.760	492.900	430.022	81 741	−302.389	−220.428	8.857
1400	82.813	499.035	434.735	90.020	−303.116	−214.097	7.988
1500	82.855	504.750	439.214	98.303	−303.899	−207.711	7.233
1600	82.890	510.098	443.479	106.590	−304.752	−201.271	6.571
1700	82.919	515.124	447.547	114.881	−305.690	−194.775	5.985
1800	82.943	519 865	451.435	123.174	−306.724	−188.222	5.462
1900	82.963	524.350	455.155	131.469	−307.859	−181.608	4.993
2000	82.981	528.606	458.722	139.767	−309.097	−174.931	4.569
2100	82.996	532.655	462.147	148.065	−310.435	−168.191	4.184
2200	83.009	536.516	465.441	156.366	−311.866	−161.384	3.832
2300	83.021	540.206	468.612	164.667	−313.377	−154.510	3.509
2400	83.031	543.740	471.669	172.970	−314.955	−147.570	3.212
2500	83.040	547.129	474.620	181.273	−316.583	−140.562	2.937
2600	83.047	550.386	477.472	189.578	−318.243	−133.488	2.682
2700	83.054	553.521	480.231	197.883	−319.918	−126.350	2.444
2800	83 061	556.541	482.902	206.189	−615.492	−118.183	2.205
2900	83.066	559.456	485.492	214.495	−616.052	−100.412	1.809
3000	83.071	562.272	488.005	222.802	−616.580	−82.622	1.439
3100	83.076	564.996	490.445	231.109	−617.063	−64.815	1 092
3200	83.080	567.634	492.816	239.417	−617.490	−46.994	0.767
3300	83.084	570.190	495.122	247.725	−617.852	−29.160	0.462
3400	83 087	572.671	497.367	256.034	−618.142	−11.317	0.174
3500	83.091	575.079	499.553	264.343	−618.353	6.535	−0.098
3600	83.094	577.420	501.683	272.652	−618.483	24.390	−0.354
3700	83.096	579 697	503 761	280.961	−618.528	42.249	−0.596
3800	83.099	581.913	505.789	289.271	−618.486	60.108	−0.826
3900	83 101	584.071	507.769	297.581	−618.356	77.964	−1.044
4000	83.103	586.175	509.703	305.891	−618.139	95.815	−1 251
4100	83.105	588.227	511.593	314.202	−617.836	113.661	−1.448
4200	83.107	590.230	513.441	322.512	−617.448	131.498	−1 635
4300	83.109	592.186	515.250	330.823	−616.977	149.324	−1.814
4400	83.110	594.096	517.020	339.134	−616.426	167.139	−1.984
4500	83.112	595 964	518.754	347.445	−615.794	184.940	−2.147
4600	83.113	597.791	520.452	355.756	−615.090	202.726	−2.302
4700	83.114	599.578	522.117	364.068	−614.314	220.497	−2.451
4800	83.116	601.328	523.749	372.379	−613.469	238.250	−2.593
4900	83.117	603.042	525.350	380.691	−612.558	255.985	−2.729
5000	83.118	604.721	526.921	389.003	−611.587	273.700	−2.859
5100	83.119	606.367	528.462	397.315	−610.557	291.396	−2.985
5200	83.120	607.981	529.976	405.626	−609.473	309.071	−3 105
5300	83.121	609.564	531.463	413.939	−608.337	326.724	−3.220
5400	83.122	611.118	532.924	422.251	−607.154	344.356	−3.331
5500	83.122	612.643	534.359	430.563	−605.926	361.965	−3.438
5600	83.123	614.141	535.770	438.875	−604 658	379.552	−3.540
5700	83.124	615.612	537.158	447.187	−603.352	397.116	−3.639
5800	83.125	617.058	538.524	455.500	−602.009	414.656	−3.734
5900	83.125	618.479	539.867	463.812	−600.637	432.173	−3.826
6000	83.126	619.876	541.189	472.125	−599.215	449.664	−3.915

PREVIOUS· September 1979 (1 atm) CURRENT. September 1979 (1 bar)

Lithium Aluminum Oxide ($LiAlO_2$) CRYSTAL $M_r = 65.92134$

$\Delta_f H°(0\ K) = -1180.52 \pm 2.1\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 53.31 \pm 1.2\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = -1188.67 \pm 2.1\ kJ{\cdot}mol^{-1}$

$T_{fus} = 1973 \pm 15\ K$ $\Delta_{fus}H° = [87.864 \pm 21]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation is based on the solution calorimetric studies of Coughlin.[1] From measurements of the heat of solution of $LiAlO_2(cr)$ in aqueous HCl and of four auxiliary reactions, Coughlin reported $\Delta_r H°(303.15\ K) = -89.12 \pm 0.14\ kcal{\cdot}mol^{-1}$ for $Al(cr) + LiCl(cr) + 14.731\ H_2O(l) \rightarrow LiAlO_2(cr) + HCl{\cdot}12.731\ H_2O(aq) + 3/2\ H_2(g)$. This value is corrected to $\Delta_r H°(298.15\ K) = -88.9 \pm 0.14\ kcal{\cdot}mol^{-1}$ using heat capacities of the materials. This value, when combined with auxiliary heats of formation[2,3] yields our adopted value of $\Delta_f H°(LiAlO_2,\ cr,\ 298.15\ K) = -284.1 \pm 0.5\ kcal{\cdot}mol^{-1}$ $(-1188.674\ kJ{\cdot}mol^{-1})$.

Gross *et al.*[4] measured the heats of solution of $LiAlO_2(cr)$ and of $Al_2O_3 3\ H_2O$(cr, gibbsite) + $Li_2O(cr)$ in aqueous HF. From these and the heat of solution of three moles of H_2O in HF(aq) they report $\Delta_r H°(298.15\ K) = -11.3\ kcal{\cdot}mol^{-1}$ for $Li_2O(cr) + Al_2O_3 3\ H_2O(cr,\ gibbsite) \rightarrow 2\ LiAlO_2(cr) + 3\ H_2O(l)$. Combining this $\Delta_r H°$ with auxiliary heats of formation[2,5] yields $\Delta_f H°(LiAlO_2,\ cr,\ 298.15\ K) = -283.8 \pm 0.7\ kcal{\cdot}mol^{-1}$, in excellent agreement with the adopted value.

Equilibrium studies of vapor pressure over $LiAlO_2(cr)$ by the torsion effusion technique support the adopted value of $\Delta_f H°(298.15\ K)$. Potter *et al.*[6] and Popkov and Semenov[7] both studied the equilibrium $LiAlO_2(cr) \rightarrow Li(g) + x/4\ O_2(g) + (1-x)/2\ O(g) + 1/2\ Al_2O_3(cr,\ \alpha)$ in the temperature range from 1500 to 1820 K where $1-x \cong 0.13$. Neither author reports the raw data but they do report 2nd and 3rd law values for $\Delta_r H°(298.15\ K)$. Based on these reported values and auxiliary $\Delta_f H°(298.15\ K)$ data[2] we calculate 2nd and 3rd law values for $\Delta_f H°(LiAlO_2,\ cr,\ 298.15\ K)$ of -283.9 and $-282.8\ kcal{\cdot}mol^{-1}$, respectively, from the data of Potter *et al.*[6] 2nd and 3rd law values for $\Delta_f H°(298.15\ K)$ calculated from the results of Popkov and Semenov[7] are -283.8 and $-277.9\ kcal{\cdot}mol^{-1}$, respectively. The expected uncertainty in these determinations is of the order of 2 to 5 $kcal{\cdot}mol^{-1}$.

Heat Capacity and Entropy

The adopted values of $C_p°$ below 300 K are taken from Douglas and Beckett[8] based on the low temperature $C_p°$ measurements of King (53–296 K).[9] At higher temperatures the adopted $C_p°$ data are based on the drop calorimetric enthalpy data of Christensen *et al.* (399–1795 K).[10] No transitions were detected in either study.

Phase Data

The data in this table are for the γ or tetragonal phase of $LiAlO_2$. The crystal structure is $P4_12_12$.[11,12] A hexagonal (α) phase may be prepared but converts to the γ phase on heating. Byker *et al.*[13] recently reviewed the phase data and constructed a phase diagram for the Al_2OLi_2O system. The reader is referred to their paper for details but the following comments may be informative. The α to γ phase transformation occurs above 1173 K but may occur at lower temperature. The transition has frequently been reported as irreversible although Lejus and Collongues[14] report that the γ to α transformation does occur if aided by prolonged grinding. Measurements of the heat of the α–γ transition are hampered by its slow nature but apparently imply that it is slightly exothermic near 1200 K. Based on the above data and the known density change between α and γ phases, Byker *et al.* constructed a phase diagram which indicates that the α phase is the thermodynamically stable phase below ~550 K at 1 atm pressure. This seems to support the observation of Lejus and Collongues. The uncertainties are such that this temperature may be off by several hundred Kelvin. Thus, while it is clear that the γ phase is the thermodynamically stable phase above 1200 K, its stability at low temperature may be controlled by kinetic factors.

Fusion Data

Refer to the liquid table for details.

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Lithium Aluminum Oxide ($LiAlO_2$) $Al_1Li_1O_2(cr)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.693	−1180.523	−1180.523	INFINITE
100	17.966	8.046	99.257	−9.121	−1183.834	−1165.875	608.991
200	47.999	30.154	58.942	−5.758	−1187.025	−1146.565	299.452
298.15	67.777	53.313	53.313	0.	−1188.674	−1126.303	197.324
300	68.128	53.733	53.314	0.126	−1188.693	−1125.916	196.039
400	81.546	75.421	56.180	7.697	−1189.202	−1104.891	144.284
500	88.408	94.425	61.974	16.226	−1192.298	−1083.492	113.192
600	92.688	110.947	68.790	25.294	−1192.108	−1061.744	92.433
700	95.751	125.475	75.871	34.723	−1191.706	−1040.047	77.609
800	98.165	138.424	82.896	44.423	−1191.220	−1018.414	66.496
900	100.203	150.107	89.725	54.343	−1190.737	−996.843	57.855
1000	102.006	160.759	96.303	64.455	−1200.889	−974.563	50.906
1100	103.654	170.559	102.614	74.740	−1200.170	−951.964	45.205
1200	105.198	179.645	108.660	85.183	−1199.326	−929.436	40.457
1300	106.671	188.124	114.450	95.777	−1198.363	−906.983	36.443
1400	108.089	196.082	119.999	106.515	−1197.279	−884.609	33.005
1500	109.466	203.586	125.324	117.393	−1196.075	−862.317	30.029
1600	110.813	210.694	130.439	128.408	−1194.752	−840.109	27.427
1700	112.140	217.452	135.361	139.556	−1338.549	−810.812	24.913
1800	113.449	223.899	140.102	150.835	−1336.240	−779.835	22.630
1900	114.746	230.068	144.676	162.245	−1333.827	−748.988	20.591
1973.000	115.679	234.411	147.916	170.656	--- CRYSTAL <--> LIQUID ---		
2000	116.022	235.986	149.094	173.784	−1331.309	−718.272	18.759
2100	117.294	241.678	153.368	185.449	−1328.691	−687.684	17.105
2200	118.558	247.163	157.508	197.242	−1325.971	−657.223	15.604

PREVIOUS: June 1972 CURRENT: December 1979

Lithium Aluminum Oxide ($LiAlO_2$) $Al_1Li_1O_2(cr)$

$S°(298.15\ K) = [93.711]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-1107.739]\ kJ·mol^{-1}$

$T_{fus} = 1973 \pm 15\ K$ $\Delta_{fus}H° = [87.864 \pm 21]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(LiAlO$_2$, l, 298.15 K) is calculated from $\Delta_f H°$(LiAlO$_2$, cr, 298.15 K) by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°$(1973 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of LiAlO$_2$(l) is estimated to be 30 cal·K^{-1}·mol^{-1} (125.52 J·K^{-1}·mol^{-1}) above a hypothetical glass transition temperature of 1450 K. Below this temperature the heat capacity is taken to be the same as the crystal. The adopted $C_p°$ = 30 cal·K^{-1}·mol^{-1} is based on an estimated value of $C_p°$ = 7.5 cal·K^{-1}·g·atom^{-1} recommended by Kubaschewski and Alcock.[2] $S°$(298.15 K) is calculated in a manner analogous to that used for the enthalpy formation.

Fusion Data

The adopted melting point, T_{fus} = 1973 ± 15 K, is based on the phase study of Strickler and Roy[3] and is suppported by the value 1975 K reported by Prophet.[4] The older study of Ballo and Dittler[5] reported T_{fus} to lie between 2173 and 2273 K and Hummel *et al.*[6] reported T_{fus} = 1883 ± 15 K. Hummel *et al.* also stated that their samples were only partially fused after considerable time at 1973 K. Prophet also reported that his samples slowly decomposed on fusion and that successive melting points approached that of aluminum oxide at 2308 K. After fusing seven times X-ray analysis indicated the sample was 95% α-aluminum oxide and 5% LiAl$_5$O$_8$ with Li$_2$O being lost by vaporization. The adopted $\Delta_{fus}H°$ is estimated by assuming the entropy of melting to be approximately the same on a gram-atom basis as that of BeAl$_2$O$_4$.[1]

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							
100							
200							
298.15	67.777	93.711	93.711	0.	−1107.739	−1057.412	185.254
300	68.128	94.131	93.712	0.126	−1107.758	−1057.100	184.057
400	81.546	115.820	96.578	7.697	−1108.267	−1040.115	135.825
500	88.408	134.823	102.372	16.226	−1111.362	−1022.756	106.847
600	92.688	151.345	109.189	25.294	−1111.172	−1005.048	87.497
700	95.751	165.874	116.270	34.723	−1110.771	−987.390	73.680
800	98.165	178.822	123.294	44.423	−1110.285	−969.797	63.321
900	100.203	190.505	130.124	54.343	−1109.801	−952.266	55.268
1000	102.006	201.158	136.702	64.455	−1119.953	−934.026	48.789
1100	103.654	210.958	143.013	74.740	−1119.234	−915.467	43.472
1200	105.198	220.044	149.058	85.183	−1118.391	−896.979	39.044
1300	106.671	228.523	154.848	95.777	−1117.427	−878.566	35.301
1400	108.089	236.480	160.398	106.515	−1116.343	−860.232	32.096
1450.000	108.784	240.285	163.087	111.937	GLASS <--> LIQUID		
1450.000	125.520	240.285	163.087	111.937	TRANSITION		
1500	125.520	244.541	165.732	118.213	−1114.319	−841.994	29.321
1600	125.520	252.642	170.913	130.765	−1111.459	−823.932	26.899
1700	125.520	260.251	175.947	143.317	−1253.851	−798.873	24.546
1800	125.520	267.426	180.832	155.869	−1250.271	−772.213	22.409
1900	125.520	274.212	185.570	168.421	−1246.715	−745.751	20.502
1973.000	125.520	278.945	188.937	177.584	--- CRYSTAL <--> LIQUID ---		
2000	125.520	280.651	190.164	180.973	−1243.184	−719.476	18.791
2100	125.520	286.775	194.620	193.525	−1239.679	−693.377	17.247
2200	125.520	292.614	198.943	206.077	−1236.201	−667.443	15.847
2300	125.520	298.194	203.137	218.629	−1232.750	−641.669	14.573
2400	125.520	303.536	207.210	231.181	−1229.327	−616.043	13.408
2500	125.520	308.660	211.166	243.733	−1225.934	−590.560	12.339
2600	125.520	313.583	215.011	256.285	−1222.571	−565.211	11.355
2700	125.520	318.320	218.750	268.837	−1219.240	−539.991	10.447
2800	125.520	322.885	222.388	281.389	−1509.843	−513.926	9.587
2900	125.520	327.289	225.930	293.941	−1505.483	−478.435	8.618
3000	125.520	331.545	229.380	306.493	−1501.159	−443.093	7.715
3100	125.520	335.660	232.743	319.045	−1496.871	−407.895	6.873
3200	125.520	339.645	236.021	331.597	−1492.620	−372.835	6.086
3300	125.520	343.508	239.220	344.149	−1488.408	−337.907	5.349
3400	125.520	347.255	242.343	356.701	−1484.235	−303.106	4.657
3500	125.520	350.894	245.393	369.253	−1480.103	−268.428	4.006
3600	125.520	354.430	248.373	381.805	−1476.013	−233.866	3.393
3700	125.520	357.869	251.286	394.357	−1471.966	−199.418	2.815
3800	125.520	361.216	254.135	406.909	−1467.963	−165.078	2.269
3900	125.520	364.477	256.922	419.461	−1464.005	−130.843	1.752
4000	125.520	367.654	259.651	432.013	−1460.094	−96.710	1.263

PREVIOUS: June 1972 CURRENT: December 1979

Lithium Aluminum Oxide ($LiAlO_2$) CRYSTAL-LIQUID

0 to 1973 K		crystal
above	1973 K	liquid

Refer to the individual tables for details.

M_r = 65.92134 Lithium Aluminum Oxide ($LiAlO_2$) $Al_1Li_1O_2(cr,l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.693	−1180.523	−1180.523	INFINITE
90	17.966	8.046	99.257	−9.121	−1183.834	−1165.875	608.991
200	47.999	30.154	58.942	−5.758	−1187.025	−1146.565	299.452
298.15	67.777	53.313	53.313	0.	−1188.674	−1126.303	197.324
300	68.128	53.733	53.314	0.126	−1188.693	−1125.916	196.039
400	81.546	75.421	56.180	7.697	−1189.202	−1104.891	144.284
500	88.408	94.425	61.974	16.226	−1192.298	−1083.492	113.192
600	92.688	110.947	68.790	25.294	−1192.108	−1061 744	92.433
700	95.751	125.475	75.871	34.723	−1191.706	−1040.047	77.609
800	98.165	138.424	82.896	44.423	−1191.220	−1018.414	66.496
900	100.203	150.107	89.725	54.343	−1190.737	−996 843	57.855
1000	102.006	160.759	96.303	64.455	−1200.889	−974.563	50.906
1100	103.654	170.559	102.614	74.740	−1200.170	−951.964	45.205
1200	105.198	179.645	108.660	85.183	−1199.326	−929.436	40.457
1300	106.671	188.124	114.450	95.777	−1198.363	−906.983	36.443
1400	108.089	196.082	119.999	106.515	−1197.279	−884.609	33.005
1500	109.466	203.586	125.324	117.393	−1196.075	−862.317	30.029
1600	110.813	210.694	130.439	128.408	−1194.752	−840.109	27.427
1700	112.140	217.452	135.361	139.556	−1338.549	−810.812	24.913
1800	113.449	223.899	140.102	150.835	−1336.240	−779.835	22.630
1900	114.746	230.068	144.676	162.245	−1333.827	−748.988	20.591
1973.000	115.679	234.411	147.916	170.656	CRYSTAL <--> LIQUID		
1973.000	125.520	278.945	147.916	258.520	TRANSITION		
2000	125.520	280.651	149.696	261.909	−1243.184	−719.476	18.791
2100	125.520	286.775	156.079	274.461	−1239.679	−693.377	17.247
2200	125.520	292.614	162.154	287.013	−1236.201	−667.444	15.847
2300	125.520	298.194	167.948	299.565	−1232.750	−641.669	14.573
2400	125.520	303.536	173.487	312.117	−1229.327	−616.044	13.408
2500	125.520	308.660	178.792	324.669	−1225.934	−590.560	12.339
2600	125.520	313.583	183.882	337.221	−1222.571	−565.211	11.355
2700	125.520	318.320	188.774	349.773	−1219.240	−539.991	10 447
2800	125.520	322.885	193.483	362.325	−1509.843	−513.926	9.587
2900	125.520	327.289	198.021	374.877	−1505.483	−478.436	8.618
3000	125.520	331.545	202.402	387.429	−1501.159	−443.094	7 715
3100	125.520	335.660	206.634	399.981	−1496.871	−407.895	6.873
3200	125.520	339.646	210.729	412.533	−1492.621	−372.836	6.086
3300	125.520	343.508	214.694	425.085	−1488.408	−337 908	5.349
3400	125.520	347.255	218.538	437.637	−1484.235	−303.106	4.657
3500	125.520	350.894	222.268	450.189	−1480.104	−268.428	4 006
3600	125.520	354.430	225.891	462.741	−1476.013	−233.866	3.393
3700	125.520	357.869	229.411	475.293	−1471.966	−199.419	2.815
3800	125.520	361.216	232.836	487.845	−1467.963	−165.078	2.269
3900	125.520	364.477	236.170	500.397	−1464.005	−130.843	1.752
4000	125.520	367.654	239.417	512.949	−1460.094	−96.710	1.263

PREVIOUS: CURRENT: December 1979

Lithium Aluminum Oxide ($LiAlO_2$) $Al_1Li_1O_2(cr,l)$

Aluminum Nitride (AlN) CRYSTAL $M_r = 40.98824$ Aluminum Nitride (AlN) $Al_1N_1(cr)$

$\Delta_fH°(0\ K) = -312.98 \pm 2.5\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = 20.14 \pm 0.21\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -317.98 \pm 2.5\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalps of formation is the average value of the calorimetric determinations of Neugebauer and Margrave[1] and Mah *et al.*[2] Neugebauer and Margrave obtained $\Delta_fH°(298.15\ K) = -76.47 \pm 0.2\ kcal\cdot mol^{-1}$ by direct nitridation. Mah *et al.* obtained $\Delta_fH°(298.15\ K) = -75.6 \pm 0.4\ kcal\cdot mol^{-1}$ via oxygen combustion calorimetry. The older direct nitridation study of Neumann *et al.*[3] yields $\Delta_fH°(298.15\ K) = -57.4 \pm 0.8\ kcal\cdot mol^{-1}$; the source of bias in this study is not apparent. Fichter and Jenny[4] also made measurements using oxygen combustion calorimetry; our recalculation of their data using the modern accepted value for the heat of formation of $Al_2O_3(cr, \alpha)$[5] yields $\Delta_fH°(298.15\ K) = -71.5 \pm 1.0\ kcal\cdot mol^{-1}$.

Equilibrium data supports the calorimetric determinations but is less certain due largely to corrections for a condensation coefficient significantly different from unity. We have adopted a condensation coefficient (fraction of incident molecules which condense on the vaporizing surface) of $\alpha = 2 \times 10^{-3}$ from Hildenbrand and Hall[6] and used that value to convert measured pressures to equilibrium pressures, $P_e = P_m/\alpha$. This is a large correction, equivalent in some cases to 50 kcal·mol⁻¹ in the $\Delta_fH°(298.15\ K)$ values. The data below corresponds to the dissociation of $2\ AlN(cr) = 2\ Al(g) + N_2(g)$.

Source	Method	Data Point	T/K	$\Delta_rH°(298.15\ K)\ kcal\cdot mol^{-1}$ 2nd law	3rd law	Drift $cal\cdot K^{-1}\cdot mol^{-1}$	$\Delta_fH°(298.15\ K)\ kcal\cdot mol^{-1}$
Hildenbrand and Hall[a 6]	torsion–effusion	29[b]	1776–1972	309.3 ± 6.0	307.2 ± 1.5	−1.1 ± 3.2	−74.8 ± 1.2
Hoch and White[a 7]	Langmuir	13[b]	1660–1948	342.6 ± 18.5	307.6 ± 7.6	−19.3 ± 10.2	−75.0 ± 3.9
Dreger *et al.*[a 8]	Knudsen–effusion	11[c]	1450–1870	391.5 ± 17.6	308.9 ± 12.0	−48.2 ± 10.2	−75.6 ± 6.1
Bolgar *et al.*[a 9]	Langmuir	10	1718–1829	388.5 ± 9.7	315.3 ± 4.2	−41.5 ± 5.5	−78.8 ± 2.3
Linevsky[10]	atomic resonance	7	1641–1707	290.1 ± 18.8	299.7 ± 1.8	5.8 ± 11.2	−71.0 ± 1.4

[a] Raw pressure data corrected using $\alpha = 2 \times 10^{-3}$

[b] Two points rejected by a statistical test.

[c] One point rejected by a statistical test.

Studies not re–evaluated above include those of Blank[11] and Wu.[12] Blank's[11] Knudsen and Langmuir effusion studies yield a third law value of $\Delta_rH°(298.15\ K) = -306.4\ kcal\cdot mol^{-1}$ ($\Delta_fH°(AlN, cr, 298.15\ K) = -74.4\ kcal\cdot mol^{-1}$) when corrected for condensation coefficient according to the author. We have not reanalyzed this data since not all of the measured points from the graph are given in tabular form. Wu's Knudsen effusion study[12] leads to a value of $\Delta_fH°(AlN, cr, 298.15\ K) = -62.2 \pm 1.1\ kcal\cdot mol^{-1}$ as reported by the author based on a second–law analysis. The data are presented graphically only. Wu also suggests that AlN decomposes incongruently with loss of N_2 until a composition of Al_2N is reached.

Heat Capacity and Entropy

The adopted heat capacity data is derived by using orthogonal polynomials to smoothly merge the heat capacity–enthalpy data of Mah *et al.*[2] These authors reported heat capacity data in the 53–296 K range and enthalpy data (via drop calorimetry) in the 399–1799 K range. The entropy is based on $S°(50\ K) = 0.0692\ cal\cdot K^{-1}\cdot mol^{-1}$. The $C_p°$ data above 1799 K are a smooth extrapolation of the merged data and will approach a constant $C_p° = 12.521\ cal\cdot K^{-1}\cdot mol^{-1}$ at very high temperature Demidenko *et al.*[13] measured heat capacity over the range 55 to 330 K and their values for $S°(298.15\ K) = 4.804\ cal\cdot K^{-1}\cdot mol^{-1}$ and $H°(298.15\ K)-H°(0\ K) = 925\ cal\ K^{-1}\ mol^{-1}$ are in excellent agreement with the adopted values; their complete data are not available. Mezaki *et al.*[14] measured enthalpies via drop calorimetry over the range 478 to 1113 K; their values are −1.5% lower than the adopted values.

References

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−3.871	−312.980	−312.980	INFINITE
100	5.678	2.164	39.274	−3.711	−314.756	−306.283	159.986
200	19.332	10.267	22.581	−2.463	−316.764	−296.990	77.566
298.15	30.097	20.142	20.142	0.	−317.984	−286.995	50.280
300	30.254	20.329	20.143	0.056	−318.000	−286.803	49.937
400	36.692	29.987	21.416	3.428	−318.594	−276.301	36.081
500	40.799	38.647	24.013	7.317	−318.808	−265.697	27.757
600	43.538	46.341	27.106	11.541	−318.811	−255.072	22.206
700	45.434	53.201	30.353	15.994	−318.727	−244.455	18.241
800	46.791	59.361	33.601	20.608	−318.648	−233.850	15.269
900	47.792	64.932	36 777	25.339	−318.647	−223.252	12.957
1000	48.550	70.008	39.850	30.158	−329.363	−211.887	11.068
1100	49.136	74 664	42.807	35.043	−329.302	−200.142	9.504
1200	49.598	78.960	45.643	39.981	−329.214	−188.404	8.201
1300	49.970	82.945	48.361	44.960	−329.107	−176.674	7.099
1400	50.272	86.660	50.965	49.972	−328.986	−164.953	6.154
1500	50.521	90.137	53.462	55.012	−328.856	−153.240	5.336
1600	50.728	93.404	55.857	60.075	−328.717	−141.537	4.621
1700	50.903	96.485	58.157	65.157	−328.573	−129.843	3.990
1800	51.052	99.399	60.368	70.255	−328.425	−118.157	3.429
1900	51.180	102.162	62.496	75.366	−328.273	−106.480	2.927
2000	51.290	104.790	64.545	80.490	−328.119	−94.810	2.476
2100	51.385	107.295	66.522	85.624	−327.963	−83.149	2.068
2200	51.469	109.688	68.430	90.767	−327.805	−71.495	1.697
2300	51.543	111.977	70.274	95.917	−327.646	−59.848	1.359
2400	51.609	114.172	72.058	101.075	−327.486	−48.208	1.049
2500	51.666	116.280	73.785	106.239	−327.325	−36.574	0.764
2600	51.718	118.308	75.458	111.408	−327.165	−24.948	0.501
2700	51.765	120.260	77.082	116.582	−327.003	−13.327	0.258
2800	51.807	122.144	78.658	121.761	−620.743	−0.744	0.014
2900	51.845	123.962	80.189	126.943	−619.486	21.376	−0.385
3000	51.878	125 721	81.677	132.130	−618.229	43 454	−0.757

PREVIOUS: December 1962   CURRENT: December 1979

Aluminum Nitride (AlN) IDEAL GAS $M_r = 40.98824$ Aluminum Nitride (AlN) $Al_1N_1(g)$

$\Delta_f H°(0\ K) = 523 \pm 3\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 228.6 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = 523 \pm 38\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3\Pi$	0	6
$^1\Pi$	19727.4	6

$\omega_e = 746.9\ cm^{-1}$ $\omega_e x_e = [5.59]\ cm^{-1}$ $\sigma = 1$

$B_e = 0.5730\ cm^{-1}$ $\alpha_e = 0.0056\ cm^{-1}$ $r_e = 1.65\ Å$

Enthalpy of Formation

The enthalpy of formation is calculated from the adopted dissociation energy using auxiliary JANAF data.[1] Simmons and McDonald[2] observed an apparent predissociation from the $J=47$ rotational level during their emission spectroscopic study of AlN. They have shown that it is possible to assign this predissociation as being from the excited $^3\Pi$ state of AlN(g) to ground state Al(g) + N(g). If this assignment is correct, we calculate $D_0° = 21{,}000\ cm^{-1}$ using their value of $B_o = 0.5811\ cm^{-1}$ for the excited $^3\Pi$ state rotational constant. A linear Birge–Sponer extrapolation using the adopted molecular constant data yields $D_0° = 25{,}000\ cm^{-1}$. Considering the nature of the uncertainties in these calculations, we adopt an average value of $D_0° = 23{,}000 \pm 3{,}000\ cm^{-1}$ or $D_0° = 66 \pm 9\ kcal \cdot mol^{-1}$. With auxiliary JANAF data[1] this yields an adopted value of $\Delta_f H°(298.15\ K) = 125 \pm 9\ kcal \cdot mol^{-1}$ ($523.000 \pm 38\ kJ \cdot mol^{-1}$).

Heat Capacity and Entropy

The adopted molecular constant data are taken from the emission spectroscopy work of Simmons and McDonald[2] except for $\omega_e x_e$ which we estimate from the Pekeris relationship $\omega_e x_e = B_e(1 + \omega_e \alpha_e / 6B^2_e)^2$.[3] Although the energy difference between the two $^3\Pi$ states is well established, it is not certain that the lowest $^3\Pi$ state is the ground state since it has only been studied in emission. We assume it to be the ground state by analogy with the BN molecule where the $^1\Pi$ state has been shown theoretically and exp,uccirclerimentally (via absorption spectroscopy) to be the ground state.[4] For BN, SCF calculations[5] indicate $^3\Sigma$, $^1\Sigma$ and $^1\Pi$ states lying between 3400 and 4800 cm^{-1}. If these states lie at the same energy for AlN, they would have no effect on the thermochemical properties below 500 K but would increase the entropy at 6000 K by 5.0 J·K^{-1}·mol^{-1}.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.942	522.933	522.933	INFINITE
100	29 134	195.617	255.951	−6.033	523.906	513.034	−267.981
200	30.316	216.062	231.448	−3.077	523.605	502.220	−131.166
250	31.378	222.940	229.080	−1.535	523.306	496.908	−103.823
298.15	32.367	228.553	228.553	0.	523.000	491.851	−86.170
300	32.403	228.753	228.553	0.060	522.988	491.658	−85.605
350	33.288	233.817	228.951	1.703	522.668	486.462	−72.600
400	34.019	238.311	229.846	3.386	522.348	481.311	−62.853
450	34.612	242.353	231.015	5.102	522.028	476.201	−55.276
500	35.093	246.026	232.335	6.845	521 704	471.126	−49.218
600	35.808	252.491	235.170	10.393	521.025	461.074	−40.140
700	36.304	258.051	238.051	14.000	520.263	451.141	−33.665
800	36.663	262.923	240.862	17.649	519.377	441.325	−28.816
900	36.934	267.258	243.558	21.330	518.328	431.630	−25.051
1000	37.147	271.160	246.127	25.034	506.497	422.821	−22.086
1100	37.320	274.709	248.566	28.758	505.396	414.507	−19.683
1200	37.465	277.963	250.882	32.497	504.286	406.293	−17.685
1300	37.589	280.967	253.082	36.250	503.167	398.172	−15.999
1400	37.699	283.756	255.175	40.014	502.040	390.138	−14.556
1500	37.797	286.361	257.168	43.789	500.905	382.184	−13.309
1600	37.886	288.803	259.070	47.573	499.765	374.307	−12.220
1700	37.969	291.102	260.887	51.366	498.620	366.501	−11.261
1800	38.046	293.275	262.627	55.167	497.471	358.762	−10.411
1900	38.119	295.334	264.294	58.975	496.320	351 087	−9.652
2000	38.189	297.291	265.896	62.791	495.166	343.473	−8.971
2100	38.257	299.156	267.435	66.613	494.011	335.917	−8.355
2200	38.322	300.937	268.918	70.442	492.855	328.416	−7.798
2300	38.387	302.642	270.347	74.278	491.698	320.967	−7.289
2400	38.450	304.277	271.727	78.119	490.542	313.569	−6.825
2500	38.514	305.848	273.061	81.968	489.387	306.219	−6.398
2600	38.577	307.360	274.351	85.822	488.234	298.915	−6.005
2700	38.641	308.817	275.601	89.683	487.082	291.655	−5.642
2800	38.706	310.223	276.812	93.550	192.031	285.406	−5.324
2900	38.772	311.583	277.988	97.424	191.979	288.742	−5.201
3000	38.840	312.898	279.130	101.305	191.930	292.079	−5.086
3100	38.910	314.173	280.240	105.192	191.884	295.418	−4.978
3200	38.981	315.409	281.320	109.087	191.842	298.759	−4.877
3300	39.056	316.610	282.371	112.989	191.804	302.101	−4.782
3400	39.133	317.777	283.395	116.898	191.770	305.444	−4.693
3500	39.212	318.913	284.394	120.815	191.741	308.787	−4.608
3600	39.294	320.018	285.368	124.741	191.716	312.132	−4.529
3700	39.379	321.096	286.319	128.674	191.696	315.477	−4.454
3800	39.467	322.148	287.248	132.616	191.681	318.823	−4.383
3900	39.558	323.174	288.157	136.568	191.671	322.169	−4.315
4000	39.652	324.177	289.045	140.528	191.665	325.515	−4.251
4100	39.748	325.157	289.913	144.498	191.665	328.861	−4.190
4200	39.847	326.116	290.764	148.478	191.670	332.207	−4.132
4300	39.949	327.055	291.597	152.468	191.679	335.553	−4.076
4400	40.053	327.974	292.413	156.468	191.693	338.899	−4.023
4500	40.159	328.876	293.214	160.478	191.713	342.244	−3.973
4600	40.268	329.759	293.999	164.500	191.735	345.589	−3.924
4700	40.378	330.627	294.769	168.532	191.760	348.934	−3.878
4800	40.490	331.478	295.525	172.575	191.788	352.277	−3.834
4900	40.604	332.314	296.267	176.630	191.819	355.621	−3.791
5000	40.720	333.135	296.996	180.696	191.851	358.963	−3 750
5100	40.836	333.943	297.713	184.774	191.884	362.305	−3.711
5200	40.954	334.737	298.417	188.864	191.917	365.646	−3.673
5300	41.073	335.518	299.110	192.965	191.948	368.987	−3.637
5400	41.192	336.287	299.791	197.078	191.978	372.327	−3.602
5500	41.313	337.044	300.462	201.203	192.005	375.667	−3.568
5600	41 433	337.790	301.122	205.341	192.028	379.006	−3.535
5700	41.554	338.524	301.771	209.490	192.046	382.344	−3.504
5800	41.675	339.248	302.411	213.651	192.060	385.682	−3.473
5900	41.795	339.961	303.042	217.825	192.064	389.021	−3.444
6000	41 916	340.665	303.663	222.010	192.082	392.357	−3 416

PREVIOUS: December 1979 (1 atm) CURRENT· December 1979 (1 bar)

Sodium Aluminum Oxide ($NaAlO_2$) CRYSTAL $M_r = 81.97011$ Sodium Aluminum Oxide ($NaAlO_2$) $Al_1Na_1O_2(cr)$

$\Delta_f H°(0\ K) = -1137.32 \pm 0.71\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1133.19 \pm 0.71\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 1.297\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° =$ Unknown

$S°(298.15\ K) = 70.40 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 740\ K$
$T_{fus} = > 1923\ K$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was reported by Coughlin.[1] The value was calculated from the measured heat of solution of $NaAlO_2(cr)$ at 303.15 K in 4.360m hydrochloric acid solution.

Heat Capacity and Entropy

The low temperature heat capacities, below 350 K, were measured by Westrum.[2] Heat capacities above 350 K, 399.4–1698.6 K, were measured by Christensen *et al.*[3] These two sets of $C_p°$ data were plotted graphically and joined smoothly at 350 K. Low temperature heat capacities 51 K–298.15 K, were also determined by King[4] and agree very well with those reported by Westrum.[2] $S°(298.15\ K)$ was reported by Westrum[2] based on $S°(10\ K) = 0.01\ J \cdot K^{-1} \cdot mol^{-1}$.

Transition Data

T_{trs} and $\Delta_{trs} H°$ were obtained from Christensen *et al.*[3]

Fusion Data

T_{trs} is taken from Kammermeyer *et al.*[5]

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
0	0.	0.	INFINITE	-23.794	-1137.319	-1137.319	INFINITE
100	28.259	15.004	123.662	-10.866	-1129.119	-1110.209	579.914
200	56.907	44.279	76.663	-6.477	-1131.899	-1090.089	284.702
298.15	73.638	70.400	70.400	0.	-1133.195	-1069.248	187.328
300	73.889	70.856	70.401	0.136	-1133.209	-1068.851	186.104
400	83.412	93.498	73.424	8.030	-1136.417	-1047.095	136.737
500	89.563	112.798	79.417	16.690	-1136.549	-1024.739	107.054
600	94.270	129.554	86.408	25.888	-1136.263	-1002.398	87.267
700	98.291	144.393	93.651	35.519	-1135.686	-980.130	73.138
740.000	99.788	149.896	96.544	39.481	ALPHA <--> BETA		
740.000	97.696	151.649	96.544	40.778	TRANSITION		
800	98.751	159.306	100.967	46.671	-1133.761	-958.058	62.555
900	100.525	171.040	108.112	56.635	-1133.231	-936.128	54.331
1000	102.299	181.723	114.946	66.776	-1143.354	-913.493	47.716
1100	104.073	191.556	121.470	77.095	-1142.628	-890.541	42.288
1200	105.847	200.688	127.695	87.591	-1238.567	-865.220	37.662
1300	107.621	209.230	133.642	98.264	-1236.730	-834.182	33.518
1400	109.395	217.270	139.331	109.115	-1234.746	-803.290	29.971
1500	111.169	224.878	144.783	120.143	-1232.613	-772.545	26.902
1600	112.943	232.110	150.017	131.349	-1230.328	-741.948	24.222
1700	114.751	239.011	155.050	142.734	-1227.889	-711.498	21.862
1800	116.491	245.620	159.900	154.297	-1225.296	-681.196	19.768
1900	118.233	251.965	164.579	166.034	-1222.553	-651.042	17.898
2000	119.858	258.072	169.102	177.939	-1219.665	-621.037	16.220
2100	121.366	263.957	173.480	190.002	-1216.644	-591.179	14.705
2200	122.759	269.635	177.722	202.209	-1213.503	-561.468	13.331
2300	124.034	275.121	181.838	214.549	-1210.252	-531.903	12.080
2400	125.194	280.424	185.836	227.012	-1206.905	-502.481	10.936
2500	126.237	285.557	189.723	239.584	-1203.473	-473.200	9.887
2600	127.163	290.526	193.505	252.255	-1199.968	-444.058	8.921
2700	127.973	295.341	197.188	265.013	-1196.403	-415.052	8.030
2800	128.666	300.008	200.777	277.846	-1486.690	-385.211	7.186
2900	129.243	304.533	204.277	290.742	-1481.946	-345.957	6.231
3000	129.704	308.923	207.693	303.691	-1477.178	-306.866	5.343

PREVIOUS: December 1960   CURRENT: March 1963

Aluminum Oxide (AlO) IDEAL GAS $M_r = 42.98094$ Aluminum Oxide (AlO) $Al_1O_1(g)$

$S^\circ(298.15\ K) = 218.38 \pm 0.08\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H^\circ(0\ K) = 67.0 \pm 8\ kJ{\cdot}mol^{-1}$
$\Delta_f H^\circ(298.15\ K) = 66.9 \pm 8\ kJ{\cdot}mol^{-1}$

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

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å	Source
$X^2\Sigma^+$	0.0	2	979.23	6.97	0.64136	0.0058	1.6178	1
$A^2\Pi_i$	5282	4	728.5	4.15	0.5365	0.0050	1.769	2, 1
$B^2\Sigma^+$	20635.2	2	870.05	3.52	0.60408	0.00447	1.6670	1
$C^2\Pi_r$	33055.	4	856.	6.	[0.60]	[0.004]	[1.67]	1 3–4
$^4\Sigma^+$	[30200]	4	[820]	[5.0]	[0.565]	[0.004]	[1.724]	3–4
$^4\Delta$	[31600]	8	[820]	[5.0]	[0.565]	[0.004]	[1.724]	3–4
$^4\Sigma^-$	[33000]	4	[820]	[5.0]	[0.565]	[0.004]	[1.724]	3–4
$^2\Delta$	[34700]	4	[820]	[5.0]	[0.565]	[0.004]	[1.724]	3–4
$^2\Sigma^-$	[34900]	2	[820]	[5.0]	[0.565]	[0.004]	[1.724]	3–4
$D^2\Sigma^+$	40187	2	817.5	4.8	0.5652	0.0046	1.7234	1–2

Enthalpy of Formation

We adopt $\Delta_f H^\circ(298.15\ K) = 16.0 \pm 2\ kcal{\cdot}mol^{-1}$($D_0^\circ = 121.193 \pm 2\ kcal{\cdot}mol^{-1}$) based mainly on $D_0^\circ \geqslant 121.0 \pm 0.6\ kcal{\cdot}mol^{-1}$ [5] from laser–induced fluorescence of AlO and on $D_0^\circ = 122.0 \pm 2.5$ and $121.6\ kcal{\cdot}mol^{-1}$ [6] from recent mass spectrometry of the evaporation of Al_2O_3. The mass–spectrometric values of $D_0^{\circ 6}$ become 121.5 ± 3 and $-120.8 \pm 3\ kcal{\cdot}mol^{-1}$ when we convert to $\Delta_f H^\circ(298.15\ K) = 78.8 \pm 1\ 0\ kcal{\cdot}mol^{-1}$ for Al(g) and to a temperature scale based on $T_{fus} = 2327$ K for $\alpha{-}Al_2O_3$ instead of 2318 K.

The adopted $\Delta_f H^\circ$ was selected by Pedley and Marshall[7] from a network analysis of thermochemical data on D_0° of AlO, BO, BaO, SiO and TiO. They considered over two dozen studies on AlO plus many studies on related oxides. We concur in their selection.

Our previous JANAF Thermochemical Table[8] summarized older mass–spectrometric values of D_0° ranging from 113.5 to $119.9\ kcal{\cdot}mol^{-1}$. We now give less weight to the lower values for two reasons: they are less consistent with the network of data for other oxides and they all may have a negative bias arising from ionization cross sections. These lower values converge toward the adopted value if they are recalculated using alternative approximations for ionization cross sections[9–11] of reactants and calibrants. Ho and Burns[6] and Drowart[11] gave some examples of similar recalculations. We conclude that errors in cross sections provide a plausible, though unproved, explanation of much of the discrepancy between the mass–spectrometric and fluorescence values of D_0°. Errors in the interpretation of fluorescence data[5] appear to be less likely, though not impossible. Plausibility of the fluorescence interpretation rests in part on the spectroscopic limit $D_0^\circ \leqslant 122.1 \pm 0.6\ kcal{\cdot}mol^{-1}$ derived by Drowart[11] from reinterpretation of absorption edges observed by Tyte and previously interpreted to give $D_0^\circ \leqslant 119.9\ kcal{\cdot}mol^{-1}$.[12] Additional results on D_0° have been summarized elsewhere.[5] Gurvich *et al.*[13] selected $D_0^\circ = 121.176 \pm 1.2\ kcal{\cdot}mol^{-1}$.

Heat Capacity and Entropy

Electronic levels (ν_{00}) and vibration–rotation constants of the observed states are from Huber and Herzberg[1] and recent studies.[2] Schamps[3] made extensive predictions of the unobserved levels of AlO and MgO. We adopt these estimates since additional data for MgO[4] and the F state of AlO confirm that they are reasonably accurate. Estimated molecular constants are derived from isoconfigurational levels whenever possible. We omit levels above 40187 cm^{-1} since they will have a negligible effect. The thermodynamic functions are calculated using first–order anharmonic corrections to Q_r^i and Q_r^i in the partition function $Q = Q_t \Sigma\ Q_v^i Q_r^i g_i \exp(-c_2\epsilon_i/T)$. Functions calculated by Gurvich *et al.*[13] are in close agreement; their values of the Gibbs energy function differ by $\leqslant 0.01$ at $T \leqslant 5000$ K and by only 0.026 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$ at 6000 K.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K$_f$
0	0.	0.	INFINITE	−8.788	67.037	67.037	INFINITE
100	29.108	186.129	244.933	−5.880	68.009	58.760	−30.693
200	29.504	206.370	221.161	−2.958	67.673	49.577	−12.948
298.15	30.883	218.386	218.386	0.	66.944	40.845	−7.156
300	30.913	218.577	218.387	0.057	66.929	40.683	−7.084
400	32.489	227.691	219.619	3.229	66.107	32.057	−4.186
500	33.750	235.083	221.995	6.544	65.260	23.642	−2.470
600	34.685	241.323	224.710	9.968	64.369	15.401	−1.341
700	35.399	246.726	227.478	13.474	63.400	7.315	−0.546
800	36.001	251.492	230.187	17.044	62.321	−0.625	0.041
900	36.583	255.766	232.796	20.673	61.106	−8.422	0.489
1000	37.205	259.652	235.290	24.362	49.149	−15.315	0.800
1100	37.898	263.230	237.670	28.116	47.973	−21.704	1.031
1200	38.669	266.560	239.940	31.944	46.852	−27.988	1.218
1300	39.506	269.688	242.109	35.852	45.793	−34.182	1.373
1400	40.386	272.648	244.186	39.847	44.806	−40.296	1.503
1500	41.283	275.465	246.178	43.930	43.893	−46.343	1.614
1600	42.167	278.157	248.093	48.103	43.057	−52.331	1 708
1700	43.015	280.739	249.938	52.362	42.296	−58.269	1.790
1800	43.805	283.221	251.719	56.704	41.605	−64.164	1.862
1900	44.523	285.609	253.440	61.121	40.977	−70.023	1.925
2000	45.158	287.909	255.106	65.606	40.405	−75.850	1.981
2100	45.706	290.126	256.721	70.150	39.881	−81.649	2.031
2200	46.165	292.263	258.288	74.744	39.396	−87.425	2.076
2300	46.538	294.324	259.811	79.380	38.942	−93.179	2.116
2400	46.830	296.311	261.290	84.049	38.509	−98.914	2.153
2500	47.047	298.227	262.730	88.743	38.091	−104.632	2.186
2600	47.196	300.075	264.131	93.456	37.681	−110.333	2.217
2700	47.286	301.858	265.495	98.180	37.272	−116.018	2.244
2800	47.325	303.579	266.825	102.911	−257.042	−120.719	2.252
2900	47.321	305.240	268.121	107.644	−256.368	−115.863	2.087
3000	47.279	306.843	269.385	112.374	−255.706	−111.029	1.933
3100	47.209	308.393	270.619	117.099	−255.059	−106.217	1.790
3200	47.115	309.890	271.823	121.815	−254.430	−101.426	1.656
3300	47.003	311.338	272.998	126.521	−253.820	−96.654	1.530
3400	46.878	312.739	274.147	131.215	−253.231	−91.901	1.412
3500	46.744	314.096	275.269	135.896	−252.663	−87.164	1.301
3600	46.605	315.411	276.366	140.564	−252.118	−82.443	1.196
3700	46.464	316.686	277.438	145.217	−251.596	−77.737	1.097
3800	46.324	317.923	278.487	149.857	−251.096	−73.045	1.004
3900	46.187	319.125	279.514	154.482	−250.619	−68.365	0.916
4000	46.055	320.293	280.519	159.094	−250.163	−63 698	0.832
4100	45.930	321.428	281.503	163.694	−249.730	−59.042	0.752
4200	45.813	322.534	282.467	168.281	−249.318	−54.396	0.677
4300	45.704	323.610	283.411	172.857	−248.928	−49.760	0.604
4400	45.606	324.660	284.337	177.422	−248.557	−45.133	0.536
4500	45.518	325.684	285.244	181.978	−248.205	−40.514	0.470
4600	45.441	326.683	286.134	186.526	−247.874	−35.902	0.408
4700	45.376	327.660	287.008	191.067	−247.561	−31.297	0.348
4800	45.322	328.615	287.864	195.601	−247.268	−26.699	0.291
4900	45.280	329.549	288.706	200.131	−246.993	−22.106	0.236
5000	45.250	330.463	289.532	204.658	−246.736	−17.520	0.183
5100	45.232	331.359	290.343	209.182	−246.498	−12.937	0.133
5200	45.226	332.237	291.140	213.705	−246.278	−8.360	0 084
5300	45.231	333.099	291.924	218.227	−246.077	−3.787	0.037
5400	45.248	333.944	292.694	222.751	−245.894	0.783	−0.008
5500	45.276	334.775	293.452	227.277	−245.730	5.349	−0.051
5600	45.315	335.591	294.197	231.807	−245.585	9.913	−0.092
5700	45.365	336.394	294.930	236.341	−245.461	14.474	−0.133
5800	45.425	337.183	295.652	240.880	−245.354	19.034	−0.171
5900	45.494	337.960	296.363	245.426	−245.270	23.591	−0.209
6000	45.574	338.725	297.062	249.980	−245.186	28.145	−0.245

PREVIOUS December 1979 (1 atm) — CURRENT: December 1979 (1 bar)

Aluminum Oxide, Ion (AlO^+) IDEAL GAS *GFW* = 42.980391 Aluminum Oxide, Ion (AlO_1^+) $Al_1O_1^+(g)$

$S°(298.15 K) = [231.0 \pm 13]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_fH°(0\ K) = 986.6 \pm 20\ kJ\cdot mol^{-1}$

$\Delta_fH°(298.15\ K) = [992.993]\ kJ\cdot mol^{-1}$

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

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	ω_ex_e, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$^3\Pi$	[0]	6	[710]	[4]	[0.5066]	[0.004]	[1.82]
$^1\Pi$	[2000]	2	[710]	[4]	[0.5066]	[0.004]	[1.82]
$^1\Sigma$	[300]	1	[820]	[5]	[0.5806]	[0.005]	[1.70]
$^3\Sigma$	[12000]	3	[870]	[5]	[0.5806]	[0.005]	[1.70]
$^1\Sigma$	[20000]	1	[870]	[5]	[0.5806]	[0.005]	[1.70]

Enthalpy of Formation

$\Delta_fH°$ is calculated from that of AlO[1] using Hildenbrand's appearance potential[2] of 9.53 ± 0.15 eV (219.8 ± 3.5 kcal mol^{-1}), assuming that it is identical with the ionization potential for $AlO(g) \rightarrow AlO^+(g) + e\ (g)$. Other reported values for the appearance potential range from 9 to 10.3 ± 1 eV, including several values of 9.5.[1-5] These values are consistent with, but less precise than, the adopted value. $\Delta_fH°(0\ K)$ yields $D_0^\circ = 39.5 \pm 5$ kcal·mol for $AlO^+ \rightarrow Al^+ + O$; this is larger than the value of −26 kcal·mol^{-1} predicted by Schamps[6] from his SCF calculation of IP(AlO) = 10.08 eV. MNDO calculations[7] differ by only 3.5 kcal·mol^{-1} from our [$\Delta_fH°(AlO^+, 298.15\ K)$–$\Delta_fH°(AlO, 298.15\ K)$ even though the MNDO values of $\Delta_fH°(298.15\ K)$ deviate by −14 and −18 kcal·mol^{-1}, respectively.

$\Delta_fH°(AlO^+, g, 298.15\ K)$ is obtained from $\Delta_fH°(AlO)$ by using IP(AlO) with JANAF [1] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$, for AlO(g), $AlO^+(g)$ and $e^-(g)$. $\Delta_rH°(Al0 \rightarrow Al0^+ + e^-, 298.15\ K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_fH°(298.15\ K)$ should be changed by −1 481 kcal·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

No spectroscopic data have been observed for AlO^+ but Schamps[6] recently predicted electronic levels and molecular constants from variational calculations with semiempirical estimates of correlation energy differences. Similar calculations were reasonably accurate for MgO.[6] The predictions for AlO^+ yield almost equal energies for $^3\Pi$ and $^1\Sigma^+$; thus they do not distinquish which is the ground state. AlO^+ is isoelectronic with MgO and AlN. MgO has a $^1\Sigma^+$ ground state with the low–lying $^3\Pi$ level at 2600 cm^{-1}.[8] Triplet–triplet bands are observed for AlN[9,10] and it is quite likely that the lower $^3\Pi$ level is the ground state.[10] We conclude for AlO^+ that $^3\Pi$ is very low lying and probably the ground state; it will dominate the electronic partition function.

The adopted electronic levels are minor modifications of the predictions of Schamps.[6] Molecular constants of the $^3\Pi$ state are estimated to be intermediate between those of MgO[1] and AlN.[9] The r_e adopted for $^3\Pi$ is −0 1 Å longer than that of Al_2O.[1] Values of r_e adopted for AlO^+ are also longer than those of their Π and Σ counterparts in AlO.[1] Values of ω_e are based on force–constant comparisons. Other constants are based on comparisons with the observed and calculated values for MgO.[1,6]

The low–lying electronic levels cause an entropy uncertainty of perhaps 3 cal/(mol·K)$^{-1}$ at 298 K but <1 cal/(mol·K)$^{-1}$ at T>2000 K. Uncertainty in the enthalpy is large (perhaps 4 kcal·mol^{-1}) at high temperature. The thermodynamic functions are calculated using first–order anharmonic corrections to Q_r' and Q_v' in the partition function $Q=Q_t\Sigma Q_r'Q_v'g_i\ \exp(-c_2\epsilon_i/T)$.

References

[1] JANAF Thermochemical Tables: AlO(g), $Al_2O(g)$ 12–31–79; MgO(g) 12–31–74; $Al^+(g)$ 6–30–79; $e^-(g)$ 3–31–77.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−9.090	986.587		
100	29.445	197.312	259.050	−6.174			
200	31.118	218.161	233.943	−3.156			
298.15	33.135	230.975	230.975	0.	992.993	956.886	−167.642
300	33.168	231.180	230.975	0.061	993.021	956.661	−166.570
400	34.685	240.942	232.296	3.458	994.503	944.317	−123.315
500	35.770	248.805	234.837	6.984	995.945	931.603	−97.324
600	36.583	255.401	237.729	10.603	997.327	918.604	−79.972
700	37.206	261.090	240.669	14.294	998.622	905.379	−67.560
800	37.686	266.091	243.541	18.040	999.797	891.977	−58.240
900	38.052	270.551	246.298	21.828	1000.820	878.437	−50.983
1000	38.330	274.576	248.928	25.647	991.071	865.552	−45.212
1100	38.539	278.239	251.429	29.491	992.064	852.952	−40.503
1200	38.696	281.600	253.805	33.354	993.056	840.261	−36.576
1300	38.813	284.702	256.064	37.229	994.043	827.488	−33.249
1400	38.900	287.581	258.214	41.115	995.026	814.639	−30.395
1500	38.966	290.268	260.262	45.009	996.003	801.720	−27.918
1600	39.017	292.784	262.217	48.908	996.972	788.737	−25.750
1700	39.057	295.151	264.085	52.812	997.933	775.692	−23.834
1800	39.091	297.384	265.874	56.719	998.886	762.592	−22.130
1900	39.120	299.499	267.588	60.630	999.831	749.439	−20.604
2000	39.147	301.506	269.234	64.543	1000.766	736.236	−19.229
2100	39.174	303.417	270.817	68.459	1001.693	722.986	−17.983
2200	39.202	305.240	272.341	72.378	1002.611	709.693	−16.850
2300	39.231	306.983	273.809	76.300	1003.521	696.358	−15.815
2400	39.262	308.653	275.226	80.224	1004.423	682.984	−14.865
2500	39.295	310.256	276.596	84.152	1005.317	669.572	−13.990
2600	39.331	311.798	277.920	88.083	1006.203	656.125	−13.182
2700	39.369	313.283	279.203	92.018	1007.083	642.644	−12.433
2800	39.410	314.716	280.446	95.957	714.056	630.098	−11.755
2900	39.453	316.100	281.651	99.900	716.019	627.064	−11.295
3000	39.499	317.438	282.822	103.848	717.977	623.964	−10.864
3100	39.546	318.734	283.960	107.800	719.930	620.798	−10.460
3200	39.595	319.990	285.066	111.757	721.879	617.569	−10.081
3300	39.647	321.209	286.143	115.719	723.824	614.279	−9.723
3400	39.699	322.394	287.192	119.686	725.764	610.930	−9.386
3500	39.753	323.545	288.214	123.659	727.702	607.525	−9.067
3600	39.808	324.666	289.211	127.637	729.636	604.064	−8.765
3700	39.863	325.757	290.184	131.621	731.567	600.549	−8.478
3800	39.919	326.821	291.134	135.610	733.495	596.982	−8.206
3900	39.976	327.859	292.063	139.604	735.421	593.365	−7.947
4000	40.034	328.872	292.970	143.605	737.343	589.698	−7.701
4100	40.091	329.861	293.858	147.611	739.262	585.983	−7.466
4200	40.149	330.828	294.727	151.623	741.177	582.221	−7.241
4300	40.206	331.773	295.577	155.641	743.088	578.414	−7.026
4400	40.264	332.698	296.411	159.664	744.995	574.562	−6.821
4500	40.321	333.604	297.227	163.694	746.900	570.667	−6.624
4600	40.378	334.490	298.028	167.729	748.796	566.730	−6.435
4700	40.435	335.359	298.813	171.769	750.687	562.751	−6.254
4800	40.491	336.211	299.583	175.816	752.570	558.733	−6.080
4900	40.547	337.047	300.339	179.868	754.447	554.675	−5.913
5000	40.602	337.866	301.081	183.925	756.313	550.579	−5.752
5100	40.657	338.671	301.811	187.988	758.168	546.447	−5.597
5200	40.711	339.461	302.527	192.056	760.013	542.277	−5.447
5300	40.765	340.237	303.231	196.130	761.844	538.072	−5.303
5400	40.818	340.999	303.924	200.209	763.660	533.833	−5.164
5500	40.871	341.749	304.605	204.294	765.461	529.560	−5.029
5600	40.922	342.486	305.274	208.384	767.244	525.255	−4.899
5700	40.974	343.211	305.934	212.478	769.008	520.918	−4.774
5800	41.024	343.924	306.583	216.578	770.755	516.550	−4.652
5900	41.074	344.625	307.221	220.683	772.476	512.152	−4.534
6000	41.123	345.316	307.851	224.793	774.195	507.724	−4.420

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

Aluminum Oxide, Ion (AlO^-) IDEAL GAS $M_r = 42.98149$ Aluminum Oxide, Ion (AlO_1^-) $Al_1O_1^-(g)$

$S°(298.15\ K) = [212.81 \pm 1.7]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_fH°(0\ K) = -263.2 \pm 17\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = [-269.425]\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ, cm^{-1}	g_i
[$^1\Sigma^+$]	0	[1]
[$^3\Pi$]	[27000]	[6]

$\omega_e = [900]\ cm^{-1}$ $\omega_ex_e = [5.4]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.640]\ cm^{-1}$ $\alpha_e = [0.006]\ cm^{-1}$ $r_e = [1.62]\ Å$

Enthalpy of Formation

We adopt $\Delta_fH°(0\ K) = -62.9 \pm 4\ kcal\ mol^{-1}$ based on equilibrium data for $AlO(g) + Cl^-(g) = Cl(g) + AlO^-(g)$ obtained using effusion mass spectrometry by Srivastava *et al.*[1,2] Our analysis of the data is summarized below. For the process $AlO^-(g) \rightarrow Al(g) + O^-(g)$ we calculate a dissociation energy $D_0^o = 166.4 \pm 4\ kcal{\cdot}mol^{-1}$; this is comparable to $D_0^o(AlF) = 159.3 \pm 1.5\ kcal{\cdot}mol^{-1}$[3] and much larger than $D_0^o(AlO) = 121.2 \pm 2\ kcal{\cdot}mol^{-1}$.[3] The corresponding electron affinity, $EA(AlO) = 78.9 \pm 4\ kcal{\cdot}mol^{-1}$ (3 42 eV), is 4.4 kcal·mol⁻¹ less than $EA(Cl) = 83.3\ kcal{\cdot}mol^{-1}$.[3] Gaines and Page[4] used a semi–empirical method to predict $EA(AlO) = 60$ and $EA(BO) = 49\ kcal\ mol^{-1}$, corresponding to a difference of 11 kcal·mol⁻¹ Although this difference is comparable with the experimental difference of 9 kcal·mol⁻¹, the values predicted for EA(AlO) and EA(BO) are −20 kcal·mol⁻¹ lower than the experimental results.[1,2] MNDO calculations[5] predicted $\Delta_fH°(298.15\ K) = -55.9$ and $[\Delta_fH°(AlO^-, 298.15\ K)-\Delta_fH°(AlO, 298.15\ K)] = 54\ kcal{\cdot}mol^{-1}$, but these values have a large uncertainty. Gurvich *et al.*[6] selected $EA(AlO) = 79.8 \pm 2.4\ kcal{\cdot}mol^{-1}$ based on the equilibrium data.[1]

The value of $\Delta_rH°(AlO^- \rightarrow AlO + e^-, 298.15\ K)$ calculated from our tables will differ from a room temperature threshold energy due to inclusion of the enthalpies, $H°(0\ K)-H°(298.15\ K)$, of $AlO^-(g)$, $AlO(g)$ and $e^-(g)$ and to the threshold effects discussed by Rosenstock *et al.*[7]

Source	T/K	Data Points	δS cal·K⁻¹·mol⁻¹	$\Delta_fH°$(298.15 K), kcal·mol⁻¹ 2nd law	3rd law	$\Delta_fH°$(298.15 K) kcal·mol⁻¹
Srivastava (1972)[1,2]	2082–2222	5	−5.8 ± 3.8	−8.1 ± 8.3	4.48 ± 1.1	−64.39

Heat Capacity and Entropy

All of the molecular constants are estimated by comparison with AlF and AlO.[3] We estimate the electronic states and levels from the low–lying states of isoelectronic AlF The bond distance is taken equal to that in AlO and slightly shorter than that in AlF B_e is calculated from r_e. We derive $\omega_e = 900 \pm 100\ cm^{-1}$ from k = 4 8 mdyn/Å estimated from k(AlF) = 4.23 and k(AlO) = 5.68. Similar comparisons of ω_ex_e/ω_e and α_e/B_e are used to estimated ω_ex_e and α_e.

Gurvich *et al.*[6] calculated $C_p°$, $S°$ and $H°$ using somewhat larger estimates for ω_e and B_e. Their values of $S°$ differ from ours by −0.21 (298 15 K), −0.56 (2000 K) and −0.63 (4000 K) cal K⁻¹·mol⁻¹.

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

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_fH°$ (kJ·mol⁻¹)	$\Delta_fG°$ (kJ·mol⁻¹)	log K$_f$
0	0.	0.	INFINITE	−8.826	−263.172		
100	29.112	180.387	239.570	−5.918			
200	29 690	200.668	215.615	−2.989			
250	30.453	207.371	213.318	−1.487			
298.15	31.303	212.807	212.807	0.	−269.424	−287.606	50.387
300	31.335	213.001	212.808	0.058	−269.477	−287.718	50 096
350	32.194	217.897	213.193	1.646	−270.901	−290.646	43.377
400	32.961	222.247	214.057	3.276	−272.332	−293.369	38.310
450	33.622	226.168	215.189	4.941	−273.768	−295.913	34.349
500	34 179	229 740	216.468	6.636	−275.212	−298.296	31 163
600	35.041	236.053	219.220	10.100	−278.142	−302.639	26.347
700	35.654	241.503	222.023	13.636	−281.159	−306.484	22.870
800	36.102	246.295	224.763	17.225	−284.298	−309.890	20.234
900	36 439	250.567	227.397	20.853	−287.593	−312.893	18 160
1000	36.699	254.420	229.910	24.510	−301.660	−314 759	16.441
1100	36.907	257.928	232.300	28.191	−304.988	−315.908	15.001
1200	37.077	261.147	234.572	31.890	−308.317	−316.754	13.788
1300	37.219	264.121	236.732	35.605	−311.647	−317.322	12.750
1400	37.341	266.883	238.788	39.334	−314.979	−317.633	11.851
1500	37 446	269.463	240 748	43.073	−318.314	−317.706	11.064
1600	37.539	271 883	242.619	46.822	−321.652	−317.557	10.367
1700	37.623	274.161	244.408	50.581	−324.993	−317.199	9.746
1800	37.699	276.314	246.122	54.347	−328.339	−316.644	9 189
1900	37 769	278.354	247.765	58.120	−331.688	−315.903	8.685
2000	37.835	280.293	249.343	61.900	−335.043	−314 985	8.227
2100	37 896	282.141	250.861	65.687	−338.403	−313.900	7 808
2200	37 954	283.905	252.323	69.479	−341 768	−312.654	7.423
2300	38.009	285.593	253.734	73.278	−345.139	−311.255	7.069
2400	38.062	287.212	255.095	77.081	−348.516	−309.710	6.741
2500	38.113	288.767	256.411	80.890	−351.898	−308.023	6 436
2600	38 164	290.263	257.684	84.704	−355.286	−306.202	6.152
2700	38.213	291.704	258.918	88.523	−358.679	−304.249	5.886
2800	38.262	293.095	260.114	92.346	−655.979	−301.203	5 619
2900	38.312	294 438	261.274	96.175	−658.287	−288.492	5.196
3000	38.362	295 738	262.402	100.009	−660.601	−275.701	4.800
3100	38.414	296.997	263.497	103.848	−662.918	−262.833	4 429
3200	38.467	298.217	264.563	107.692	−665.240	−249.890	4.079
3300	38.523	299 402	265.601	111.541	−667.565	−236.874	3.749
3400	38.582	300.552	266.612	115.396	−669.893	−223.788	3 438
3500	38.645	301.672	267.598	119.258	−672.224	−210.634	3 144
3600	38.712	302.761	268.560	123.126	−674.557	−197.412	2.864
3700	38.784	303.823	269.499	127.000	−676.892	−184.126	2.599
3800	38.861	304 858	270.416	130.882	−679.228	−170.777	2.347
3900	38.944	305.869	271.312	134.773	−681.565	−157.366	2.108
4000	39 035	306.856	272.188	138.672	−683.902	−143.895	1.879
4100	39.132	307.821	273.045	142.580	−686.238	−130.366	1.661
4200	39.237	308.765	273.885	146.498	−688.573	−116.780	1.452
4300	39.350	309.690	274.707	150.427	−690.908	−103.138	1.253
4400	39.471	310.596	275.512	154.368	−693.241	−89.442	1.062
4500	39.602	311.484	276.302	158.322	−695.569	−75 694	0.879
4600	39 741	312.356	277.076	162.289	−697.897	−61.893	0.703
4700	39.890	313.212	277.836	166.271	−700.223	−48.042	0.534
4800	40 048	314.054	278.581	170.267	−702.546	−34.141	0.372
4900	40.216	314 881	279.314	174.281	−704.866	−20.192	0.215
5000	40.393	315.696	280.033	178.311	−707.184	−6.195	0.065
5100	40.580	316 497	280.741	182.359	−709.500	7.848	−0.080
5200	40.776	317.287	281.436	186.427	−711.814	21.935	−0.220
5300	40.982	318.066	282.120	190.515	−714.126	36.069	−0.355
5400	41.197	318.834	282.792	194.624	−716.437	50.245	−0.486
5500	41.420	319.592	283.455	198.755	−718.747	64.463	−0.612
5600	41.652	320.340	284.107	202.908	−721.057	78.725	−0.734
5700	41.893	321.080	284.749	207.085	−723.368	93.027	−0.852
5800	42.141	321.810	285.381	211.287	−725.677	107.370	−0.967
5900	42.397	322.533	286.005	215.514	−727.991	121.752	−1.078
6000	42.660	323.248	286.620	219.767	−730.286	136.172	−1.185

PREVIOUS· December 1979 (1 atm) CURRENT: December 1979 (1 bar)

Aluminum Oxide, Ion (AlO_1^-) $Al_1O_1^-(g)$

Aluminum Oxide (AlO_2) IDEAL GAS M_r = 58.98034 Aluminum Oxide (AlO_2) $Al_1O_2(g)$

$\Delta_{at}H°(0\ K)$ = 216.52 ± 8 kJ·mol⁻¹
$S°(298.15\ K)$ = [251.83 ± 8] J·K⁻¹·mol⁻¹

$\Delta_fH°(0\ K)$ −85.01 ± 32 kJ·mol⁻¹
$\Delta_fH°(298.15\ K)$ = −86.19 ± 32 kJ·mol⁻¹

Electronic Levels and Quantum Weights		Vibrational Frequencies and Degeneracies
ϵ_i, cm⁻¹	g_i	ν, cm⁻¹
0	[4]	[700](1)
[15000]	[4]	[200](2)
[20000]	[2]	[930](1)

Point Group: [$D_{\infty h}$] $\sigma = 2$
Bond Distance: Al–O = [1.69] Å
Bond Angle: O–Al–O = [180]°
Rotational Constant: B_0 = [0.184455] cm⁻¹

Enthalpy of Formation

We adopt $\Delta_fH°(298.15\ K)$ = −20.6 ± 8 kcal·mol⁻¹ and $\Delta_{at}H°(0\ K)$ = 216.52 kcal·mol⁻¹ derived from mass–spectrometric data measured by Ho and Burns[1] during laser evaporation of single crystals of Al_2O_3. $\Delta_fH°$ and $\Delta_{at}H°$ are consistent with limiting values from studies in two other laboratories that were unable to detect AlO_2^+.[2-3] AlO_2 appears to be much less stable than predicted by earlier data;[4-5] those differ from the adopted $\Delta_fH°$ by −19 to −23 kcal·mol⁻¹ Our analyses of the data are given below.

AlO_2 is the least abundant of the five Al–containing species identified in the vapor over Al_2O_3. Ho and Burns,[1] unlike Farber *et al.*,[4-5] identified AlO_2 as the source of the mass = 59 ion by accurate mass data combined with intensities and appearance potentials of AlO_2^+ and conceivable impurity ions. Their partial pressure[1] should be free of large error from mass = 59 ions other than AlO_2^+. Error does arise from uncertainties in the evaporation coefficients, ionization cross sections and total flux of species.[1] An extreme example of this error is the formation of α–Al_2O_3, which is biased by −9 kcal·mol⁻¹ if calculated from the reported[1] pressures of Al and O. Our assigned uncertainty includes contributions from this error and that of the Gibbs–energy function.

Semiempirical calculations predicted $\Delta_fH°(298.15\ K)$ = −14.6 and −24.3 kcal·mol⁻¹ by the MNDO half–electron[6] and unrestricted Hartree–Fock[7] methods. These values agree with our adopted $\Delta_fH°$ but may be too uncertain to exclude the more negative value. Recent summaries[1,8] cite many other AlO_2 papers, including emission spectra and kinetic data that may not involve AlO_2. New studies[9] reassign much of the emission to an aluminum hydrate. We discount the bond–dissociation energies estimated from kinetics since formation of AlO_2 was inferred only from disappearance of AlO. Gurvich *et al.*[10] selected $\Delta_{at}H°$ = 215.1 ± 7.2 kcal·mol⁻¹ based on different Gibbs–energy functions.

Source	Method	Reaction[a]	T/K	δS[b] cal·K⁻¹·mol⁻¹	$\Delta_rH°(298.15)$, kcal·mol⁻¹ 2nd law	3rd law	$\Delta_fH°(298.15\ K)$ kcal·mol⁻¹	$\Delta_{at}H°(0\ K)$
1	Mass spec.	A	2221–2327[c]	−26 ± 5	−279 ± 12	−218.5 ± 2.7	−20.6 ± 8	216.5
2	Eff. mass spec.	B	2600	—	—	>25.1[d]	>−21.7 ± 8	<216.6
3	Mass spec.	B	2450	—	—	>24.9[d]	>−18.9 ± 8	<214.8
4	Eff. mass spec.	B	1943–2093	−1 ± 1	2.5 ± 1.4	3.6 ± 0.2	−43.2 ± 8	239.1
4	Flow eff. mass spec	B	1663–1983	−9 ± 6	−14 ± 12	3.2 ± 3.8	−43.6 ± 8	239.5
5	Flame mass spec.	C	2250	—	—	2.5	−39.3 ± 12	235.2

[a] Reactions: A) $Al(g) + 2\ O(g) = AlO_2(g)$; B) $AlO(g) = AlO_2(g) + Al(g)$; C) $AlO(g) + H_2O(g) = AlO_2(g) + H_2(g)$.

[b] $\delta S = \Delta_rS°$(2nd law) − $\Delta_rS°$(3rd law). [c] Temperature scale adjusted.

[d] AlO_2 not detected, detection limits estimated as $P(AlO_2)<P(Al_2O_2)/10$ in[3] and $P(AlO_2)<P(Al_2O_2$, 2300 K) in.[2]

Heat Capacity and Entropy

We adopt a linear OAlO structure and estimate the bond length by correcting the predicted value[6] for OAlO using the bias[6,11] in predicted values for AlO and Al_2O. Electronic states are estimated from BO_2 and vibrational frequencies from several related molecules. The adopted frequencies correspond to $k_1 \approx 14.2$, $k_{12} \approx 0.5$ and $(k_\delta/l) \approx 0.086$ mdyn/Å. The Al–O stretching constant k_1 may be compared to 3.6 for Al_2O,[11] 4.0 for AlOH,[12] 5.5 for AlO[11] and 6.6 for FAlO.[12] We assume that $k_1/(k_\delta/l^2)$49 compared to 31 in BO_2 and 39 in FBO.

Linear OAlO is the most stable structure according to MNDO[6] and unrestricted Hartree–Fock[7] calculations. The latter predicts that linear AlOO and cyclic AlO_2 are less stable by 22 and 38 kcal·mol⁻¹.[7] These predictions are not decisive but they are the best available. Spectral assignments are conflicting. IR bands in gas–plus–O_2 matrices have been assigned to each of three structures. A band at 523 cm⁻¹ in neon was tentatively assigned[11] to OAlO, but comparison with GaO_2[14] suggests that it is more likely to be ν_2 of cyclic AlO_2. Assignments for ν_2 in argon include 496[15] and 717[16] cm⁻¹. Other assignments for cyclic AlO_2 include ν_1 = 1096[15] (Ar), 1177[16] (Ar), 1116[17] (Ar) and 1096[17] (N_2). and ν_3 = 525 cm⁻¹,[16] (Ar). Assignments to AlOO include 1336 and 1091 cm⁻¹,[18] (N_2). Gurvich *et al.*[10] calculated functions for cyclic AlO_2 using 1096, 496 and 550 cm⁻¹; their values of the Gibbs energy function differ from ours by 1.4 and 0.2 J·K⁻¹·mol⁻¹ at 298 and 2000 K.

Continued on page 172

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−12.042	−85.010	−85.010	INFINITE
100	37.838	204.213	292.685	−8.847	−85.203	−87.595	45.755
200	44.987	232.915	256.245	−4.666	−85.735	−89.792	23.451
250	47.638	243.244	252.641	−2.349	−85.990	−90.776	18.967
298.15	49.892	251.832	251.832	0.	−86.190	−91.679	16.062
300	49.972	252.140	251.833	0.092	−86.197	−91.713	15.969
350	51.950	259.997	252.448	2.642	−86.359	−92.619	13.823
400	53.583	267.044	253.840	5.282	−86.487	−93.504	12.210
450	54.914	273.435	255.668	7.995	−86.594	−94.375	10.955
500	55.998	279.279	257.741	10.769	−86.692	−95.234	9.949
600	57.605	289.640	262.216	16.454	−86.901	−96.924	8.438
700	58.700	298.607	266.789	22.273	−87.185	−98.573	7.356
800	59.469	306.499	271.269	28.184	−87.592	−100.174	6.541
900	60.025	313.537	275.582	34.160	−88.162	−101.714	5.903
1000	60.438	319.883	279.700	40.184	−99.515	−102.421	5.350
1100	60.753	325.659	283.619	46.244	−100.139	−102.681	4.876
1200	60.997	330.956	287.346	52.332	−100.775	−102.885	4.478
1300	61.190	335.847	290.891	58.442	−101.424	−103.034	4.140
1400	61.346	340.387	294.267	64.569	−102.085	−103.133	3.848
1500	61.473	344.624	297.484	70.710	−102.760	−103.185	3.593
1600	61.578	348.595	300.556	76.863	−103.450	−103.191	3.369
1700	61.667	352.331	303.493	83.025	−104.154	−103.153	3.170
1800	61.744	355.858	306.305	89.196	−104.875	−103.074	2.991
1900	61.812	359.198	309.001	95.374	−105.611	−102.953	2.830
2000	61.873	362.370	311.591	101.558	−106.365	−102.794	2.685
2100	61.930	365.390	314.082	107.748	−107.135	−102.597	2.552
2200	61.984	368.273	316.480	113.944	−107.923	−102.362	2.430
2300	62.038	371.029	318.792	120.145	−108.727	−102.091	2.319
2400	62.092	373.670	321.024	126.351	−109.549	−101.786	2.215
2500	62.148	376.206	323.181	132.563	−110.387	−101.445	2.120
2600	62.207	378.645	325.268	138.781	−111.240	−101.070	2.031
2700	62.269	380.994	327.288	145.005	−112.109	−100.663	1.947
2800	62.335	383.260	329.247	151.235	−406.892	−99.255	1.852
2900	62.405	385.448	331.148	157.472	−406.693	−88.272	1.590
3000	62.480	387.565	332.993	163.716	−406.505	−77.295	1.346
3100	62.560	389.615	334.787	169.968	−406.329	−66.323	1.118
3200	62.644	391.603	336.531	176.228	−406.162	−55.359	0.904
3300	62.734	393.532	338.229	182.497	−406.005	−44.399	0.703
3400	62.828	395.406	339.884	188.775	−405.856	−33.443	0.514
3500	62.927	397.228	341.496	195.063	−405.714	−22.492	0.336
3600	63.030	399.003	343.069	201.361	−405.578	−11.545	0.168
3700	63.137	400.731	344.604	207.669	−405.448	−0.601	0.008
3800	63.247	402.416	346.104	213.988	−405.322	10.340	−0.142
3900	63.361	404.061	347.569	220.319	−405.201	21.277	−0.285
4000	63.478	405.666	349.001	226.661	−405.084	32.210	−0.421
4100	63.596	407.235	350.402	233.014	−404.971	43.141	−0.550
4200	63.717	408.769	351.774	239.380	−404.861	54.069	−0.672
4300	63.840	410.270	353.117	245.758	−404.755	64.995	−0.790
4400	63.963	411.739	354.432	252.148	−404.653	75.918	−0.901
4500	64.088	413.178	355.722	258.551	−404.553	86.838	−1.008
4600	64.212	414.588	356.986	264.966	−404.460	97.757	−1.110
4700	64.337	415.970	358.227	271.393	−404.372	108.674	−1.208
4800	64.461	417.326	359.444	277.833	−404.291	119.589	−1.301
4900	64.585	418.656	360.639	284.285	−404.217	130.503	−1.391
5000	64.707	419.962	361.812	290.750	−404.153	141.415	−1.477
5100	64.828	421.245	362.965	297.227	−404.099	152.326	−1.560
5200	64.947	422.505	364.098	303.715	−404.058	163.235	−1.640
5300	65.065	423.743	365.212	310.216	−404.030	174.145	−1.716
5400	65.180	424.960	366.307	316.728	−404.018	185.053	−1.790
5500	65.293	426.157	367.384	323.252	−404.024	195.961	−1.861
5600	65.403	427.335	368.444	329.787	−404.049	206.871	−1.930
5700	65.511	428.493	369.488	336.332	−404.098	217.781	−1.996
5800	65.615	429.634	370.515	342.889	−404.167	228.692	−2.060
5900	65.717	430.756	371.526	349.455	−404.267	239.602	−2.121
6000	65.816	431.861	372.523	356.032	−404.373	250.515	−2.181

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

Aluminum Oxide, Ion (AlO_2^-) IDEAL GAS $M_r = 58.98089$ Aluminum Oxide, Ion (AlO_2^-) $Al_1O_2^-(g)$

$\Delta_{at}H°(AlO_2^- \rightarrow Al + 2O + e^-) = 311.2 \pm 12$ kJ·mol^{-1}
$S°(298.15\ K) = [235\ 09 \pm 6.3]$ J·K^{-1}·mol^{-1}

$\Delta_fH°(0\ K) = -481 \pm 50$ kJ mol^{-1}
$\Delta_fH°(298.15\ K) = [-489.210]$ kJ·mol^{-1}

Vibrational Frequencies and Degeneracies
ν, cm^{-1}

[780](1)
[270](2)
[1120](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distance: Al–O = [1.68] Å
Bond Angle: O–Al–O = [180]°
Rotational Constant: $B_0 = [0.186657]$ cm^{-1}

Enthalpy of Formation

We adopt the rounded value $\Delta_fH°(0\ K) = -115 \pm 12$ kcal·mol^{-1}, which corresponds to the electron affinity EA = 94.68 kcal·mol^{-1} for AlO_2.[1] This is based on equilibrium data[2-3] that yield [EA(AlO_2)–EA(Cl)] = 11.6 kcal·mol^{-1} and EA(AlO_2) = 94.9 kcal·mol^{-1}. Data for the reaction $AlO_2(g) + Cl^-(g) = AlO_2^-(g) + Cl(g)$ at 2080–2222 K were obtained by Srivastava, Uy and Farber[2-3] using effusion mass spectrometry From their data we derive the values $\Delta_rH°(298.15\ K) = -11.7 \pm 0.9$ (3rd law) and $-8\ 7 \pm 8.6$ (2nd law) kcal·mol^{-1} plus [$\Delta_rS°$(2nd law)–$\Delta_rS°$(3rd law)] = 1.4 ± 4.0 cal·K^{-1}·mol^{-1}). The third–law $\Delta_rH°$ yields $\Delta_fH°(AlO_2^-, g, 0\ K) = -115.2$ and EA(AlO_2) = 94 9 kcal·mol^{-1}. Gurvich *et al.*[9] selected $\Delta_fH°(0\ K) = -115.7 \pm 14.3$ and EA = 96.8 ± 12 kcal·mol^{-1} based on Srivastava *et al.*[2]

It is conceivable that this electron affinity is biased. New data show that similar studies of Farber *et al*. on $\Delta_{at}H°(AlO_2, g, 0\ K)$ may be biased by >20 kcal·mol^{-1}.[1] Two calculations[4-5] provide a test for bias in EA = $\Delta_rH°(AlO_2^- \rightarrow AlO_2 + e^-) = 94.9$ kcal·mol^{-1}. Vertical ionization potentials of 85.3 and 78.4 kcal·mol^{-1} were calculated for AlO_2^- by Gutsev and Boldyrev[4] using two different bases in the non–empirical discrete–variation Xα method. MNDO calculations of Davis *et al.*[5] gave 76.0 kcal mol^{-1} instead of our adopted difference [$\Delta_fH°(AlO_2)$–$\Delta_fH°(AlO_2^-)$] = 96.3 kcal·mol^{-1} at 298.15 K. Although both calculations favor smaller values of EA, they may be too uncertain to yield a definite conclusion. New data are desirable for both AlO_2^- and AlO^-.[1]

The value of $\Delta_rH°(AlO_2^- \rightarrow AlO_2 + e^-, 298.15\ K)$ calculated from our tables will differ from a room temperature threshold energy due to inclusion of JANAF[1] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$ of $AlO_2^-(g)$, $AlO_2(g)$ and $e^-(g)$ and to threshold effects discussed by Rosenstock *et al.*[6]

Heat Capacity and Entropy

We adopt a linear, symmetric structure and estimate the bond length to be 0.01 Å shorter than in AlO_2.[1] MNDO calculations[5] support this linear structure and also predict that the bond length of AlO_2^- is 0.007 Å shorter than in AlO_2. AlO_2^- is isoelectronic with SiO_2 and MgF_2, which are also believed to be linear.

We estimate the vibrational frequencies of AlO_2^-, together with those of AlO_2, from comparisons with SiO_2, OAlF, MgF_2, CO_2, OBF, BeF_2, BO_2^-, and BO_2. Our adopted values correspond to $k_1 \approx 5.6$, $k_{12} \approx 0.2$ and $(k_\delta/l^2) \approx 0.16$ mdyn/Å. The Al–O stretching constant k_1 may be compared to 5.5 in AlO,[1] 6.6 in OAlF and OAlCl[7] and 4.2 assumed in AlO_2.[1] We assume that $k_1/(k_\delta/l^2) \approx 35$. We take the ground state to be $^1\Sigma^+$ by analogy to other triatomics with 16 valence electrons.[8]

Gurvich *et al.*[9] calculated functions that differ by −1.3 cal·K^{-1}·mol^{-1} in entropy and Gibbs energy function.

References

[1] JANAF Thermochemical Tables: $AlO_2(g)$, AlO(g), and AlO (g), 12–31–79; e (g), 3–31–77.
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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	−11.368	−481.158		
100	34.491	190.471	273.699	−8.323			
200	42.492	217.143	239.288	−4.429			
250	45.226	226.927	235.864	−2.234			
298.15	47.528	235.094	235.094	0.	−489.210	−483.454	84.699
300	47.611	235.388	235.095	0.088	−489.260	−483.418	84 171
350	49.683	242.887	235.682	2.522	−490.577	−482.339	71 985
400	51.455	249.640	237.012	5.051	−491.854	−481.075	62.822
450	52.950	255.789	238.761	7.662	−493.103	−479.652	55.677
500	54.203	261 435	240.750	10.342	−494.334	−478.092	49.946
600	56.131	271.498	245.057	15.865	−496.785	−474.613	41.319
700	57.493	280.259	249.474	21.550	−499.280	−470.722	35.126
800	58.475	288.004	253.815	27.351	−501.876	−466.466	30.457
900	59.198	294.935	258.006	33.236	−504.615	−461.877	26.807
1000	59 743	301.201	262.017	39.184	−518.123	−456.214	23.830
1100	60.161	306.916	265.843	45.180	−520.890	−449.889	21.363
1200	60.489	312.165	269.487	51.214	−523.659	−443.312	19.297
1300	60.750	317.018	272.959	57.276	−526.434	−436.504	17.539
1400	60.960	321.528	276.269	63.362	−529.215	−429.482	16.024
1500	61.133	325.739	279.428	69.467	−532.005	−422.261	14.704
1600	61.275	329.690	282.447	75.587	−534.805	−414.853	13.544
1700	61.395	333.408	285.337	81.721	−537.617	−407.270	12.514
1800	61 496	336.920	288.106	87.866	−540.442	−399.522	11.594
1900	61.582	340.248	290.763	94.020	−543.281	−391.615	10.766
2000	61.656	343.408	293.317	100.182	−546.135	−383.559	10.018
2100	61.719	346.418	295.775	106.350	−549.005	−375.360	9.337
2200	61.775	349.290	298.143	112.525	−551.893	−367.023	8.714
2300	61.824	352.038	300.427	118.705	−554.797	−358.555	8.143
2400	61.867	354.670	302.632	124.890	−557.719	−349.961	7.617
2500	61 904	357.196	304.765	131.078	−560.659	−341.244	7.130
2600	61.938	359.625	306.828	137.271	−563.617	−332.409	6.678
2700	61.968	361.963	308.827	143.466	−566.592	−323.459	6.258
2800	61.995	364.217	310.765	149.664	−863.486	−313.432	5.847
2900	62.020	366.393	312.646	155.865	−865.401	−293.754	5.291
3000	62.042	368.496	314.473	162.068	−867.334	−274.009	4.771
3100	62.061	370.530	316.249	168.273	−869.283	−254.199	4.283
3200	62.079	372.501	317.976	174.480	−871.248	−234.327	3.825
3300	62.096	374.412	319.657	180.689	−873.230	−214.392	3.394
3400	62.111	376.266	321.295	186.899	−875.227	−194.397	2.987
3500	62.125	378.066	322.892	193.111	−877.239	−174.344	2.602
3600	62.137	379.816	324.449	199.324	−879.267	−154.232	2.238
3700	62.149	381.519	325.968	205.539	−881.309	−134.065	1.893
3800	62.160	383.177	327.452	211.754	−883.366	−113.841	1.565
3900	62.170	384.791	328.902	217.971	−885.437	−93.563	1.253
4000	62.179	386.366	330.319	224 188	−887.523	−73.232	0.956
4100	62.188	387.901	331.704	230.406	−889.624	−52.849	0.673
4200	62.196	389.400	333.060	236.626	−891.739	−32.414	0.403
4300	62.203	390.863	334.388	242.845	−893.869	−11.929	0.145
4400	62.210	392.293	335.687	249.066	−896.016	8.606	−0.102
4500	62.217	393.692	336.961	255.287	−898.175	29.189	−0.339
4600	62.223	395.059	338.209	261.509	−900.354	49.821	−0.566
4700	62.228	396.397	339.433	267.732	−902.550	70.501	−0.784
4800	62.234	397.707	340.633	273.955	−904.764	91.227	−0.993
4900	62.239	398.991	341.811	280.179	−906 998	112.001	−1.194
5000	62.243	400.248	342.968	286 403	−909.252	132.820	−1.388
5100	62.248	401.481	344.103	292.627	−911.529	153.684	−1.574
5200	62.252	402.690	345.218	298.852	−913.830	174.592	−1.754
5300	62.256	403.875	346.314	305.078	−916.156	195.546	−1.927
5400	62.260	405 039	347.390	311.303	−918.509	216.543	−2.095
5500	62.263	406.182	348.449	317.530	−920.891	237.584	−2.256
5600	62.266	407.303	349.490	323.756	−923.304	258.670	−2.413
5700	62.270	408.406	350.514	329.983	−925.750	279.798	−2.564
5800	62.273	409.489	351.521	336.210	−928.227	300.970	−2.711
5900	62.276	410.553	352.513	342.437	−930.744	322.183	−2.852
6000	62.278	411.600	353.489	348.665	−933.279	343.439	−2.990

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

Aluminum Oxide, Ion (AlO_2^-) $Al_1O_2^-(g)$

Aluminum Sulfide (AlS) IDEAL GAS $M_r = 59.04154$ Aluminum Sulfide (AlS) $Al_1S_1(g)$

$S°(298.15\ K) = 230.601 \pm 0.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 238.4 \pm 8.5\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 238.5 \pm 8.5\ kJ{\cdot}mol^{-1}$

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

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Sigma^+$	0	2	617.1	3.33	0.2799	0.0018	2.029
$A^2\Pi_i$	[4500]	4	[459]	[2]	[0.234]	[0.001]	
$B^2\Sigma^+$	23381.1	2	510.9	1.45	0.2461	0.0012	2.164
$C\ ^2\Pi_{r1/2}$	29942.5	2	545	6	[0.2600]	[0.0028]	3.090
$C^2\Pi_{r3/2}$	30059.7	2	559	14	[0.2539]	[0.0044]	3.127
$D^2\Sigma^+$	35714.9	2	430	14	0.2402	0.0036	2.190

Enthalpy of Formation

The adopted value of $\Delta_f H°$(298.15 K) is an average of 3rd law values from the equilibrium studies of Ficalora *et al.*[1] and Uy and Drowart.[2] Ficalora *et al.*[1] used mass spectrometric ion intensity data to study the equilibrium Al(g) + 1/2 S_2(g) AlS(g) and they reported 2nd and 3rd law values for $\Delta_f H°$(298.15 K) of −37.3 ± 3.0 kcal mol^{-1} and −35 4 ± 2.0 kcal·mol^{-1}, respectively. Uy and Drowart[2] used mass spectrometric ion intensity data to study two different equilibria and report an average value of D_0° = 88.4 ± 1 9 kcal mol^{-1} via 3rd law techniques. Using auxiliary JANAF data[3] we calculate 3rd law values of $\Delta_f H°$(298.15 K) = 58.8 ± 2.0 kcal mol^{-1} and $\Delta_f H°$(298.15 K) = 55.2 ± 1.9 kcal·mol^{-1} from the data of Ficalora *et al.*[1] and Uy Drowart[2] respectively. A complete reanalysis is impossible since neither set of authors report their raw data. Reanalysis is desirable since the free energy functions in this table differ from those in the older table[4] used by both sets of authors, due to inclusion of excited electronic states. A crude calculation shows that these differences are large enough to affect third-law results by as much as ±0.2 kcal·mol^{-1} which is within the uncertainty of the reported values. The adopted value of $\Delta_f H°$(298.15 K), coupled with auxiliary JANAF data,[3] yields an adopted D_0° = 86.9 ± 2.0 kcal·mol^{-1}.

Heat Capacity and Entropy

With the exception of the two $^2\Pi$ states the adopted molecular constant data are from Huber and Herzberg[5] based on earlier absorption and emission spectroscopic studies by several authors. We have adopted a modified nomenclature system consistent with states for AlO,[3] but different from that of Huber and Herzberg for AlS.[5] This is desirable to accommodate the predicted low lying $^2\Pi_i$ state which is unobserved for AlS but has been observed for AlO. The energy of this $A^2\Pi$ state for AlS is predicted from relative energies of the two $^2\Pi$ states for AlO[3] and is consistent with INDO/S calculations[6] if the bias in these calculations for AlO is directly transferable to AlS. Molecular constant data for the $A^2\Pi$ state is predicted assuming the same relative differences between this state and the ground state as in AlO.

We adopt Lavendy's[7] molecular constant data for the $C^2\Pi$ state, except we use his experimental values of B_0 = 0.2572 cm^{-1} and B_0 = 0.2495 cm^{-1} for the 1/2 and 3/2 components in conjunction with the Pekeris relationship[8] to estimate values of B_e and α_e. Lavendy's emission spectroscopy measurements indicate that this state is highly perturbed and this is reflected in the unusually large differences between molecular constant data for the 1/2 and 3/2 components. The nature of the perturbing state was not identified. We treat the $C^2\Pi$ state as two separate electronic states separated by the spin–orbit coupling constant of 117.2 cm^{-1}. This approximation introduces little uncertainty since the entire $C^2\Pi$ state makes an entropy contribution of less than 0.1 cal·mol^{-1}·K^{-1} at 6000 K.

The largest uncertainty in the table is due to uncertainty in the estimated $A^2\Pi$ state. This state makes no contribution to the thermochemical functions below 500 K so its uncertainty is not reflected in that given for the S°(298.15 K) value. This state makes the following entropy contributions in cal·K^{-1}·mol^{-1}: 0 05 at 1000 K, 0.9 at 2000 K, 1.8 at 3000 K, 2.2 at 4000 K, 2 4 at 5000 K and 2.5 at 6000 K.

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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	−9.087	238.352	238.352	INFINITE
100	29.206	196.985	258.754	−6.177	240.089	222.341	−116.139
200	31.167	217.716	233.589	−3.175	239.647	204.661	−53.452
298.15	33.398	230.601	230.601	0.	238.488	187.722	−32.888
300	33.432	230.807	230.601	0.062	238.463	187.407	−32.630
400	34.871	240.640	231.932	3.483	234.779	170.692	−22.290
500	35.749	248.523	234.488	7.017	231.752	155.008	−16.194
600	36.348	255.096	237.390	10.624	229.039	139.919	−12.181
700	36.861	260 738	240.332	14.284	226.505	125.267	−9.348
800	37.417	265.695	243.199	17.997	224.026	110.974	−7.246
900	38.085	270.140	245.949	21.771	168.402	98.073	−5.692
1000	38.884	274.193	248.574	25.619	156.478	91.088	−4.758
1100	39.797	277.941	251.075	29.552	155.365	84.604	−4.018
1200	40.783	281.445	253.462	33.581	154.331	78.218	−3.405
1300	41.794	284.750	255.742	37.709	153.382	71.914	−2.890
1400	42.782	287.883	257.927	41.939	152.519	65.680	−2.451
1500	43.708	290.867	260.025	46.264	151.735	59.505	−2.072
1600	44.543	293.715	262.042	50.677	151.025	53.380	−1.743
1700	45.266	296.438	263.986	55.169	150.379	47.297	−1.453
1800	45.870	299.043	265.862	59.726	149.785	41.251	−1.197
1900	46.353	301.536	267.674	64.339	149.233	35.236	−0.969
2000	46.720	303.924	269.427	68.993	148.711	29.250	−0.764
2100	46.979	306.210	271.125	73.679	148.209	23.289	−0.579
2200	47 144	308.400	272.770	78.386	147 719	17.352	−0.412
2300	47.225	310.497	274.365	83.105	147.231	11.437	−0.260
2400	47.235	312.508	275.912	87.828	146.738	5.544	−0.121
2500	47.188	314.435	277.415	92.550	146.236	−0.329	0.007
2600	47.094	316.284	278.875	97.264	145.720	−6.181	0.124
2700	46.963	318.059	280.293	101.968	145.186	−12.014	0.232
2800	46.804	319.764	281.673	106.656	−149.270	−16.858	0.314
2900	46 624	321.404	283.015	111.328	−148.751	−12.138	0 219
3000	46.431	322.981	284.321	115.980	−148.257	−7.436	0.129
3100	46.229	324.500	285.593	120.614	−147.787	−2.750	0.046
3200	46.024	325.965	286.831	125.226	−147.342	1.922	−0.031
3300	45.818	327.378	288.039	129.818	−146.922	6.580	−0.104
3400	45.614	328.742	289.216	134.390	−146.528	11.225	−0.172
3500	45 415	330.062	290.364	138.941	−146.159	15.860	−0.237
3600	45.223	331.338	291.485	143.473	−145.814	20.484	−0.297
3700	45.039	332.575	292.579	147.986	−145.494	25.099	−0.354
3800	44.864	333.774	293.647	152.481	−145.197	29.705	−0.408
3900	44.698	334.937	294.691	156.959	−144.923	34.304	−0.459
4000	44.543	336.067	295.711	161.421	−144.672	38.897	−0.508
4100	44.399	337.165	296.709	165.868	−144.443	43.483	−0.554
4200	44.265	338.233	297.685	170.301	−144.236	48.064	−0.598
4300	44.142	339.273	298.640	174.721	−144.050	52.640	−0.639
4400	44.031	340.287	299.575	179.130	−143.885	57.213	−0.679
4500	43.930	341.275	300.491	183.528	−143.739	61.781	−0.717
4600	43.840	342.239	301.388	187.916	−143.615	66.347	−0.753
4700	43 761	343.181	302.267	192.296	−143.511	70.910	−0.788
4800	43.692	344.102	303.129	196.669	−143 427	75.471	−0.821
4900	43.633	345.002	303.975	201.035	−143.363	80.031	−0.853
5000	43.584	345.883	304.804	205.396	−143.319	84.590	−0.884
5100	43.545	346.746	305.618	209.752	−143.296	89.148	−0.913
5200	43.515	347.591	306.417	214.105	−143.293	93.705	−0.941
5300	43.495	348.420	307.202	218.456	−143.311	98.263	−0.968
5400	43.484	349.233	307.973	222.804	−143.350	102.821	−0.995
5500	43.481	350.031	308.730	227.153	−143.409	107.381	−1.020
5600	43.487	350.814	309.475	231.501	−143.490	111.941	−1.044
5700	43.501	351.584	310.207	235.850	−143.593	116.503	−1.068
5800	43.524	352.341	310.927	240.201	−143.715	121.067	−1.090
5900	43.554	353.085	311.635	244.555	−143.862	125 634	−1.112
6000	43.592	353.817	312.332	248.912	−144.010	130.201	−1.133

PREVIOUS. December 1979 (1 atm) CURRENT December 1979 (1 bar)

Aluminum (Al$_2$) IDEAL GAS $M_r = 53.96308$ Aluminum (Al$_2$) Al$_2$(g)

$S°(298.15\ \mathrm{K}) = 233.5 \pm 0.3\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$

$\Delta_f H°(0\ \mathrm{K}) = 486.3 \pm 3.5\ \mathrm{kJ{\cdot}mol^{-1}}$
$\Delta_f H°(298.15\ \mathrm{K}) = 487.0 \pm 3.5\ \mathrm{kJ{\cdot}mol^{-1}}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^3\Sigma_g^-$	0	3
$^5\Sigma_u^-$	[1000.]	[5]
$1\,^3\Sigma_u^-$	[10000]	[3]
$2\,^3\Sigma_u^-$	17269.36	3

$\omega_e = 350.01\ \mathrm{cm^{-1}}$ $\omega_e x_e = 2.022\ \mathrm{cm^{-1}}$ $\omega_e y_e = -0.0105\ \mathrm{cm^{-1}}$ $\sigma = 2$
$B_e = 0.2054\ \mathrm{cm^{-1}}$ $\alpha_e = 0.0012\ \mathrm{cm^{-1}}$ $D_e = 3.07\mathrm{x}10^{-7}\ \mathrm{cm^{-1}}$ $r_e = 2.4668$ Å

Enthalpy of Formation

From a mass–spectrometric investigation of the equilibria

$$\mathrm{AlAu(g) + Al(g) = Al_2(g) + Au(g)}$$
$$\mathrm{2\ AlAu(g) = Al_2(g) + Au_2(g)}$$

at 1921–2032 K and a 2nd law and 3rd law treatment of the data, Sterns and Kohl[1] derived the dissociation energy, $D_0° = 1.55 \pm 0.15$ eV for Al$_2$. Using current auxiliary data for Al$_2$(g) and Al(g),[7] this value is corrected to 1.56 eV. As discussed by Stearns and Kohl,[1] it is likely that all of the previous mass spectrometic determinations[2,3,4] resulted in slightly high values for $D_0°$ (<1.96 ± 0.4 eV, 1.78 ± 0.19 eV and 1.80 eV, respectively) because of interferences due to the measurement of Al$^+$ ion intensities from extraneous sources The dissociation energy of Al$_2$ has also been evaluated by a linear Birge–Sponer extrapolation[5] as 1.87 ± 0.2 eV and a graphical Birge–Sponer extrapolation[6] as 1.6 ± 0.2 eV. An ab initio calculation (LCAO–STO–MO–SCF–CI) by Leleyter and Joyes[9] yielded a dissociation energy of 1.03 eV. Based on the Stearns and Kohl result and auxiliary JANAF data,[7] we adopt $\Delta_f H°(298.15\ \mathrm{K}) = 116\ 4 \pm 3.5$ kcal mol for Al$_2$(g).

Heat Capacity and Entropy

The bond spectrum of Al$_2$ was first reported by Zeeman[6] who wrongly attributed the emission to the AlC molecule. The vibrational constants are those reported by him. Values for the rotational constants are taken from Ginter *et al.*[5] who also assigned the upper and lower $^3\Sigma$ state configurations and energies. The electronic energies for the $^5\Sigma$ state and 1 $^3\Sigma$ state have been estimated by analogy with B_2. An ab initio SCF calculation of the ground state potential curve for Al$_2$[8] is reported but without inclusion of configuration interaction the calculated separations between states are not reliable.

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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	−9.816	486.280	486.280	INFINITE
100	30.569	196.386	265.163	−6.878	488.251	470.010	−245.508
200	34.832	218.934	236.936	−3.600	487.925	451.796	−117.997
298.15	38.448	233.531	233.531	0.	487.018	434.251	−76.079
300	38.511	233.769	233.532	0.071	486.999	433.923	−75.553
400	41.208	245.250	235.079	4.068	485.980	416.384	−54.374
500	42.539	254.607	238.079	8.264	484.910	399.107	−41.694
600	42.884	262.401	241.502	12.539	483 715	382.056	−33.261
700	42.718	269.002	244.971	16.821	482.301	365.221	−27.253
800	42.350	274.682	248.339	21.075	480.594	348.608	−22.762
900	41.941	279.646	251.547	25.289	478.526	332.230	−19.282
1000	41.559	284.045	254.581	29.464	454.869	317.624	−16.591
1100	41.230	287.990	257.442	33.603	452.658	304.006	−14 436
1200	40.961	291.566	260.139	37.712	450.417	290.591	−12.649
1300	40.749	294.836	262.684	41.797	448.152	277.363	−11.145
1400	40.587	297.849	265.090	45.863	445.868	264.311	−9.862
1500	40.470	300.645	267.368	49.916	443.571	251.423	−8.755
1600	40.392	303.255	269.530	53.959	441.263	238.688	−7.792
1700	40.348	305.702	271.587	57.995	438.950	226.098	−6.947
1800	40.334	308.008	273.547	62.029	436.634	213.645	−6.200
1900	40.345	310.188	275.418	66.063	434.317	201.319	−5.535
2000	40.380	312.259	277.209	70.099	432.003	189.116	−4.939
2100	40.435	314.230	278.925	74.140	429.694	177.029	−4.403
2200	40.507	316.113	280.573	78.187	427.391	165.051	−3.919
2300	40.595	317.915	282.158	82.242	425.096	153.178	−3.479
2400	40.697	319.645	283.684	86.306	422.810	141.404	−3.078
2500	40.810	321.309	285.156	90.382	420.535	129.726	−2.710
2600	40.934	322.912	286.578	94.469	418.272	118.138	−2.373
2700	41.066	324.459	287.952	98.569	416.022	106.638	−2.063
2800	41.207	325.955	289.283	102.682	−174.017	97.155	−1.812
2900	41.355	327.404	290.572	106.810	−174.048	106.841	−1.924
3000	41.509	328.808	291.824	110.953	−174 064	116.527	−2 029
3100	41.668	330.172	293.039	115.112	−174.065	126.213	−2.127
3200	41.831	331.497	294.220	119.287	−174.050	135.899	−2.218
3300	41.999	332.787	295.369	123.479	−174.020	145.585	−2.304
3400	42.169	334.043	296.488	127.687	−173.974	155.269	−2.385
3500	42.343	335.268	297.579	131.913	−173.912	164.952	−2.462
3600	42.519	336.464	298.643	136.156	−173.834	174.633	−2.534
3700	42.696	337.631	299.681	140.416	−173.741	184.311	−2.602
3800	42.876	338.772	300.694	144.695	−173.634	193.987	−2.667
3900	43.056	339.888	301.685	148.992	−173.511	203.659	−2.728
4000	43.238	340.980	302.654	153.306	−173.375	213.329	−2.786
4100	43.420	342.050	303.602	157.639	−173.225	222.995	−2.841
4200	43.604	343.099	304.530	161.990	−173.064	232.657	−2.894
4300	43.787	344.127	305.439	166.360	−172.890	242.314	−2.944
4400	43.970	345.136	306.329	170.748	−172.707	251.968	−2.991
4500	44.155	346.126	307.203	175.154	−172.510	261.617	−3.037
4600	44.338	347.098	308.060	179.579	−172.308	271.263	−3.080
4700	44.522	348.054	308.900	184.022	−172.100	280.903	−3.122
4800	44.706	348.993	309.726	188.483	−171.886	290.539	−3.162
4900	44.889	349 917	310.537	192.963	−171.668	300.171	−3.200
5000	45.073	350.826	311.333	197.461	−171.449	309 798	−3.236
5100	45.255	351 720	312.117	201.977	−171.229	319.421	−3.272
5200	45 438	352.600	312.887	206.512	−171.012	329.039	−3.305
5300	45.620	353 468	313.644	211.065	−170.799	338.653	−3.338
5400	45.802	354.322	314.390	215.636	−170.592	348.264	−3.369
5500	45 984	355.164	315.123	220.225	−170.393	357.870	−3.399
5600	46.165	355.994	315.846	224.833	−170.204	367.473	−3.428
5700	46.346	356.813	316.557	229.458	−170.028	377.073	−3.455
5800	46.526	357.621	317.258	234.102	−169.862	386.669	−3.482
5900	46.707	358.418	317 949	238.764	−169.717	396.264	−3.508
6000	46.887	359.204	318.630	243.443	−169.548	405.851	−3.533

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

Beryllium Aluminum Oxide ($BeAl_2O_4$) CRYSTAL M_r = 126.97286 Beryllium Aluminum Oxide ($BeAl_2O_4$) $Al_2Be_1O_4(cr)$

$\Delta_fH°(0\ K) = -2285.5 \pm 3.8\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 66.29 \pm 0.13\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = -2300.78 \pm 3.8\ kJ{\cdot}mol^{-1}$

$T_{fus} = 2146 \pm 10\ K$ $\Delta_{fus}H° = 170.008 \pm 3.8\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The adopted value of $\Delta_fH°(298.15\ K)$ is calculated from $\Delta_rH°(968\ K) = -4.0 \pm 0.3\ kcal{\cdot}mol^{-1}$ for BeO(cr, α) + Al_2O_3(cr, α) → $BeAl_2O_4$(cr) using current values of $\Delta_fH°$ for the reactants.[1] The value of $\Delta_rH°(968\ K)$ was determined by Holm and Kleppa[2] from the difference in heats of solution of the three components in an oxide melt.

For comparison, a second-law treatment of the equilibrium data of Young[3] yields $\Delta_rH°(298.15\ K) = -2\ 3\ kcal{\cdot}mol^{-1}$ for the same reaction. This is obtained from a suitable linear combination of the three equilibria studied by Young and leads to $\Delta_fH°(298.15\ K) = -548.2\ kcal{\cdot}mol^{-1}$ in good agreement with the adopted value.

Heat Capacity and Entropy

Heat capacity and derived properties at and below 298.15 K are taken from the calorimetric data (16–380 K) of Furukawa and Saba.[4] The entropy is based on $S°(16\ K) = 0.004\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ Above 298 15 K the adopted $C_p°$ are based on Ishihara and West's[5] merging of enthalpy data of Ditmar and Douglas[6] (323–1173 K) and Ishihara and West[5] (1182–2137) with the $C_p°$ data of Furukawa and Saba.[4] Values above 2137 K are our extrapolation. Ishihara and West report a sharp rise in enthalpy data above 2030 K, apparently associated with premelting phenomena. Data in this region was ignored by Ishihara and West during their treatment.

Fusion Data

Refer to the liquid table for details.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−13.088	−2285.491	−2285.491	INFINITE
100	16.365	5.523	132.214	−12.669	−2291.889	−2256.332	1178.587
200	66.430	31.982	74.785	−8.560	−2297.784	−2218.294	579.359
298.15	105.380	66.291	66.291	0.	−2300.782	−2178.542	381.672
300	105.940	66.945	66.293	0.195	−2300.815	−2177.784	379.186
400	130.280	101.047	70.777	12.108	−2301.703	−2136.594	279.011
500	145.250	131.854	79.971	25.942	−2301.355	−2095 338	218.899
600	154.970	159.252	90 946	40.983	−2300.371	−2054.220	178.836
700	161.750	183 668	102 480	56.832	−2299.118	−2013.292	150.234
800	166.830	205.612	114.024	73.271	−2297.811	−1972.550	128.794
900	170 870	225.503	125.322	90.163	−2296.605	−1931.966	112.128
1000	174.200	243.683	136.263	107.421	−2316.784	−1889.987	98.723
1100	177.030	260.423	146.799	124 986	−2315.359	−1847.375	87 725
1200	179.480	275.934	156.922	142.814	−2313.836	−1804 898	78.565
1300	181.670	290.388	166.639	160.873	−2312.239	−1762.550	70 820
1400	183.750	303.927	175.967	179.144	−2310.577	−1720.329	64.186
1500	185.910	316.677	184.926	197.625	−2308.849	−1678.228	58.441
1600	188 410	328.752	193.541	216.337	−2321.567	−1635.720	53.401
1700	191.560	340.263	201.836	235.326	−2319.211	−1592.925	48.945
1800	195.790	351.326	209.835	254.683	−2316.556	−1550.278	44.988
1900	201.570	362.058	217.566	274.535	−2313.473	−1507.788	41.452
2000	209.490	372.588	225.054	295.068	−2309.778	−1465.476	38.274
2100	220.190	383.055	232.329	316.525	−2305.227	−1423.369	35 404
2146.000	226.250	387.890	235.612	326.790	--- CRYSTAL <--> LIQUID ---		
2200	233.098	393.597	239.419	339.191	−2299.533	−1381.503	32.801
2300	248.548	404.290	246.354	363.252	−2292.510	−1339.927	30.431
2400	266.455	415.238	253.162	388.982	−2283.885	−1298.690	28.265

PREVIOUS: June 1972 CURRENT December 1979

Beryllium Aluminum Oxide ($BeAl_2O_4$) LIQUID $M_r = 126.97286$

$S°(298.15\ K) = [126.406]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 2146 \pm 10\ K$

$\Delta_f H°(298.15\ K) = [-2163.842]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 170.008 \pm 3.8\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(BeAl_2O_4, l, 298\ 15\ K)$ is calculated from $\Delta_f H°(BeAl_2O_4, cr, 298.5\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(2146\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Ishihara and West[2] reported enthalpy data from 2177 to 2355 K and reported a quadratic enthalpy equation for the liquid. This equation yields a temperature dependence for $C_p°$ which is unreasonably large Therefore we have fit their enthalpy data to a linear equation which fits their measured points with an average deviation of 0.15 $kcal{\cdot}mol^{-1}$ and a maximum deviation of 0.35 $kcal{\cdot}mol^{-1}$ Based on the scatter in the data we believe higher fits are unjustified and adopt the resulting constant value of $C_p° = 58.893\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ ($246.408\ J{\cdot}K^{-1}{\cdot}mol^{-1}$) above the assumed glass transition at 1450 K. Below T_{gls}, $C_p°$ is taken to be the same as the crystal.

$S°$(298 15 K) is calculated in a manner analagous to that used for enthalpy of formation.

Fusion Data

The adopted melting point is taken from the phase study of Lang *et al.*[3] after adjustment to IPTS–68. We calculate $\Delta_{fus}H°$ from the difference between $H°(2146; 298.15)$ for the crystal[1] and liquid using our adopted linear enthalpy equation for the liquid.

References

[1] JANAF Thermochemical Tables: $BeAl_2O_4(cr)$, 12–31–79.
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Beryllium Aluminum Oxide ($BeAl_2O_4$) $Al_2Be_1O_4(l)$

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298 15	105.380	126.406	126.406	0.	−2163.842	−2059.526	360.820
300	105.940	127.060	126.408	0 195	−2163.876	−2058.879	358.483
400	130.280	161.162	130.892	12.108	−2164.764	−2023.701	264.268
500	145.250	191.969	140.086	25.942	−2164.416	−1988.456	207.733
600	154.970	219.367	151.061	40.983	−2163.431	−1953.350	170.054
700	161.750	243.783	162.595	56.832	−2162.179	−1918.434	143.155
800	166.830	265.727	174.139	73.271	−2160.872	−1883.703	122.993
900	170.870	285.618	185.438	90.163	−2159.665	−1849.131	107.321
1000	174.200	303.799	196.378	107.421	−2179.845	−1813.163	94.710
1100	177.030	320.538	206.914	124.986	−2178.419	−1776.562	84.362
1200	179.480	336 049	217.037	142.814	−2176.897	−1740.096	75.744
1300	181.670	350.503	226.754	160.873	−2175.299	−1703.761	68.458
1400	183.750	364.042	236.082	179.144	−2173.638	−1667.550	62.217
1450 000	184.800	370.508	240.606	188.358	——— GLASS <−−> LIQUID ———		
1450.000	246.409	370.508	240.606	188.358	TRANSITION		
1500	246.409	378.862	245.076	200 679	−2168.857	−1631.514	56.814
1600	246.409	394 765	253 940	225.320	−2175 646	−1595.419	52.085
1700	246.409	409.703	262.668	249.960	−2167.637	−1559.400	47.915
1800	246.409	423.788	271.231	274.601	−2159.697	−1523.851	44.221
1900	246.409	437.110	279.615	299.242	−2151.827	−1488.741	40.928
2000	246.409	449.750	287.808	323.883	−2144.023	−1454.044	37.976
2100	246.409	461.772	295.808	348.524	−2136.288	−1419.736	35.314
2146 000	246.409	467.111	299.423	359.859	−−− CRYSTAL <−−> LIQUID −−−		
2200	246.409	473.235	303.614	373.165	−2128.619	−1385.793	32.903
2300	246.409	484.188	311.229	397.806	−2121.017	−1352.200	30.709
2400	246.409	494.675	318.656	422.447	−2113.480	−1318.935	28.706
2500	246.409	504.734	325.899	447.088	−2106.009	−1285.983	26.869
2600	246.409	514.399	332.964	471.729	−2098.603	−1253.328	25 180
2700	246.409	523.698	339.858	496.370	−2091.260	−1220.956	23.621
2800	246.409	532.660	346.584	521 011	−2962.738	−1180.698	22.026
2900	246.409	541.306	353.151	545.652	−2952.264	−1117.240	20.124
3000	246 409	549.660	359.562	570.293	−2941.834	−1054.141	18.354
3100	246.409	557.740	365.826	594.934	−2931.448	−991.388	16.705
3200	246.409	565.563	371.946	619.575	−2921.107	−928.972	15.164
3300	246.409	573.145	377.929	644.216	−2910.809	−866.877	13.722
3400	246 409	580.501	383.779	668.857	−2900.558	−805.093	12.369
3500	246 409	587.644	389.502	693.498	−2890.353	−743.611	11.098
3600	246.409	594.586	395.103	718.139	−2880.194	−682.419	9.902
3700	246.409	601.337	400.586	742.779	−2870.085	−621.510	8.774
3800	246.409	607.909	405.956	767.420	−2860.026	−560.871	7.710
3900	246.409	614.309	411.216	792.061	−2850.018	−500.497	6.703
4000	246.409	620.548	416.372	816.702	−2840.064	−440.380	5.751

PREVIOUS. June 1972   CURRENT December 1979

Beryllium Aluminum Oxide ($BeAl_2O_4$) CRYSTAL-LIQUID

0 to 2146 K crystal
above 2146 K liquid

Refer to individual tables for details

M_r= 126.97286 Beryllium Aluminum Oxide ($BeAl_2O_4$) $Al_2Be_1O_4(cr,l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−13.088	−2285.491	−2285.491	INFINITE
100	16.365	5.523	132.214	−12.669	−2291.889	−2256.332	1178.587
200	66.430	31.982	74.785	−8.560	−2297.784	−2218.294	579.359
298.15	105.380	66.291	66.291	0.	−2300.782	−2178.542	381.672
300	105.940	66.945	66.293	0.195	−2300.815	−2177.784	379.186
400	130.280	101.047	70.777	12.108	−2301.703	−2136.594	279.011
500	145.250	131.854	79.971	25.942	−2301.355	−2095.338	218.899
600	154.970	159.252	90.946	40.983	−2300.371	−2054.220	178.836
700	161.750	183.668	102.480	56.832	−2299.118	−2013.292	150.234
800	166.830	205.612	114.024	73.271	−2297.811	−1972.550	128.794
900	170.870	225.503	125.322	90.163	−2296.605	−1931.966	112.128
1000	174.200	243.683	136.263	107.421	−2316.784	−1889.987	98.723
1100	177.030	260.423	146.799	124.986	−2315.359	−1847.375	87.725
1200	179.480	275.934	156.922	142.814	−2313.836	−1804.898	78.565
1300	181.670	290.388	166.639	160.873	−2312.239	−1762.550	70.820
1400	183.750	303.927	175.967	179.144	−2310.577	−1720.329	64.186
1500	185.910	316.677	184.926	197.625	−2308.849	−1678.228	58.441
1600	188.410	328.752	193.541	216.337	−2321.567	−1635.720	53.401
1700	191.560	340.263	201.836	235.326	−2319.211	−1592.925	48.945
1800	195.790	351.326	209.835	254.683	−2316.556	−1550.278	44.988
1900	201.570	362.058	217.566	274.535	−2313.473	−1507.788	41.452
2000	209.490	372.588	225.054	295.068	−2309.778	−1465.476	38.274
2100	220.190	383.055	232.329	316.525	−2305.227	−1423.369	35.404
2146.000	226.250	387.890	235.612	326.790	CRYSTAL <--> LIQUID		
2146.000	246.409	467.111	235.612	496.798	TRANSITION		
2200	246.409	473.235	241.369	510.105	−2128.619	−1385.793	32.903
2300	246.409	484.188	251.690	534.745	−2121.017	−1352.200	30.709
2400	246 409	494.675	261.598	559.386	−2113.480	−1318.935	28.706
2500	246 409	504.734	271.123	584.027	−2106.009	−1285.983	26.869
2600	246.409	514.399	280.295	608.668	−2098.603	−1253.328	25.180
2700	246.409	523.698	289.139	633.309	−2091.260	−1220.957	23.621
2800	246.409	532.660	297.677	657.950	−2962.738	−1180.698	22.026
2900	246.409	541.306	305.930	682.591	−2952.264	−1117.240	20.124
3000	246.409	549.660	313.916	707.232	−2941.834	−1054 141	18.354
3100	246.409	557.740	321.652	731.873	−2931.448	−991.388	16.705
3200	246.409	565.563	329.152	756.514	−2921.107	−928.972	15.164
3300	246.409	573.145	336.432	781.155	−2910.810	−866.878	13.722
3400	246.409	580.501	343.503	805.796	−2900.558	−805.093	12.369
3500	246.409	587.644	350.377	830.437	−2890.353	−743.611	11.098
3600	246.409	594.586	357.064	855.078	−2880.194	−682.419	9.902
3700	246.409	601.337	363.575	879.719	−2870.085	−621.510	8.774
3800	246.409	607.909	369.919	904.360	−2860 026	−560.871	7.710
3900	246.409	614.309	376.104	929.001	−2850.018	−500.497	6.703
4000	246.409	620.548	382.137	953.642	−2840.064	−440.380	5.751

PREVIOUS: CURRENT: December 1979

Beryllium Aluminum Oxide ($BeAl_2O_4$) $Al_2Be_1O_4(cr,l)$

Aluminum Bromide ((AlBr$_3$)$_2$) IDEAL GAS $M_r = 533.38708$ Aluminum Bromide ((AlBr$_3$)$_2$) Al$_2$Br$_6$(g)

$\Delta_f H^\circ(0\ \mathrm{K}) = -892.9 \pm 3.4\ \mathrm{kJ \cdot mol^{-1}}$

$S^\circ(298.15\ \mathrm{K}) = 547.2 \pm 4.2\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ $\Delta_f H^\circ(298.15\ \mathrm{K}) = -937.2 \pm 3.4\ \mathrm{kJ \cdot mol^{-1}}$

Vibrational Frequencies and Degeneracies					
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
409 (1)	59 (1)	76 (1)	[8] (1)	346 (1)	376 (1)
203 (1)	[30](1)	500 (1)	489 (1)	90 (1)	199 (1)
139 (1)	[250](1)	[110](1)	114 (1)	[67](1)	112 (1)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: D_{2h}
Bond Distances. Al–Br = 2.222 ± 0.005 Å; Al–Br(bridge) = 2.414 ± 0.007 Å
Bond Angles: Br–Al–Br = 122.8 ± 3.3°; Br(bridge)–Al–Br(bridge) = 92.3 ± 0.9°
Product of the Moments of Inertia: $I_A I_B I_C = 8\,865729 \times 10^{-110}\ \mathrm{g^3 \cdot cm^6}$

Enthalpy of Formation

Vapor pressures over AlBr$_3$(cr) and AlBr$_3$(l) have been measured by Dunne and Gregory,[1] Fischer *et. al.*[2] and Sulzmann.[3] The vapor pressures were corrected for vapor non–ideality by means of the equation $\Delta G^\circ/T = -R\ln P - BP/T$. The Bertholot equation of state and critical constants T_c=763 K and P$_c$=28.5 atm reported by Johnson, Silva and Cubicciotti[4] were used to calculate B. The corrected vapor pressures were used to calculate $\Delta_r H^\circ(298.15\ \mathrm{K})$ by both 2nd and 3rd law methods. The results of the calculations are as follows with reaction (A) corresponding to 2 AlBr$_3$(cr)=Al$_2$Br$_6$(g) and reaction (B) corresponding to 2 AlBr$_3$(l)=Al$_2$Br$_6$(g).

Source	Reaction	Method	Data Points	T/K	$\Delta_r H^\circ(298.15\ \mathrm{K})$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H^\circ(298.15\ \mathrm{K})$ kcal·mol^{-1}
[3]	A	Manometric	13	302–334	21.2 ± 0.2	20.54 ± 0.1	−2.2 ± 0.5	−223.86
[1]	A	Effusion	3	273–310	19.6 ± 0.7	20.26 ± 0.1	2.2 ± 2.4	−224.14
[2]	B	Mass Loss	18[a]	413–522	15.6 ± 0.0	15.62 ± 0.0	0.1 ± 0.1	−223.98
[2]	B	Transport	4	396–470	16.0 ± 0.1	15.61 ± 0.1	−0.9 ± 0.3	−223.99

[a] Point at 436.2 K rejected due to statistical test.

Heat Capacity and Entropy

Structural assignments for the dimer of aluminum tribromide are based on the electron diffraction data reported by Shen.[5] These values are in good agreement with earlier diffraction studies by Palmer and Elliott[6] and Akishin *et al.*[7] The principal moments of inertia are $I_A = 282.4212 \times 10^{-39}$, $I_B = 502.7859 \times 10^{-39}$ and $I_C = 624.3585 \times 10^{-39}\ \mathrm{g \cdot cm^2}$. Beattie *et.al.*[8] measured the condensed phase IR and Raman bands for aluminum tribromide while Beattie and Horder[9] measured the gas phase Raman spectra. Perov *et al.*[10] investigated the IR spectra of monomeric and dimeric aluminum tribromide in a xenon matrix at 20–30 K. It has been established that the condensed phases of AlBr$_3$ are dimeric,[11] [12] thus spectroscopic studies of the crystal and liquid pertain to the structure of Al$_2$Br$_6$(g) However, gas phase values are adopted in preference to condensed phase frequencies whenever possible. Five frequencies (ν_5, ν_6, ν_9, ν_{10}, ν_{15}) adjusted not only for consistency with the frequencies chosen for Al$_2$F$_6$(g) and Al$_2$Cl$_6$(g) but also for agreement between 2nd and 3rd law $\Delta_r H^\circ(298.15\ \mathrm{K})$ values in the second data set tabulated above.

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

T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K$_f$
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−38.309	−892.918	−892.918	INFINITE
100	122.051	386.605	686.066	−29.946	−893.902	−915.011	477.953
200	154.379	482.768	562.199	−15.886	−898.150	−934.593	244.091
250	162.423	518.147	549.952	−7.951	−900.889	−943.399	197.112
298.15	167.514	547.220	547.220	0.	−937.216	−947.368	165.975
300	167.672	548.257	547.223	0.310	−937.415	−947.430	164.962
350	171.215	574.387	549.279	8.788	−1029.359	−944.065	140.894
400	173.690	597.420	553.885	17.414	−1028.768	−931.920	121.696
450	175.474	617.986	559.886	26.145	−1028.167	−919.850	106.773
500	176.796	636.546	566.639	34.954	−1027.568	−907.847	94.842
600	178.581	668.951	581.068	52.730	−1026.422	−884.012	76.960
700	179.692	696.569	595.644	70.648	−1025.414	−860.359	64.201
800	180.428	720.615	609.795	88.656	−1024.625	−836.837	54.640
900	180.939	741.898	623.313	106.726	−1024.129	−813.397	47.208
1000	181.309	760.982	636.142	124.839	−1045.169	−788.473	41.186
1100	181.584	778.276	648.290	142.985	−1044.723	−762.825	36.224
1200	181.794	794.085	659.790	161.154	−1044.280	−737.217	32.090
1300	181.959	808.643	670.688	179.342	−1043.844	−711.647	28.594
1400	182.090	822.133	681.029	197.545	−1043.419	−686.109	25.599
1500	182.195	834.699	690.860	215.759	−1043.012	−660.601	23.004
1600	182.282	846.461	700.221	233.983	−1042.625	−635.120	20.735
1700	182.354	857.514	709.152	252.215	−1042.266	−609.662	18.733
1800	182.415	867.939	717.687	270.453	−1041.940	−584.225	16.954
1900	182.466	877.803	725.857	288.698	−1041.652	−558.804	15.363
2000	182.510	887.163	733.690	306.946	−1041.410	−533.397	13.931
2100	182.548	896.069	741.212	325.199	−1041.219	−508.001	12.636
2200	182.580	904.562	748.445	343.456	−1041.085	−482.613	11.459
2300	182.609	912.678	755.411	361.715	−1041.012	−457.230	10.384
2400	182.634	920.451	762.127	379.977	−1041.002	−431.848	9.399
2500	182.656	927.906	768.610	398.242	−1041.059	−406.466	8.493
2600	182.676	935 071	774.875	416.509	−1041.182	−381 081	7.656
2700	182.693	941.965	780.937	434.777	−1041.370	−355.688	6.881
2800	182.709	948.610	786.807	453.047	−1629.423	−328.353	6 126
2900	182.723	955.022	792.498	471.319	−1627.541	−281.919	5.078
3000	182.736	961.216	798.019	489.592	−1625.713	−235.551	4.101
3100	182.747	967.208	803.381	507.866	−1623.934	−189.241	3.189
3200	182.758	973.011	808.591	526.141	−1622.196	−142.989	2.334
3300	182.767	978.634	813.659	544.417	−1620.492	−96 789	1.532
3400	182.776	984.091	818.592	562.694	−1618.815	−50.642	0.778
3500	182.784	989.389	823.397	580.972	−1617.158	−4.544	0.068
3600	182.791	994.538	828.080	599.251	−1615.512	41.508	−0.602
3700	182.798	999.547	832.647	617.531	−1613.871	87.514	−1.235
3800	182.804	1004 422	837.103	635.811	−1612.226	133.475	−1.835
3900	182.810	1009.170	841.454	654.091	−1610.572	179.393	−2.403
4000	182.815	1013.799	845.705	672.373	−1608.903	225.268	−2.942
4100	182.820	1018.313	849.861	690.654	−1607.211	271.101	−3.454
4200	182 824	1022.718	853.924	708.936	−1605.494	316.893	−3.941
4300	182.829	1027.020	857.900	727.219	−1603.744	362.644	−4.405
4400	182.833	1031.224	861.791	745.502	−1601.961	408.353	−4.848
4500	182.836	1035.332	865.602	763.786	−1600.134	454.021	−5.270
4600	182.840	1039.351	869.336	782.069	−1598.271	499.649	−5 674
4700	182.843	1043.283	872.995	800.354	−1596.364	545.235	−6.060
4800	182 846	1047 133	876.583	818.638	−1594.414	590.781	−6.429
4900	182.849	1050.903	880.102	836.923	−1592.417	636.285	−6.783
5000	182.852	1054.597	883.555	855.208	−1590.376	681.748	−7.122
5100	182.854	1058.218	886.945	873 493	−1588.290	727 171	−7 448
5200	182.857	1061.769	890.273	891.779	−1586 161	772.550	−7.760
5300	182.859	1065.252	893.541	910.064	−1583.988	817.890	−8.061
5400	182.861	1068.670	896.753	928.350	−1581.774	863.188	−8.350
5500	182.863	1072.025	899.909	946.637	−1579.520	908.444	−8.628
5600	182.865	1075.320	903.012	964.923	−1577.229	953.659	−8.895
5700	182.867	1078.557	906.064	983.210	−1574.904	998.833	−9.153
5800	182.868	1081.737	909.065	1001.496	−1572.541	1043.964	−9.402
5900	182.870	1084.863	912.018	1019.783	−1570.153	1089.056	−9.642
6000	182.872	1087.937	914.925	1038.070	−1567.695	1134.103	−9.873

PREVIOUS: September 1979 (1 atm) CURRENT. September 1979 (1 bar)

Aluminum Bromide ((AlBr$_3$)$_2$) Al$_2$Br$_6$(g)

Aluminum Chloride (($AlCl_3$)$_2$) IDEAL GAS $M_r = 266.68108$ Aluminum Chloride (($AlCl_3$)$_2$) Al_2Cl_6(g)

$S°(298.15 \text{ K}) = 475.0 \pm 4.2 \text{ J·K}^{-1}\text{·mol}^{-1}$

$\Delta_f H°(0 \text{ K}) = -1293.02 \pm 3.35 \text{ kJ·mol}^{-1}$

$\Delta_f H°(298.15 \text{ K}) = -1295.74 \pm 3.35 \text{ kJ·mol}^{-1}$

Vibrational Frequencies (all singly degenerate), cm^{-1}

A_g	A_g	A_u	B_{1g}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	B_{3g}	B_{3u}	B_{3u}
501	217	[60]	289	[10]	625	610	420	[161]	484	144
336	99		166		175		116	135		320

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

Point Group: D_{2h}

Bond Distances: Al–Cl = 2.065 ± 0.002 Å; Al–Cl(bridge) = 2.252 ± 0.004 Å

Bond Angles Cl–Al–Cl=123.4 ± 1.6°; Cl(bridge)–Al–Cl(bridge) = 91.0 ± 0.5°

Product of the Moments of Inertia: $I_A I_B I_C = 5.687094 \times 10^{-111} \text{ g}^3\text{·cm}^6$

Enthalpy of Formation

The enthalpy of formation is calculated from the value for $AlCl_3$(cr) and the heat of sublimation as derived from vapor pressure data. Vapor pressures were 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 $T_c = 620$ K[1] and $P_c = 24.3$ atm were used to calculate B. P_c is an extrapolation of the data given by Denisova and Baskova.[2] The corrected vapor pressures were used to derive $\Delta_{sub}H°$(298.15 K) by both 2nd law and 3rd law methods. The first nine data sets show good agreement between 2nd and 3rd law values and an average of $\Delta_{sub}H°(298.15 \text{ K}) = 27.61 \pm 0.55 \text{ kcal·mol}^{-1}$ Al_2Cl_6 is adopted. The remaining data sets show serious discrepancies between 2nd and 3rd law values, indicating temperature dependent errors in measurement, and are given no weight.

Source	T/K	Data Points*	$\Delta_{sub}H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
Viola *et al.*[3]	389 9–466.3	44(4)	27.48 ± 0.0	27.62 ± 0.0	0.3 ± 0.1
Viola *et al.*[3]	467.7–510.0	67(4)	26.82 ± 0.0	27.65 ± 0.1	1.7 ± 0.1
Smits and Meijering [4] liq.	444.7–464.6	7(2)	27.44 ± 0.1	27.59 ± 0.0	0.3 ± 0.3
Smits and Meijering [4]	462.4–481.8	10	27.07 ± 0.1	27.61 ± 0.0	1.1 ± 0.2
Treadwell and Terebesi [5] liq.	388.7–461.7	11	28.31 ± 0.2	27.55 ± 0.1	−1.8 ± 0.3
Treadwell and Terebesi [5]	466.5–476.2	3	27.39 ± 0.1	27.60 ± 0.0	0.5 ± 0.2
Fischer *et al.* [6] liq.	392.8–428.3	9	27.65 ± 0.4	27.61 ± 0.1	−0.1 ± 1.1
Fischer *et al.* [6]	403.8–450.4	12(2)	27.70 ± 0.1	27.60 ± 0.0	−0.2 ± 0.3
Nisel'son *et al.* [7] liq.	471.2–506.5	18(1)	27.28 ± 0.1	27.64 ± 0.0	0.7 ± 0.1
Friedel and Crafts [8]	441.0–455.9	5	29.80 ± 1.6	27.80 ± 0.1	−4.5 ± 3.5
Friedel and Crafts [8] liq.	477.4–486.2	3	29.92 ± 1.4	27.76 ± 0.0	−4.5 ± 3.0
Maier [9]	392.8–454.4	v 8(1)	25.87 ± 0.7	27.38 ± 0.2	3.5 ± 1.7
Dunne and Gregory [10]	294.2–322.2	2	29.97 ± 0.0	27.79 ± 0.3	−7.1 ± 0.0
Denisova and Baskova [2] liq.	467.8–511.6	8	26.31 ± 0.2	27.56 ± 0.1	2.5 ± 0.3

*First number indicates number of data points used in calculation; number in parentheses indicates number of data points rejected.

Heat Capacity and Entropy

Structural assignments for the dimer of aluminum trichloride are based on the electron diffraction data reported by Shen.[11] These values are in good agreement with earlier electron diffraction studies by Palmer and Elliott[12] and Akishin *et al.*[13] and a theoretical investigation by Curtiss.[14] The principal moments of inertia are: $I_A = 108.2257 \times 10^{-39}$ $I_B = 206.7252 \times 10^{-39}$ and $I_C = 254.1948 \times 10^{-39}$ g cm^2. Klemperer[15] observed three frequencies in the infrared spectrum of Al_2Cl_6 vapor, Beattie and Horder[16] and Maroni *et al.*[17] reported gas phase Raman spectra, and Gerding and Smit[18] and Pershina and Raskin[19] measured liquid phase Raman frequencies. These earlier vibrational assignments were supplemented by matrix isolated/IR and Raman studies reported by Beattie et al[20] and Perov *et al.*[21] and the detailed vibrational analysis given by Tranquille and Fouassier.[22] Normal coordinate calculations have been reported by several investigators[23,24,17,25] but their basis on incomplete data makes many assignments doubtful. The new vibrational assignment incorporates the additional frequencies observed by Tranquille and Fouassier and differs with earlier calculations primarily in reassignment of the frequencies at 289 cm^{-1} and 161 cm^{-1}. The estimated fundamentals are based on comparisons with Al_2F_6, Al_2Br_6, and Al_2I_6 and are adjusted such that the entropy is consistent for the 2nd and 3rd law calculations above.

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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	−33.898	−1293.019	−1293.019	INFINITE
100	101.982	330.759	602.707	−27.195	−1296.020	−1270.996	663.900
200	140.807	415.028	489.094	−14.813	−1296.355	−1245.724	325.350
250	151.631	447.687	477.628	−7.485	−1296.111	−1233.091	257.640
298.15	158.858	475.050	475.050	0.	−1295.743	−1220.985	213.912
300	159.089	476.033	475.053	0.294	−1295.727	−1220.522	212.512
350	164.322	500.973	477.011	8.387	−1295.260	−1208.023	180.288
400	168.079	523.174	481.419	16.702	−1294.746	−1195.596	156.129
450	170.844	543.138	487.186	25.178	−1294.204	−1183.234	137.346
500	172.925	561.251	493.701	33.775	−1293.652	−1170.934	122.327
600	175.775	593.052	507.683	51.221	−1292.573	−1146.493	99.811
700	177.576	620.293	521.871	68.895	−1291.609	−1122.224	83 741
800	178.779	644.089	535.692	86.717	−1290.848	−1098.082	71 697
900	179.621	665.197	548.931	104.639	−1290.369	−1074.018	62.334
1000	180.232	684.155	561.522	122.633	−1311 416	−1048.469	54 766
1100	180.688	701.356	573.464	140.680	−1310.969	−1022.196	48.540
1200	181.038	717.093	584.787	158.768	−1310.518	−995.964	43.353
1300	181.312	731.595	595.529	176.886	−1310.067	−969.770	38.966
1400	181.530	745 040	605 734	195.028	−1309.620	−943.610	35.207
1500	181.707	757.571	615.444	213.190	−1309.181	−917.482	31.950
1600	181.852	769.302	624.697	231.368	−1308.752	−891.382	29.101
1700	181.972	780.331	633.531	249.560	−1308.336	−865.310	26.588
1800	182.074	790.735	641.978	267.762	−1307.937	−839.261	24.355
1900	182.159	800.582	650 069	285.974	−1307.557	−813.234	22.357
2000	182.233	809.927	657.830	304.194	−1307.200	−787.226	20.560
2100	182.296	818.820	665.286	322.420	−1306.869	−761.236	18.935
2200	182.351	827.302	672.459	340.653	−1306.569	−735.260	17.457
2300	182.399	835.408	679.369	358.890	−1306.304	−709.298	16.109
2400	182.441	843.172	686.034	377.132	−1306.078	−683.346	14.873
2500	182.478	850.621	692.469	395.378	−1305.897	−657.403	13.736
2600	182.511	857.778	698.691	413.628	−1305.763	−631.466	12.686
2700	182.541	864.667	704.711	431.880	−1305.681	−605.533	11.715
2800	182.567	871.306	710.543	450.136	−1893.454	−577.667	10 777
2900	182.591	877.713	716.198	468.393	−1891.290	−530.713	9.559
3000	182.612	883.903	721.685	486.654	−1889.183	−483.832	8 424
3100	182.631	889.891	727.015	504.916	−1887.132	−437.021	7 364
3200	182.649	895 690	732.196	523.180	−1885.136	−390.276	6.371
3300	182.665	901.311	737.236	541.445	−1883.193	−343.591	5.439
3400	182.679	906.764	742.142	559.713	−1881.300	−296.965	4.562
3500	182.693	912.059	746.922	577.981	−1879.451	−250.394	3.737
3600	182.705	917.206	751.581	596.251	−1877.644	−203.875	2.958
3700	182.716	922.212	756.125	614.522	−1875.870	−157 406	2.222
3800	182 727	927.085	760.560	632.794	−1874.126	−110.985	1.526
3900	182 736	931.832	764.891	651.068	−1872.403	−64 609	0.865
4000	182.745	936.458	769.123	669.342	−1870.696	−18.277	0.239
4100	182.753	940.971	773.260	687.617	−1868.996	28.013	−0.357
4200	182.761	945.375	777.305	705.892	−1867.299	74.261	−0.924
4300	182.768	949.675	781.264	724.169	−1865.595	120.468	−1.463
4400	182.775	953.877	785.140	742.446	−1863.880	166.636	−1.978
4500	182.781	957.985	788.935	760.724	−1862.143	212.764	−2.470
4600	182.787	962.002	792.654	779.002	−1860.385	258.854	−2.939
4700	182.792	965.933	796.299	797.281	−1858.597	304.905	−3.389
4800	182.798	969.782	799.873	815.561	−1856.776	350.918	−3.819
4900	182.802	973.551	803.379	833.841	−1854.914	396.893	−4.231
5000	182.807	977.244	806.820	852.121	−1853.011	442.828	−4.626
5100	182.811	980.864	810.197	870.402	−1851.063	488.726	−5.006
5200	182.815	984.414	813.513	888.683	−1849.067	534.584	−5.370
5300	182.819	987.896	816.771	906.965	−1847.020	580.404	−5.720
5400	182.823	991.314	819.972	925.247	−1844.922	626.185	−6.057
5500	182.826	994.668	823.118	943.530	−1842.771	671.927	−6.381
5600	182.829	997.963	826.211	961.812	−1840.567	717.629	−6.694
5700	182.832	1001.199	829.252	980.095	−1838.311	763.291	−6.995
5800	182.835	1004.379	832.244	998.379	−1835.995	808.913	−7.285
5900	182.838	1007.504	835.188	1016.662	−1833.633	854.494	−7.565
6000	182.841	1010.577	838.086	1034.946	−1831.175	900.030	−7.835

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

Potassium Aluminum Chloride ($K_3Al_2Cl_9$) CRYSTAL $M_r = 490.33498$

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K)$ = [468.608] J·K^{-1}·mol^{-1} $\Delta_f H°(298.15\ K) = -2860 \pm 12$ kJ·mol^{-1}

T_{fus} = Unknown

Enthalpy of Formation

$\Delta_f H°(K_3Al_2Cl_9$, cr, 298.15 K) is calculated from the heat of solution, $\Delta_r H° = -112.07$ kcal·mol^{-1}, of $K_3Al_2Cl_9$(cr) in water (one mole of solute in 36 l. of water), as determined by Baud.[1]

Heat Capacity and Entropy

Heat capacities are estimated based on the assumption that the property of the mixed chloride ($2AlCl_3 + 3KCl$) is the sum of the corresponding values for its component chlorides, i.e. AlCl(cr) and KCl(cr). In a similar manner, $S°(298.15\ K)$ is estimated to be 112 cal·K^{-1}·mol^{-1}.

Reference

[1] E. Baud, Ann. chim. Phys. **1**, 8 (1904).

Potassium Aluminum Chloride ($K_3Al_2Cl_9$) $Al_2Cl_9K_3$(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							
250							
298.15	337.230	468.608	468.608	0.	−2860.182	−2625.893	460.046
300	337.858	470 696	468.614	0 624	−2860.094	−2624.440	456.956
400	353.130	570.010	482.052	35.183	−2862.602	−2545.238	332.374
500	367.272	650.359	507.925	71.217	−2857.227	−2466.497	257.673
600	379.740	718.443	537 478	108.579	−2850.799	−2388.938	207.976
700	390.807	777.827	567.660	147.116	−2843.468	−2312.529	172.563
800	400.660	830.668	597.294	186.700	−2835.425	−2237.222	146.076
900	407.940	878.265	625.912	227 117	−2826.979	−2162.952	125.534
1000	416.726	921.687	653.349	268.338	−2839.443	−2088.115	109.072
1100	427.019	961.876	679.592	310.513	−3066.550	−1999.618	94.954
1200	438 818	999.527	704.700	353.792	−3052.785	−1903.224	82.845
1300	452.123	1035.166	728.761	398.327	−3037.812	−1808.025	72.647
1400	466.934	1069.205	751.871	444.267	−3021.478	−1714.029	63.951
1500	483.252	1101 968	774.125	491 764	−3003.629	−1621.254	56.457

PREVIOUS: June 1962 CURRENT: September 1964

Potassium Aluminum Chloride ($K_3Al_2Cl_9$) $Al_2Cl_9K_3$(cr)

Aluminum Fluoride ((AlF$_3$)$_2$) IDEAL GAS M_r = 167.953498 Aluminum Fluoride ((AlF$_3$)$_2$) Al$_2$F$_6$(g)

$\Delta_f H°(0\ K) = -2624.08 \pm 16\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 387.3 \pm 12\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -2633.62 \pm 16\ kJ \cdot mol^{-1}$

Vibrational Frequencies, ν, cm^{-1}(all single degenerate)					
[830]	[200]	[210]	[30]	600	805
[600]	[90]	980	[970]	[230]	575
[370]	[630]	340	[260]	[310]	300

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

Point Group: [D$_{2h}$]

Bond Distances: Al–F = [1.63] Å; Al–F(bridge) = [1.80] Å

Bond Angles: F–Al–F = [120°]; F(bridge)–Al–F(bridge) = [90]°

Product of the Moments of Inertia: $I_A I_B I_C = [2.669982 \times 10^{-112}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The existence of small amounts of dimer in the saturated vapor was inferred from the intensities of AlF_2^+, AlF_3^+ and $Al_2F_5^+$ observed by mass spectrometry.[1 2,3] Buchler *et al.*[1] concluded that the precursor of the first two ions was mainly AlF$_3$, while the dimer was the precursor of $Al_2F_5^+$. Intensities of $Al_2F_5^+$ relative to those of AlF_2^+ were observed as 0 0057,[1] 0.007[2] and 0.025[3] at ionizing energies of 60, 90 and 100 V for vapor at 1025, 1100 and 1025 K, respectively.

The temperature dependence of ion intensities was used to derive 2nd law values of $\Delta_{sub}H°$ for monomer and dimer[1 2] and a value of $\Delta_{dim}H°$ based on an estimate for the $\Delta_{dim}S°$.[3] The absolute pressure of the monomer was obtained[2] from the relative ion intensity assuming a relative ionization cross section equal to two and neglecting other effects. Krause and Douglas[4] reported values for $\Delta_{sub}H°$(monomer), $\Delta_{dim}H°$, and $\Delta_{dim}S°$, these were derived by combination of $\Delta_{sub}H°$(dimer)[1] with precise sublimation pressures from entrainment data near 1200 K, where the dimer is more abundant. After reduction to 1000 K with JANAF functions, these results may be summarized as follows:

Source	Method	$\Delta_r H°$, kcal·mol^{-1*}			$\Delta_r S°$, cal·K^{-1}·mol^{-1*}		
		c → m	2c → d	2m → d	c → m	2c → d	2m → d
[4]	Entrainment	68.1 ± 0.4	[86]	−50 ± 3	[44.04]	—	−35 ± 3
[1]	Ion Intensities	67.3 ± 3	85.8 ± 3	−4.8 ± 3	—	—	—
[2]	Ion Intensities	70.5	92.1	−49.0	46.4	55.1	−37.7
[3]	Ion Intensities	—	—	−48.0 ± 4	—	—	[−32 ± 3]
JANAF	Adopted	68.4	87.8	[−49]	[44.37]	[52.83]	[−35.9]

*Reactions are abbreviated by c = crystal, d = dimer gas and m = monomer gas. Brackets enclose those values assumed in deriving the other values.

JANAF values are given in the last line. These are based on JANAF entropies, on $\Delta_{dim}H° = -49\ kcal\ mol^{-1}$ for which there is close agreement, and on the entrainment pressures of Krause and Douglas.[4] Reduction of the dimer value to 298.15 K gives $\Delta_{sub}H° = 92.55 \pm 4$ and $\Delta_f H° = -629.45 \pm 4\ kcal \cdot mol^{-1}$. The table for AlF$_3$(g) gives a detailed comparison of observed and predicted total pressure along with predictions of the mole fraction of dimer in the saturated vapor. The latter are reasonably consistent with the relative ion intensities.

Heat Capacity and Entropy

The molecular structure is assumed to be similar to that of Al$_2$Cl$_6$. Bond distances and bond angles are estimated by comparison with AlF$_3$,[5] AlCl$_3$[5] and Al$_2$Cl$_6$.[5] The principal moments of inertia are $I_A = 35.3676 \times 10^{-39}$, $I_B = 79\ 7440 \times 10^{-39}$, $I_C = 94.6684 \times 10^{-39}\ g \cdot cm^2$.

Six observed vibrational frequencies are from infrared spectra of the dimer isolated in rare–gas matrices.[6] Unobserved fundamentals (2 in infrared, 9 in Raman and 1 inactive) are estimated such that the entropy is consistent with the result of Krause and Douglas[4] as given above. The estimated fundamentals are based on comparisons with Al$_2$Cl$_6$, Al$_2$Br$_6$ and Al$_2$I$_6$. Assignments used in the comparisons are minor modifications of those given by Beattie *et al.*[7]

References

[1] A.Buchler, E. P Marram and J. L. Stauffer, J. Phys. Chem. **71**, 4139 (1967).

[2] E. V. Erokhin, N. A. Zhegul'skaya, L. N. Sidorov and P. A. Akishin, Izv. Akad. Nauk SSSR, Neorg. Mater. 3 (5), 873 (1967).

[3] R. F. Porter and E. E. Zeller, J. Chem. Phys. **33**, 858 (1960).

[4] R. F. Krause and T. B. Douglas, J. Phys. Chem. **72**, 475 (1968).

[5] JANAF Thermochemical Tables: AlF$_3$(g), AlCl$_3$(g), Al$_2$Cl$_6$(g), Al$_2$Br$_6$(g), and Al$_2$I$_6$(g), 9–30–79.

[6] A. Snelson, J. Phys. Chem. **71**, 3202 (1967).

[7] I. R. Bettie and J. R. Horder, J. Chem. Soc. **A1969**, 2655; I. R. Beattie, T. Gilson and G. A. Ozin, ibid., **A1968**, 813.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K$_f$
0	0.	0.	INFINITE	−26.015	−2624.080	−2624.080	INFINITE
100	70.831	277.577	487.750	−21.017	−2628.771	−2604.020	1360.201
200	108.448	339.120	398 728	−11.922	−2632.066	−2577.841	673.263
250	122.124	364.842	389.423	−6.145	−2633.025	−2564.166	535.753
298.15	132.744	387.294	387.294	0.	−2633.619	−2550.845	446.897
300	133.107	388.117	387.297	0.246	−2633.636	−2550.331	444.052
350	141.826	409.316	388.951	7.128	−2633.991	−2536.416	378.539
400	148.717	428.722	392.727	14.398	−2634.158	−2522.464	329.400
450	154 175	446.566	397.731	21.976	−2634.188	−2508.499	291.179
500	158.525	463.044	403.449	29.797	−2634.122	−2494.536	260.602
600	164.854	492.546	415.899	45.988	−2633.822	−2466.645	214.741
700	169.093	518.297	428.727	62.699	−2633.461	−2438.810	181.986
800	172.039	541.080	441.375	79.764	−2633.186	−2411.024	157.424
900	174.155	561.472	453.606	97.079	−2633.115	−2383.260	138.321
1000	175.720	579.906	465.329	114.577	−2654.519	−2353.970	122.959
1100	176.906	596.712	476.521	132.211	−2654.394	−2323.921	110.354
1200	177.826	612.146	487.188	149.949	−2654.244	−2293.884	99.850
1300	178.551	626.410	497.356	167.770	−2654.082	−2263.861	90.963
1400	179.134	639.664	507.053	185.655	−2653.918	−2233.850	83.346
1500	179.608	652.039	516.311	203.593	−2653.762	−2203.851	76.745
1600	179.999	663.644	525.160	221.574	−2653.618	−2173.861	70.969
1700	180.325	674.566	533.631	239.590	−2653.487	−2143.880	65.873
1800	180.600	684.881	541.750	257.637	−2653.370	−2113.907	61.344
1900	180.833	694.652	549.542	275.709	−2653.264	−2083.940	57.292
2000	181.033	703.933	557.032	293.802	−2653.164	−2053.978	53.644
2100	181.206	712.770	564.239	311.915	−2653.063	−2024.022	50.345
2200	181.356	721.203	571.184	330.043	−2652.953	−1994.070	47.345
2300	181.487	729.268	577.883	348.185	−2652.826	−1964.123	44 607
2400	181.602	736.994	584.353	366.340	−2652.671	−1934.183	42.096
2500	181.704	744.410	590.608	384.505	−2652.480	−1904.249	39.787
2600	181.795	751.538	596.661	402.680	−2652.242	−1874.325	37.656
2700	181.876	758.401	602.525	420.864	−2651.947	−1844.410	35.682
2800	181.948	765.016	608.211	439.055	−3239.391	−1812.572	33.814
2900	182.013	771.402	613.729	457.253	−3236.769	−1761.660	31.731
3000	182.072	777.574	619.088	475.458	−3234.068	−1710.841	29.788
3100	182.126	783.545	624.297	493.668	−3231.281	−1660.112	27.973
3200	182.174	789.328	629.365	511.883	−3228.404	−1609.475	26.272
3300	182.218	794.934	634.297	530.102	−3225.433	−1558.929	24.676
3400	182.258	800.375	639.102	548.326	−3222.365	−1508.475	23.175
3500	182.295	805.659	643.786	566.554	−3219.196	−1458.112	21.761
3600	182.329	810.794	648.354	584.785	−3215.926	−1407.841	20.427
3700	182.360	815.791	652.812	603.019	−3212.553	−1357.663	19.167
3800	182.389	820.654	657.165	621.257	−3209.078	−1307.578	17.974
3900	182.416	825.392	661.418	639.497	−3205.501	−1257.584	16.843
4000	182.440	830.011	665.576	657.740	−3201.824	−1207.683	15 771
4100	182.463	834.516	669.642	675.985	−3198.047	−1157.877	14 752
4200	182.485	838.913	673.620	694.233	−3194.173	−1108.163	13.782
4300	182.504	843.207	677.514	712.482	−3190.204	−1058.544	12.859
4400	182.523	847.403	681.327	730.733	−3186.143	−1009.017	11.979
4500	182.540	851.505	685.064	748.987	−3181.989	−959.583	11.139
4600	182.556	855.518	688.726	767.241	−3177.752	−910.243	10.336
4700	182.571	859.444	692.317	785.498	−3173.433	−860.996	9.569
4800	182.586	863.288	695.839	803 756	−3169.036	−811.841	8.835
4900	182.599	867.053	699.294	822.015	−3164.562	−762.779	8.131
5000	182.612	870.742	702.687	840.275	−3160.019	−713.809	7.457
5100	182.623	874.358	706.017	858.537	−3155.409	−664.931	6 810
5200	182.635	877.904	709.289	876.800	−3150.737	−616.143	6.189
5300	182.645	881.383	712.503	895.064	−3146.007	−567.446	5.593
5400	182.655	884.797	715.662	913.329	−3141.224	−518.839	5.019
5500	182.664	888.149	718.768	931.595	−3136.392	−470.321	4.467
5600	182.673	891.440	721.822	949.862	−3131.515	−421 890	3.935
5700	182.682	894.674	724.826	968.130	−3126.599	−373.549	3.423
5800	182.690	897.851	727.782	986.398	−3121.640	−325.294	2.930
5900	182.697	900.974	730.691	1004.668	−3116.657	−277.122	2.453
6000	182 705	904.045	733.555	1022.938	−3111.601	−229.042	1.994

PREVIOUS September 1979 (1 atm) CURRENT. September 1979 (1 bar)

Aluminum Iodide ($(AlI_3)_2$) **IDEAL GAS** **M_r = 815.39008** **Aluminum Iodide ($(AlI_3)_2$)** **$Al_2I_6(g)$**

$S°(298.15\ K) = [597.38 \pm 1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -481.80 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -489.53 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies					
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
339 (1)	42 (1)	54 (1)	[7](1)	296 (1)	316 (1)
145 (1)	[20](1)	416 (1)	408 (1)	65 (1)	141 (1)
93 (1)	[220](1)	[100](1)	82 (1)	[50] (1)	75 (1)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: D_{2h}
Bond Distances. Al–I = 2.449 ± 0.013 Å; Al–I (bridge) = 2.634 ± 0.03 Å
Bond Angles: I–Al–I = 115.0 ± 7.4°; I (bridge)–Al–I (bridge) = 99.6 ± 4.5°
Product of the Moments of Inertia: $I_A I_B I_C = 5.884591 \times 10^{-109}\ g^3\ cm^6$.

Enthalpy of Formation

The vapor pressure over $AlBr_3(l)$ has been measured by Fischer, Rahlfs and Benze.[1] The vapor consists of both $Al_2I_6(g)$ and $AlI_3(g)$. Equilibrium constants for the reaction $Al_2I_6(g) = 2\ AlI_3(g)$ have also been determined by Fischer *et al.*[1] in the temperature range 614–843 K. From this data equilibrium constants at other temperatures were estimated and the partial pressures of $Al_2I_6(g)$ over $AlI_3(l)$ were calculated from the total pressure using these estimated values. The heats of reaction are calculated from the vaporization data using 2nd and 3rd law methods. The results of the calculations are as follows, where the $\Delta_f H°(298.15\ K)$ value is based on the 3rd law value of $\Delta_r H°(298.15\ K)$ and $\Delta_f H°(AlI_3,\ l,\ 298.15\ K) = -69.2\ kcal \cdot mol^{-1}$.

Method	T/K	Data Points	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Mass Loss	513.15–645.35	19[a]	21.50 ± 0.1	21.34 ± 0.0	−0.3 ± 0.1	−117.06
Transport	513.95–578.15	7[b]	20.80 ± 0.1	21.51 ± 0.1	1.3 ± 0.3	−116.89

[a] One point at 493.95 rejected due to statistical test.
[b] One point at 482.95 rejected due to statistical test.

The adopted enthalpy of formation is $\Delta_f H°(Al_2I_6,\ g,\ 298.15\ K) = -117.0 \pm 2.0\ kcal \cdot mol^{-1}$ ($-489.528 \pm 8.4\ kJ \cdot mol^{-1}$)

Heat Capacity and Entropy

The molecular structure, bond distances and angles were obtained from the electron diffraction work of Shen.[2] These values are in good agreement with the earlier electron diffraction work by Akishin, Rambidi and Zasorin[3] and Palmer and Elliot.[4] The principal moments of inertia are $I_A = 530.1962 \times 10^{-39}$, $I_B = 963.2338 \times 10^{-39}$, and $I_C = 1152.2532 \times 10^{-39}\ g \cdot cm^2$. Beattie, Gilson and Ozin[5] measured the condensed phase IR and Raman bonds for Al_2I_6 and Beattie and Horder[6] measured the gas phase Raman spectra. Five frequencies (ν_5, ν_6, ν_9, ν_{10}, ν_{15}) were adjusted not only for consistency with the frequencies chosen for $Al_2F_6(g)$, $Al_2Cl_6(g)$ and $Al_2Br_6(g)$,[7] but also for agreement between 2nd and 3rd law $\Delta_r H°(298\ 15\ K)$ values in the data sets tabulated above.

References

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[5] I. R. Beattie, T. Gilson and G. A Ozin, J. Chem. Soc. (London) A1968, 813.
[6] I. R Beattie and J. R. Horder, J. Chem. Soc. (London)A 1969, 2655.
[7] JANAF Thermochemical Tables. $Al_2F_6(g)$, $Al_2Cl_6(g)$ and $Al_2Br_6(g)$, 9–30–79.

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	−40.941	−481.796	−481.796	INFINITE
100	133.463	427.756	742.263	−31.451	−482.424	−505.504	264.048
200	161 741	530.588	612.847	−16.452	−485.826	−527.310	137.719
250	168.093	567.419	600.192	−8.193	−487.677	−537.470	112.298
298.15	171.953	597.380	597.380	0.	−489.528	−546.893	95.813
300	172.071	598.444	597.384	0.318	−489.602	−547.249	95.285
350	174.684	625.179	599.489	8.991	−491.834	−556.688	83.081
400	176.475	648.629	604.196	17.773	−542.078	−564.151	73.671
450	177.749	669.492	610.313	26.630	−547.927	−566.559	65.764
500	178.685	688.270	617.186	35.542	−674.164	−556.918	58.181
600	179.935	720.969	631.838	53.479	−672.960	−533.585	46.453
700	180.707	748.768	646.606	71.514	−671.923	−510.440	38.090
800	181.215	772.934	660.920	89.611	−671.124	−487.429	31.826
900	181.567	794.299	674.575	107.751	−670.637	−464.500	26.959
1000	181.820	813.443	687.522	125.921	−691.704	−440.085	22.988
1100	182.009	830.782	699.769	144.113	−691.308	−414.943	19.704
1200	182.153	846.625	711.357	162.322	−690.948	−389.835	16.969
1300	182.265	861.210	722.330	180.543	−690.644	−364.755	14.656
1400	182.354	874.720	732.739	198.774	−690.424	−339.696	12.674
1500	182.426	887.304	742.628	217.013	−690.317	−314.648	10.957
1600	182.485	899.079	752.043	235.259	−690.353	−289.603	9.455
1700	182.534	910.144	761.021	253.510	−690.559	−264.551	8.129
1800	182.576	920.579	769.598	271.765	−690.957	−239.481	6.950
1900	182.611	930.451	777.806	290.025	−691.558	−214.384	5.894
2000	182.640	939.818	785.675	308.287	−692.367	−189.249	4.943
2100	182.666	948 730	793.229	326.553	−693.376	−164.069	4.081
2200	182.688	957.228	800.492	344.820	−694.570	−138.838	3.296
2300	182.708	965.349	807.484	363.090	−695.926	−113.547	2.579
2400	182.725	973.126	814.225	381.362	−697.414	−88.195	1.920
2500	182.740	980.585	820.731	399.635	−699.003	−62.778	1.312
2600	182.753	987 753	827.018	417.910	−700.658	−37.296	0.749
2700	182.765	994.650	833.100	436.186	−702.342	−11.750	0.227
2800	182.776	1001.297	838.989	454.463	−1291.825	15.793	−0.295
2900	182.785	1007.711	844.697	472.741	−1291.280	62.484	−1.125
3000	182.794	1013.908	850.235	491.020	−1290.670	109.156	−1.901
3100	182.802	1019.902	855.612	509.299	−1289.971	155.805	−2.625
3200	182.809	1025.706	860.837	527.580	−1289.160	202.430	−3.304
3300	182.815	1031.331	865.919	545.861	−1288.219	249.028	−3.942
3400	182.821	1036.789	870.864	564.143	−1287.134	295.596	−4.541
3500	182.826	1042.088	875.681	582.425	−1285.893	342.129	−5.106
3600	182.831	1047.239	880.375	600.708	−1284.488	388.624	−5.639
3700	182.836	1052.248	884.953	618.992	−1282.913	435.079	−6.142
3800	182.840	1057.124	889.420	637.276	−1281.164	481.488	−6.619
3900	182.844	1061.874	893.781	655.560	−1279.241	527.849	−7 070
4000	182.848	1066.503	898.042	673.844	−1277.143	574.158	−7.498
4100	182.851	1071.018	902.206	692.129	−1274.873	620.412	−7.904
4200	182.854	1075 424	906.278	710.415	−1272.432	666 610	−8.291
4300	182.857	1079.727	910.262	728.700	−1269.826	712 747	−8.658
4400	182.860	1083.931	914.161	746.986	−1267.060	758.822	−9.008
4500	182.862	1088.040	917.980	765.272	−1264.133	804.831	−9.342
4600	182.865	1092.059	921.720	783.558	−1261.060	850 774	−9.661
4700	182.867	1095.992	925.387	801.845	−1257.844	896.650	−9 965
4800	182.869	1099.842	928.981	820.132	−1254.491	942.456	−10.256
4900	182.871	1103.613	932.507	838.419	−1251.006	988.189	−10.534
5000	182 873	1107.307	935 966	856.706	−1247.399	1033.850	−10.801
5100	182.874	1110.928	939.361	874.993	−1243.676	1079.439	−11.056
5200	182.876	1114.480	942.695	893.281	−1239.844	1124.953	−11.300
5300	182.878	1117.963	945.969	911.568	−1235.909	1170.391	−11.535
5400	182.879	1121.381	949.186	929.856	−1231.879	1215.756	−11.760
5500	182.880	1124 737	952.347	948.144	−1227.760	1261.045	−11.976
5600	182.882	1128.032	955.455	966.432	−1223.560	1306.259	−12.184
5700	182.883	1131.269	958.511	984.721	−1219.284	1351.396	−12.384
5800	182.884	1134.450	961.517	1003.009	−1214.935	1396.457	−12.576
5900	182.885	1137.576	964.475	1021.297	−1210.528	1441.443	−12.762
6000	182.886	1140.650	967.386	1039.586	−1206.021	1486.350	−12.940

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

Magnesium Aluminum Oxide ($MgAl_2O_4$) CRYSTAL $M_r = 142.26568$ Magnesium Aluminum Oxide ($MgAl_2O_4$) $Al_2Mg_1O_4(cr)$

$S°(298.15\ K) = 88.7 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2048 \pm 20\ K$

$\Delta_f H°(0\ K) = -2283.07 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2299.11 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [192.464 \pm 21]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

From differences in heats of solution of MgO(cr), Al_2O_3(cr, α) and $MgAl_2O_4$(cr) in a melt of $2PbOB_2O_3$ at 970 K, Charlu *et al.*,[1] derived $\Delta_r H°(970\ K) = -5.38 \pm 0.18\ kcal \cdot mol^{-1}$ for $Al_2O_3(cr, \alpha) + MgO(cr) \rightarrow MgAl_2O_4(cr)$. When combined with auxiliary JANAF data,[2] this yields our adopted heat of formation. This value is within 3 $kcal \cdot mol^{-1}$ of earlier values determined via a similar method.[3 4] The direct measurement for formation from the elements, $\Delta_f H°(298.15\ K) = -567\ 1 \pm 0.3\ kcal \cdot mol^{-1}$, by Zaionchkovskii and Rubalskaya[5] appears to be widely discordant with other values.

Our 2nd and 3rd law analysis of all the equilibrium data is given below. Heats of formation based on the 3rd law analysis support the adopted heat of formation even though agreement between 2nd and 3rd law values is only fair The two studies by Grojtheim *et al.* involving reaction 1 require significant activity corrections since the Al(l) is not pure as indicated but is alloyed with Mg[6] or Si.[8] Activities were obtained assuming the AlMg(l) solution is ideal as stated by the authors[6] and supported independently.[13] Activities used to correct the other study[8] are given by the authors in their paper.

Source	Reaction	T/K	Data Points	$\Delta_r H°$(298.15 $kcal \cdot mol^{-1}$) 2nd law	3rd law	Drift $J \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°$(298.15 K) $kcal \cdot mol^{-1}$
Grjotheim *et al.*[6]	1	1143–1414	9	140.2 ± 1.7	126.0 ± 2.3	−10.8 ± 1.3	−549.5 ± 2.4
Grjotheim *et al.*[7]	2	1324–1452	7	307.8 ± 6.6	306.6 ± 1.0	−0.8 ± 4.8	−553.1 ± 1.1
Grjotheim *et al.*[8]	1	1216–1423	7	133.5 ± 0.7	127.0 ± 0.8	−5.0 ± 0.5	−548.5 ± 1.0
Rao and Dadape[9]	3	1025–1192	7	25.9 ± 3.4	25.3 ± 0.7	−0.5 ± 2.5	−552.6 ± 4.6
Taylor and Schmalzreid[10]	4	803	1	—	−0.4	—	−544.6
Rein and Chipman[11]	4	1873	1	—	−2.2	—	−546.4
Rosen and Muan[12]	4	1673	1	—	−4.0	—	−548.2

Reactions:

(1) $4\ MgO(cr) + 2\ Al(l) \rightarrow MgAl_2O_4(cr) + 3\ Mg(g)$
(2) $8\ MgO(cr) + Al_4C_3(cr) \rightarrow 2\ MgAl_2O_4(cr) + 3\ C(ref) + 6\ Mg(g)$
(3) $4\ MgO(cr) + 3\ AlCl(g) \rightarrow MgAl_2O_4(cr) + AlCl_3(g) + 3\ Mg(g)$
(4) $MgO(cr) + Al_2O_3(cr, \alpha) \rightarrow MgAl_2O_4(cr)$

Heat Capacity and Entropy

The adopted low temperature $C_p°$ to 300 K is taken from the analysis of Douglas and Beckett[14] and based on the measurements of King[15] (54–296 K). The high temperature heat capacities are calculated from the equation given by Landa and Naumova[16] based on their enthalpy measurements (1500–2200 K) as well as those of Bonnickson[17] (421–1805 K) Enthalpies in the overlapping regions of these two studies agree within ±1%.

Integration of the low temperature heat capacity data leads to $S°(50\ K) = 0.299\ cal \cdot K^{-1} \cdot mol^{-1}$ and $S°(298.15\ K) = 19.268\ cal \cdot K^{-1} \cdot mol^{-1}$.[14] We assume that $S°(0\ K) = 1.93\ cal \cdot K^{-1} \cdot mol^{-1}$ to correct for the ~0.15 mole fraction of inverted cations present in synthetic samples of $MgAl_2O_4$; the method of calculation is given by Navrostsky and Kleppa.[18] This configurational entropy term cannot be determined from integration of the $C_p°$ data since the disorder remains at zero Kelvin.

Fusion Data

Refer to the liquid table for details.

Phase Data

This table refers to $MgAl_2O_4$ (spinel) with 15% inversion. Navrotsky and Kleppa[18] have discussed the thermodynamics of spinels in detail and the 15% inversion is typical of most synthetic spinels or of natural spinel after heating above ~1300 K. Natural spinel which has been annealed through geologic time may have the completely normal (ordered) structure. If so its entropy will be $1.93\ cal \cdot K^{-1} \cdot mol^{-1}$ less than in this table and its heat of formation will be ~0.9 $kcal \cdot mol^{-1}$ more exothermic than given here based on annealing–heat of solution experiments on natural spinel.[18] These measurements found the order–disorder transition to occur in the range 973–1300 K. There have been recent reports of second–order phase transitions in the 723–873 K range detected by X–ray[19] and thermal expansion studies[20] but these are not obvious in the enthalpy data given above.

References

[1] V. Charlu, R. C. Newton and O. J. Kleppa, Geochim Cosmochim. Acta 39, 1487 (1975).
[2] JANAF Thermochemical Tables· Al_2O_3(cr, α), 12–31–79; MgO(cr), 12–31–74; Al(l), 6–30–79; Mg(g), 9–30–72; Al_4C_3(cr), 9–30–65; C(ref. st.), 3–31–78, AlCl(g), 9–30–79; $AlCl_3$(g), 9–30–79.
[3] A. Navrotsky and O. J. Kleppa, J. Inorg. Nucl. Chem. 30, 479 (1968); A Navrotsky and O. J. Kleppa, Inorg Chem. 5, 192 (1966).
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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ ($J \cdot K^{-1} mol^{-1}$)	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ ($kJ \cdot mol^{-1}$)	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	8.075	INFINITE	−15.411	−2283.075	−2283.075	INFINITE
100	22.669	16.757	164.497	−14.774	−2289.857	−2254.524	1177.642
200	78.069	49.819	98.221	−9.681	−2296.197	−2216.480	578 885
298.15	116.198	88.692	88.692	0.	−2299.108	−2176.621	381.335
300	116.533	89.412	88.695	0.215	−2299.137	−2175.861	378.851
400	137.988	126.244	93.571	13.069	−2299.797	−2134.626	278.754
500	149.829	158.409	103.398	27.506	−2299.410	−2093.365	218.692
600	157.887	186.474	114.956	42.911	−2298.562	−2052.230	178.663
700	164.155	211.299	126.980	59.023	−2297.527	−2011.255	150.082
800	169.473	233.573	138.935	75.710	−2296.463	−1970.433	128.656
900	174.238	253 814	150.592	92.899	−2295.485	−1929.739	111.999
1000	178.657	272.403	161.856	110.546	−2324.450	−1886.914	98.562
1100	182.853	289.629	172.698	128.623	−2323.172	−1843.219	87.527
1200	186.895	305 713	183.120	147.112	−2321.562	−1799.655	78.337
1300	190.828	320.829	193.137	165.999	−2319.622	−1756.239	70.567
1400	194.686	335.112	202.773	185.275	−2444.763	−1709.818	63.794
1500	198.485	348.674	212.051	204 934	−2440.816	−1657.458	57.718
1600	202.238	361.604	220.997	224.970	−2436.542	−1605.372	52.410
1700	205.962	373.976	229.635	245.381	−2431.944	−1553.563	47.735
1800	209.652	385.853	237.986	266.162	−2427.024	−1502.034	43.588
1900	213.325	397.287	246.071	287.311	−2421 783	−1450.787	39.885
2000	216.982	408.322	253.909	308.826	−2416.221	−1399.824	36.560
2100	220.622	418.997	261.518	330.706	−2410.341	−1349.148	33.558
2200	224.254	429.344	268.912	352.950	−2404.143	−1298.758	30.836
2300	227.877	439.393	276.107	375.557	−2397.627	−1248.658	28.358
2400	231.488	449.167	283.115	398.525	−2390.796	−1198.849	26.092
2408.000	231.777	449.938	283.668	400.378	--- CRYSTAL <--> LIQUID ---		
2500	235.095	458.690	289.949	421.854	−2383.648	−1149.330	24.014
2600	238.697	467.981	296.618	445.544	−2376.185	−1100.104	22.101
2700	242.291	477.057	303.133	469.594	−2368.406	−1051.170	20.336
2800	245.885	485.934	309.504	494.002	−2948.114	−1000.595	18.666

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Magnesium Aluminum Oxide ($MgAl_2O_4$) LIQUID $M_r = 142.26568$ Magnesium Aluminum Oxide ($MgAl_2O_4$) $Al_2Mg_1O_4(l)$

$S°(298.15\ K) = [168.473]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 2408 \pm 20\ K$

$\Delta_fH°(298.15\ K) = [-2106.527]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = [192.464 \pm 21]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the liquid is calculated from that of the crystal by adding the enthalpy of $\Delta_{fus}H°$, and the difference in enthalpy, $H°(2408\ K)-H°(298.15\ K)$, *between the crystal and liquid.*

Heat Capacity and Entropy

The adopted $C_p°$ for the liquid is estimated to be 52.5 cal $K^{-1}{\cdot}mol^{-1}$ (219.66 J $K^{-1}{\cdot}mol^{-1}$) above an assumed glass transition at 1750 K. Below T_{gls}, the heat capacity is taken to be that of the crystal.[1] The heat capacity is estimated by assuming $C_p° = 7.5$ cal$\cdot K^{-1}\cdot$g$\cdot$atom^{-1} as suggested by Kubaschewski and Alcock.[2]

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

Fusion Data

Rankin and Merwin[3] *studied the binary system* alumina + magnesia and reported $T_{fus} = 2408 \pm 20$ K for $MgAl_2O_4$(cr) Wilde and Rees[4] confirm this value in a later paper. The adopted heat of melting is 46 ± 5 kcal$\cdot$mol^{-1}. This is estimated assuming that the entropy of melting per g–atom^{-1} (2 7 cal$\cdot K^{-1}$) is the same as that of Be_2O_4(cr).[1]

References

[1] JANAF Thermochemical Tables. $MgAl_2O_4$(cr), 12–31–79; Be_2O_4(l), 12–31–79.
[2] O. Kubaschewski and C B. Alcock, "Metallurgical Thermochemistry", 5th ed., Pergamon, Oxford, 449 pp. (1979).
[3] G. A. Rankin and H. E. Merwin, J. Amer. Chem. Soc. 38, 568 (1916).
[4] W. T. Wilde and W. J. Rees, Trans. Brit. Ceramic Soc. 42, 123 (1943).

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	116 198	168.473	168.473	0.	−2106.527	−2007.826	351.763
300	116.533	169.193	168.475	0.215	−2106.556	−2007.214	349.487
400	137.988	206 024	173.351	13.069	−2107.216	−1973.957	257 772
500	149.829	238.190	183.178	27.506	−2106.829	−1940.674	202.741
600	157.887	266.255	194.736	42.911	−2105 981	−1907.517	166.064
700	164.155	291.079	206.760	59.023	−2104.945	−1874.521	139 878
800	169 473	313.354	218.716	75.710	−2103.882	−1841.676	120.249
900	174.238	333.594	230.373	92.899	−2102.904	−1808.961	104.989
1000	178.657	352 183	241.637	110.546	−2131.868	−1774.113	92.670
1100	182.853	369.409	252.479	128.623	−2130.591	−1738.396	82.550
1200	186.895	385.494	262 900	147.112	−2128.981	−1702.811	74.121
1300	190.828	400 609	272.918	165 999	−2127 041	−1667 373	66.996
1400	194.686	414.893	282.553	185.275	−2252.182	−1628.930	60 776
1500	198 485	428.454	291.832	204.934	−2248.234	−1584.548	55.179
1600	202.238	441.384	300.778	224.970	−2243 961	−1540.439	50.290
1700	205.962	453 757	309.415	245.381	−2239.363	−1496.608	45 985
1750 000	207 811	459.754	313.625	255.725	GLASS <−−> LIQUID TRANSITION		
1750 000	219.660	459.754	313.625	255 725			
1800	219.660	465.942	317.771	266.708	−2233.896	−1453.066	42.167
1900	219.660	477.818	325.885	288.674	−2227.838	−1409.852	38.760
2000	219.660	489.085	333 765	310.640	−2221.826	−1366.955	35.701
2100	219.660	499.803	341.419	332 606	−2215.860	−1324.359	32.942
2200	219.660	510.021	348.852	354.572	−2209.940	−1282.044	30.440
2300	219 660	519.785	356.073	376.538	−2204.065	−1239 999	28.161
2400	219.660	529.134	363.091	398.504	−2198.236	−1198.209	26.078
2408.000	219.660	529.865	363.644	400.261	−−− CRYSTAL <−−> LIQUID −−−		
2500	219.660	538.101	369.913	420 470	−2192.452	−1156 661	24.167
2600	219.660	546.716	376.549	442.436	−2186.712	−1115.342	22.408
2700	219 660	555.006	383.006	464.402	−2181.016	−1074.243	20.782
2800	219.660	562.995	389.292	486.368	−2763.167	−1031.419	19.241
2900	219.660	570.703	395.415	508.334	−2755.368	−969.710	17.466
3000	219.660	578.150	401.383	530.300	−2747.614	−908.268	15.814
3100	219.660	585.352	407.202	552.266	−2739.904	−847.082	14.273
3200	219.660	592.326	412.879	574.232	−2732.239	−786.147	12.833
3300	219 660	599.086	418.420	596.198	−2724.618	−725.450	11.483
3400	219.660	605.643	423.830	618.164	−2717.043	−664.982	10.216
3500	219.660	612.010	429.116	640.130	−2709.515	−604.738	9.025
3600	219 660	618.199	434.283	662.096	−2702.035	−544.707	7.903
3700	219.660	624.217	439.335	684.062	−2694.603	−484.885	6.845
3800	219 660	630.075	444.278	706.028	−2687.223	−425.260	5.846
3900	219.660	635.781	449.116	727.994	−2679.895	−365.830	4.900
4000	219.660	641.342	453.852	749.960	−2672.622	−306.588	4 004

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Magnesium Aluminum Oxide ($MgAl_2O_4$) CRYSTAL-LIQUID

0 to 2408 K crystal
above 2408 K liquid

Refer to the individual tables for details.

M_r = 142.26568 Magnesium Aluminum Oxide ($MgAl_2O_4$) $Al_2Mg_1O_4(cr,l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	8.075	INFINITE	−15.411	−2283.075	−2283.075	INFINITE
100	22.669	16.757	164.497	−14.774	−2289.857	−2254.524	1177.642
200	78.069	49.819	98.221	−9.681	−2296.197	−2216.480	578.885
298.15	116.198	88.692	88.692	0.	−2299.108	−2176.621	381.335
300	116.533	89.412	88.695	0.215	−2299.137	−2175.861	378.851
400	137.988	126.244	93.571	13.069	−2299.797	−2134 626	278.754
500	149.829	158.409	103.398	27.506	−2299.410	−2093.365	218.692
600	157.887	186.474	114.956	42.911	−2298.562	−2052.230	178.663
700	164.155	211.299	126.980	59.023	−2297.527	−2011.255	150.082
800	169.473	233.573	138.935	75.710	−2296.463	−1970.433	128.656
900	174.238	253.814	150.592	92.899	−2295.485	−1929.739	111.999
1000	178.657	272.403	161.856	110.546	−2324.450	−1886.914	98.562
1100	182.853	289.629	172.698	128.623	−2323.172	−1843.219	87.527
1200	186.895	305.713	183.120	147.112	−2321.562	−1799.655	78.337
1300	190.828	320.829	193.137	165.999	−2319.622	−1756.239	70.567
1400	194.686	335.112	202.773	185.275	−2444.763	−1709.818	63.794
1500	198.485	348.674	212.051	204.934	−2440.816	−1657.458	57.718
1600	202.238	361.604	220.997	224.970	−2436.542	−1605.372	52.410
1700	205.962	373.976	229.635	245.381	−2431.944	−1553.563	47.735
1800	209.652	385.853	237.986	266.162	−2427.024	−1502.034	43.588
1900	213.325	397.287	246.071	287.311	−2421.783	−1450.787	39.885
2000	216.982	408.322	253.909	308.826	−2416.221	−1399.824	36.560
2100	220.622	418.997	261.518	330.706	−2410.341	−1349.148	33.558
2200	224.254	429.344	268.912	352.950	−2404.143	−1298.758	30.836
2300	227.877	439.393	276.107	375.557	−2397.627	−1248.658	28.358
2400	231.488	449.167	283.115	398.525	−2390.796	−1198.849	26.092
2408.000	231.777	449.938	283.668	400.378	CRYSTAL <−−> LIQUID TRANSITION		
2408.000	219.660	529.865	283.668	592.842			
2500	219.660	538.101	292.881	613.051	−2192.452	−1156.661	24.167
2600	219.660	546.716	302.479	635.017	−2186.712	−1115.343	22.408
2700	219.660	555.006	311.679	656.983	−2181.016	−1074.244	20.782
2800	219.660	562.995	320.513	678.949	−2763.167	−1031.420	19.241
2900	219.660	570.703	329.008	700.915	−2755.369	−969.711	17.466
3000	219.660	578.150	337.189	722.881	−2747.614	−908.268	15.814
3100	219.660	585.352	345.079	744.847	−2739.904	−847.083	14.273
3200	219.660	592.326	352.697	766.813	−2732.239	−786.148	12.833
3300	219.660	599.086	360.062	788.779	−2724.618	−725.451	11.483
3400	219.660	605.643	367.189	810.745	−2717.043	−664.983	10.216
3500	219.660	612.011	374.093	832.711	−2709.515	−604.739	9.025
3600	219.660	618.199	380.788	854.677	−2702.035	−544.708	7.904
3700	219.660	624.217	387.286	876.643	−2694.603	−484.885	6.845
3800	219.660	630.075	393.599	898.609	−2687.223	−425.260	5.846
3900	219.660	635.781	399.736	920.575	−2679.895	−365.830	4.900
4000	219.660	641.342	405.707	942.541	−2672.622	−306.589	4.004

PREVIOUS: CURRENT December 1979

Aluminum Oxide (Al_2O) IDEAL GAS $M_r = 69.96248$ Aluminum Oxide (Al_2O) $Al_2O_1(g)$

$\Delta_{at}H^\circ = 250 \pm 4$ kJ·mol^{-1}
$S^\circ(298.15\ K) = 252.33 \pm 3.3$ J·K^{-1}·mol^{-1}

$\Delta_fH^\circ(0\ K) = -144.5 \pm 17$ kJ·mol^{-1}
$\Delta_fH^\circ(298.15\ K) = -145.2 \pm 17$ kJ·mol^{-1}

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
471(1)	[160](2)	994(1)

Electronic Levels and Quantum Weights					
State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
X	0	1	B	34331	[3]
A	23286	[1]	C	36233	[1]

Point Group. $D_{\infty h}$ $\sigma = 2$
Bond Distance: Al–O = 1.73 Å
Bond Angle: Al–O–Al = 180° ± 10°
Rotational Constant: $B_o = 0.104378$ cm^{-1}

Enthalpy of Formation

We adopt the heat of atomization $\Delta_{at}H^\circ = 250 \pm 4$ kcal·mol^{-1} and $\Delta_fH^\circ(298.15\ K) = -34.7 \pm 4$ kcal·mol^{-1}. Six reactions analyzed below yield D° values ranging from 247.4 to 252.7 kcal·mol^{-1}.[1–10] These values show no obvious dependence on the reaction and eight of the eleven fall in the range 250 ± 2 kcal·mol^{-1}. The overall uncertainty is about twice this range due to possible error in the data and the thermodynamic functions. The mass–spectrometric methods are uncertain due to use of several different approximations for ionization cross sections; some of these must be significantly in error Other methods have their own uncertainties. We omit below two studies that were recently revised by Ho and Burns[1] and others, such as,[11] that we believe to be seriously biased.

Source	Method	Reaction[a]	T/K	δS cal·K^{-1}·mol^{-1}	Δ_rH°(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Δ_fH°(298.15 K) kcal·mol^{-1}	$\Delta_{at}H^\circ$(0 K)
[1]Ho (1980)	Mass spec.	A	2221–2327[b]	4.6 ± 3.2	−240.6 ± 7.3	−251.0 ± 0.6	−33.9 ± 4	249.2
[1]Fu (1976)	Mass spec.	A	2056–2327[b]	0.4 ± 1.3	−251.4 ± 3.0	−252.4 ± 0.8	−35.2 ± 4	250.5
[2]Smoes (1976)	Mass spec.v	B	1198–1461	−0.2 ± 0.3	18.8 ± 0.4	19.1 ± 0.2	−34.8 ± 3	250.1
[3]Hildenbrand (1973)	Mass spec.	C	2104–2256	−0.5 ± 1.4	−10.0 ± 3.1	−9.0 ± 0.4	−36.6 ± 5	251.9
[4]Farber (1972)	Mass spec.	D	1943–2093	0.0 ± 5.5	−129 ± 11	−128.8 ± 1.3	−34.0 ± 5	249.3
[5]Thompson (1973)	Mass spec.	E	1438–1580	−0.2 ± 1.9	92.3 ± 2.8	92.7 ± 0.6	−37.4 ± 4	252.7
[6]Rao (1970)	Knudsen eff.	E	1556	–	–	97.4	−32.7 ± 5	248.0
[7]Kulifeev (1969)	Knudsen eff.	E	1443–1576	19 ± 5	123 ± 7	93.6 ± 2.0	−36.5 ± 5	251.8
[8]Herstad (1966)	K.E. + P.C.[c]	E	1585–2129	0.0 ± 1.0	96.5 ± 2.0	96.4 ± 1.1	−33.7 ± 4	249.0
[9]DeMaria (1968)	Mass spec.	F	1313–1511	−1.0 ± 0.5	−5.1 ± 0.7	−3.7 ± 0.3	−32.1 ± 5	247.4
[10]Brewer (1951)	Volatilization	F	1466–1725	5.1 ± 2.7	−0.5 ± 4.3	−8.6 ± 1.4	−37.0 ± 5	252.3

[a] Reactions: A) $2\ Al(g) + O(g) \rightarrow Al_2O(g)$; B) $1/3\ Al_2O_3(cr) + 1/3\ Al(l) + Al(g) = Al_2O(g)$; C) $2AlO(g) = Al_2O(g) + O(g)$
D) $Al(g) + AlO(g) = Al_2O(g)$; E) $1/3\ Al_2O_3(cr) + 4/3\ Al(l) = Al_2O(g)$; F) $1/3\ Al_2O_3(cr) + 4/3\ Al(g) = Al_2O(g)$.

[b] Temperature scale adjusted. [c] Knudsen effusion plus pressure compensation.

Heat Capacity and Entropy

We adopt a linear Al–O–Al structure with a low bending frequency. The long–standing controversy over these properties has been greatly resolved by Douglas[12] who studied electronic absorption and emission spectra of Al_2O in Kr and Ar matrices. Vibrational progressions in the spectra[12] gave 471 ± 15, ~482 and ~452 cm^{-1} for ν_1 of the X, A and C states, respectively, plus ~133 and ~170 cm^{-1} for ν_2 of the A and C states This supplements previous evidence of linearity, i e. absence of ν_1 in IR spectra[13–18] absence of deflection by an inhomogenous electric field[19] and theoretical predictions.[20] IR spectra[13–18] also failed to show ν_2, which has been estimated as 102 or 120 ± 30 cm^{-1} from SCF calculations[20] or force constants.[17] The evidence suggests that the X state has $\nu_2 \leq 170$ cm^{-1} implying that the equilibrium bond angle[21] is much closer to 180° than the uncorrected angle of 141° derived from electron diffraction. Likewise, the angle of 140°–150°[15] derived from the isotopic shift of ν_3 becomes nearly 180°[12] if corrected for anharmonicity.

We conclude that the bond angle is 180° ± 10° and adopt the bond distance from electron diffraction.[21] Frequencies ν_1 and ν_3 are from[12] and,[13–18] while $\nu_2 = 160$ cm^{-1} is chosen to reproduce the entropy derived from equilibria (see δS in the table above). Electronic levels are from;[12] states A and C probably are bent. The band found[18] at ~24400 cm^{-1} is from Al_2.[12] Values of Gibbs energy function from Gurvich *et al.*[22] are 1.0 cal·K^{-1}·mol^{-1} larger than ours at T>1400 K.

References

[1] P. Ho and R. P Burns, High Temp. Sci. **12**, 31 (1980); C. M. Fu and R. P. Burns, ibid., **8**, 353 (1976).
[2] S. Smoes and J. Drowart, personal communication from J. Drowart, Free Univ. Brussels, Brussels, Belgium, (September 9, 1976).

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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})	Δ_fH° (kJ·mol^{-1})	Δ_fG° (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−12.710	−144.474	−144.474	INFINITE
100	40.424	201.813	295.494	−9.368	−143.552	−153.671	80.269
200	47.795	232.403	256.967	−4.913	−144.156	−163.630	42.736
250	50.162	243.332	253.179	−2.462	−144.662	−168.442	35.194
298.15	52.032	252.332	252.332	0.	−145.185	−172.975	30.304
300	52.098	252.654	252.333	0.096	−145.205	−173.147	30.148
350	53.696	260.809	252.973	2.742	−145.767	−177.760	26.529
400	55.010	268.068	254.415	5.461	−146.342	−182.291	23.805
450	56.087	274.611	256.301	8.239	−146.929	−186.750	21.677
500	56.971	280.568	258.435	11.067	−147.532	−191.142	19.968
600	58.297	291.080	263.023	16.834	−148.815	−199.746	17.389
700	59.213	300.139	267.693	22.713	−150.259	−208.123	15.530
800	59.863	308.091	272.256	28.668	−151.933	−216.278	14.121
900	60.337	315.171	276.638	34.679	−153.907	−224.206	13.013
1000	60.691	321.547	280.815	40.732	−177.417	−230.375	12.034
1100	60.961	327.345	284.786	46.815	−179.438	−235.573	11.186
1200	61.172	332.658	288.557	52.922	−181.456	−240.587	10.472
1300	61.339	337.562	292.140	59.048	−183.472	−245.433	9.862
1400	61.473	342.112	295.549	65.188	−185.488	−250.124	9.332
1500	61.583	346.357	298.796	71.341	−187.505	−254.670	8.868
1600	61.674	350.335	301.895	77.504	−189.526	−259.082	8.458
1700	61.750	354.076	304.855	83.676	−191.551	−263.368	8.092
1800	61.814	357.608	307.689	89.854	−193.581	−267.534	7.764
1900	61.869	360.951	310.405	96.038	−195.616	−271.587	7.466
2000	61.915	364.126	313.012	102.227	−197.658	−275.532	7.196
2100	61.956	367.148	315.519	108.421	−199.708	−279.376	6.949
2200	61.991	370.031	317.931	114.618	−201.764	−283.121	6.722
2300	62.022	372.787	320.257	120.819	−203.829	−286.773	6.513
2400	62.050	375.427	322.501	127.023	−205.902	−290.335	6.319
2500	62.075	377.961	324.669	133.229	−207.984	−293.810	6.139
2600	62.097	380.396	326.766	139.438	−210.073	−297.202	5.971
2700	62.118	382.740	328.796	145.649	−212.171	−300.513	5.814
2800	62.138	384.999	330.763	151.861	−802.079	−301.811	5.630
2900	62.156	387.180	332.671	158.076	−802.003	−283.946	5.114
3000	62.174	389.288	334.523	164.293	−801.934	−266.083	4.633
3100	62.192	391.327	336.323	170.511	−801.873	−248.222	4.183
3200	62.210	393.301	338.073	176.731	−801.820	−230.363	3.760
3300	62.229	395.216	339.776	182.953	−801.775	−212.506	3.364
3400	62.248	397.074	341.434	189.177	−801.737	−194.650	2.990
3500	62.269	398.879	343.049	195.403	−801.707	−176.795	2.639
3600	62.291	400.633	344.625	201.631	−801.684	−158.941	2.306
3700	62.315	402.340	346.162	207.861	−801.669	−141.087	1.992
3800	62.341	404.002	347.662	214.094	−801.661	−123.233	1.694
3900	62.369	405.622	349.127	220.329	−801.661	−105.380	1.411
4000	62.399	407.202	350.560	226.567	−801.669	−87.526	1.143
4100	62.433	408.743	351.960	232.809	−801.685	−69.673	0.888
4200	62.470	410.248	353.330	239.054	−801.710	−51.818	0.644
4300	62.509	411.718	354.671	245.303	−801.744	−33.963	0.413
4400	62.553	413.156	355.984	251.556	−801.788	−16.108	0.191
4500	62.600	414.562	357.270	257.814	−801.839	1.749	−0.020
4600	62.651	415.938	358.530	264.076	−801.904	19.607	−0.223
4700	62.705	417.286	359.766	270.344	−801.983	37.467	−0.416
4800	62.764	418.607	360.978	276.617	−802.075	55.328	−0.602
4900	62.827	419.902	362.168	282.897	−802.180	73.192	−0.780
5000	62.895	421.172	363.335	289.183	−802.303	91.058	−0.951
5100	62.967	422.418	364.481	295.476	−802.445	108.927	−1.116
5200	63.044	423.641	365.607	301.777	−802.606	126.798	−1.274
5300	63.125	424.843	366.714	308.085	−802.789	144.673	−1.426
5400	63.211	426 024	367.801	314.402	−802.995	162.551	−1.572
5500	63.301	427.184	368.870	320.727	−803.227	180.434	−1.714
5600	63.396	428.326	369.922	327.062	−803.487	198.321	−1.850
5700	63 496	429 449	370.956	333.407	−803.776	216.213	−1.981
5800	63.601	430.554	371.974	339.761	−804.092	234.110	−2.108
5900	63.710	431 642	372.977	346.127	−804.448	252.012	−2.231
6000	63.823	432.714	373.963	352.503	−804.796	269.918	−2.350

PREVIOUS. December 1979 (1 atm) CURRENT: December 1979 (1 bar)

Aluminum Oxide (Al_2O) $Al_2O_1(g)$

Aluminum Oxide, Ion (Al_2O^+) IDEAL GAS $M_r = 69.961931$ Aluminum Oxide, Ion ($Al_2O_1^+$) $Al_2O_1^+(g)$

$S°(298.15\ K) = [260.6 \pm 8]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 646.7 \pm 25\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [652.436]\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm $^{-1}$
[450] (1)
[140] (2)
[900] (1)

Ground State Quantum Weight: [2] $\sigma = 2$
Point Group: $[D_{\infty h}]$
Bond Distance: Al–O = [1.73] Å
Bond Angle: Al–O–Al = [180]°
Rotational Constant: $B_0 = [0.104379]\ cm^{-1}$

Enthalpy of Formation

$\Delta_f H°(Al_2O^+, g, 0\ K)$ is calculated from that of Al_2O[1] using Hildenbrand's appearance potential[2] of 8.20 ± 0.15 eV (189.1 ± 3.5 kcal·mol^{-1}. We assume that the appearance potential is identical with the ionization potential for $Al_2O(g) \rightarrow Al_2O^+(g) + e^-(g)$. Other values reported for the appearance potential include 7.7 ± 0.5,[3] [4] 7.9 ± 0.3,[5] 8.0 ± 0.5,[6] 8.5 ± 0.5[7] and 8.5 ± 0.2 eV.[8] These values are consistent with, but less precise than, the adopted value.

$\Delta_f H°(298.15\ K)$ is obtained from $\Delta_f H°(Al_2O)$ by using $IP(Al_2O)$ with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for $Al_2O(g)$, $Al_2O^+(g)$ and e^- (g). $\Delta_r H°(Al_2O \rightarrow Al_2O^+ + e^-, 298.15\ K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[9] $\Delta_f H°(298.15\ K)$ should be changed by −1.481 kcal·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron. MNDO calculations[10] differ by only −9.9 kcal·mol^{-1} from our value of $[\Delta_f H°(Al_2O^+, 298.15\ K) - \Delta_f H°(Al_2O, 298.15\ K)]$ even though the MNDO values of $\Delta_f H°(298.15\ K)$ differ by −47 and −37 kcal·mol^{-1}.

Heat Capacity and Entropy

Al_2O^+ is assumed to be linear as predicted by MNDO calculations[10] and by the correlation of Walsh.[11] We assume that the bond distance is the same as that in Al_2O[1] since the change in bond length on ionization was predicted to be only 0.004 Å.[10] Vibrational frequencies are estimated to be somewhat lower than those of Al_2O since the ion has one less bonding electron. The electronic ground state is doublet due to the odd number of electrons.

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	−12.981	646.679		
100	41.629	209.128	304.597	−9.547			
200	48.639	240.389	265.373	−4.997			
250	51.019	251.507	261.521	−2.503			
298.15	52.897	260.660	260.660	0.	652.436	615.909	−107.905
300	52.962	260.987	260.661	0.098	652.456	615.682	−107.200
350	54.537	269.274	261.312	2.787	652.976	609.512	−90.965
400	55.804	276.642	262.776	5.546	653.481	603.268	−78.779
450	56.821	283.276	264.691	8.363	653.972	596.961	−69.293
500	57.641	289.306	266.856	11.225	654.444	590.602	−61.700
600	58.846	299.930	271.507	17.054	655.300	577.750	−50.298
700	59.661	309.066	276.235	22.982	655.984	564.769	−42.144
800	60.231	317.072	280.850	28.978	656.429	551.704	−36.023
900	60.642	324.191	285.277	35.023	656.567	538.602	−31.260
1000	60.947	330.597	289.494	41.103	635.164	527.023	−27.529
1100	61.179	336 417	293.499	47.210	635.245	516.205	−24.513
1200	61.358	341.748	297.301	53.337	635.326	505.379	−21.999
1300	61.500	346.665	300.912	59.480	635.406	494.547	−19.871
1400	61.615	351.227	304.345	65.636	635.484	483.709	−18.047
1500	61 708	355.482	307.614	71.802	635.558	472.865	−16.467
1600	61.784	359.467	310.731	77.977	635.628	462.017	−15.083
1700	61 848	363.214	313.709	84.159	635.692	451.164	−13.863
1800	61.902	366.751	316.559	90.346	635.750	440.308	−12.777
1900	61.948	370.099	319.289	96.539	635.801	429.448	−11.806
2000	61.987	373.278	321.910	102.736	635.845	418.586	−10.932
2100	62.021	376.303	324.429	108.936	635.882	407.723	−10.142
2200	62.051	379.189	326.853	115.140	635.910	396.857	−9.423
2300	62.077	381.948	329.189	121.346	635.929	385.991	−8.766
2400	62.099	384.590	331.442	127.555	635.940	375.123	−8.164
2500	62.119	387.126	333.619	133.766	635.942	364.256	−7.611
2600	62.137	389.562	335.724	139.979	635.935	353.389	−7.100
2700	62.153	391.908	337.762	146.193	635.919	342.522	−6.626
2800	62.167	394.168	339.736	152.409	48.093	333.592	−6.223
2900	62.180	396.350	341.651	158.627	50.251	343.749	−6.192
3000	62.192	398.458	343.510	164.845	52.401	353.834	−6.161
3100	62.202	400.498	345.315	171.065	54.541	363.846	−6.131
3200	62.212	402.473	347.071	177.286	56.673	373.789	−6.101
3300	62.220	404.387	348.779	183.507	58.797	383.666	−6.073
3400	62.228	406.245	350.442	189.730	60.912	393.479	−6.045
3500	62.236	408.049	352.062	195.953	63.018	403.230	−6.018
3600	62.242	409.802	353.642	202.177	65.115	412.921	−5.991
3700	62.248	411.508	355.183	208.401	67.204	422.553	−5.965
3800	62.254	413.168	356.687	214.626	69.282	432.129	−5.940
3900	62.259	414.785	358.156	220.852	71.351	441.651	−5.915
4000	62.264	416.361	359.592	227.078	73.410	451.120	−5.891
4100	62.269	417.899	360.995	233.305	75.458	460.537	−5.867
4200	62.273	419.399	362.368	239.532	77.493	469.905	−5.844
4300	62.277	420.865	363.711	245.760	79.516	479.224	−5.821
4400	62.280	422.296	365.026	251.987	81.525	488.496	−5.799
4500	62.284	423.696	366.315	258.216	83.524	497.722	−5.777
4600	62.287	425.065	367.577	264.444	85.503	506.905	−5.756
4700	62.290	426.405	368.815	270.673	87.465	516.045	−5.735
4800	62.293	427.716	370.028	276.902	89.407	525.143	−5.715
4900	62.295	429.000	371.218	283.132	91.330	534.201	−5.695
5000	62.298	430.259	372.387	289.361	93.229	543.220	−5.675
5100	62.300	431.493	373.534	295.591	95.103	552.201	−5.656
5200	62.302	432.702	374.660	301.821	96.950	561.145	−5.637
5300	62.304	433.889	375.766	308.052	98.768	570.055	−5.618
5400	62.306	435.054	376 853	314.282	100.554	578.930	−5.600
5500	62.308	436.197	377.922	320.513	102.306	587.772	−5.582
5600	62.310	437.320	378.973	326.744	104.021	596.584	−5.565
5700	62.312	438.423	380.006	332.975	105.696	605.365	−5.548
5800	62.313	439.506	381.023	339.206	107.335	614.116	−5.531
5900	62.315	440.572	382.023	345.438	108.924	622.839	−5.514
6000	62.316	441.619	383.008	351.669	110.510	631.533	−5.498

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

Aluminum Oxide, Ion ($Al_2O_1^+$) $Al_2O_1^+(g)$

Aluminum Oxide ((AlO)$_2$) **IDEAL GAS** **M_r = 85.96188** **Aluminum Oxide ((AlO)$_2$)** **$Al_2O_2(g)$**

$\Delta_{at}H°$ = 1540 ± 32 kJ·mol^{-1}
$S°$(298.15 K) = [280.98 ± 12] J·K·mol^{-1}

$\Delta_fH°$(0 K) = −391.3 ± 32 kJ·mol^{-1}
$\Delta_fH°$(298.15 K) = −394.6 ± 32 kJ·mol^{-1}

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[600](1)	[350](1)	496 (1)
[400](1)	*[200](1)*	*[650](1)*

Ground State Quantum Weight: [1]   σ = [4]
Bond Distance: Al–O = [1.80] Å;   Point Group: [D_{2h}]
Bond Angles: O–Al–O = [90]°;   Al–O–Al = [90]°
Product of the Moments of Inertia: $I_AI_BI_C$ = [2.889675 × 10^{-114}] g^3 cm^6

Enthalpy of Formation

We adopt $\Delta_fH°$(298.15 K) = −94.3 ± 8 and $\Delta_{at}H°$ = 368 ± 8 kcal·mol^{-1} based on the mass–spectrometric studies summarized below. Data of Chervonnyi[2] and Drowart[4] are analyzed using the isomolecular reaction B instead of the atomization reaction A, which is much affected by probable bias in calibrations and relative ionization cross sections. Reaction A would give discrepancies of −16 to +5 kcal·mol^{-1} in $\Delta_{at}H°$. Use of reaction B emphasizes the consistency among the studies. Only the result of Farber *et al.*[3] appears to be discrepant. JANAF auxiliary data[5] have been used to calculate the $\Delta_fH°$ values; their uncertainties include a large contribution from possible bias in the Gibbs–energy function. Gurvich *et al.*[6] selected $\Delta_fH°$(298.15 K) = −96.96 and $\Delta_{at}H°$ = 370.5 ± 12 kcal·mol^{-1} based on somewhat different functions and without benefit of the data of Ho.[1]

Source	*Method*	Reaction[a]	*T/K*	δS cal·K^{-1}·mol^{-1}	ΔH°(298.15 K), kcal·mol 2nd law	3rd law	$\Delta_fH°$(298.15 K) kcal·mol^{-1}	$\Delta_{at}H°$
[1]Ho (1980)	Mass spec.	A	2221–2327[c]	−31 ± 1	−442 ± 3	−371.3 ± 2.8	−94.6 ± 8	368.2
[1]Fu (1976)	Mass spec.	A	2327	—	—	−368.4	−91.7 ± 8	365.4[d]
[2]Chervonnyi (1977)	Eff. mass spec.[e]	B[b]	2300–2600	−0.3 ± 3	1 ± 6	2.1 ± 1.0	−95.4 ± 10	369.0
[3]Farber (1972)	Eff. mass spec.	B	*1943–2093*	*−7.1 ± 1*	−22 ± 2	−7.3 ± 0.8	*104.8 ± 10*	378.5
[4]Drowart (1960)	Eff. mass spec.[e]	B[b]	2464–2594	31 ± 23	79 ± 57	1.3 ± 5.4	−96.2 ± 13	369 9[d]
[4]Drowart (1960)	Eff. mass spec.[f]	B[b]	2281–2466	−32 ± 17	−72 ± 39	4.1 ± 6.9	−93.4 ± 13	367.1[d]

[a] *Reactions:* A) 2 Al(g) + 2 O(g) = Al_2O_2(g); B) Al_2O(g) + AlO(g) = Al(g) + Al_2O_2(g).

[b] Reaction B used instead of A to minimize bias from calibrations and ionization cross sections.

[c] Temperature scale adjusted to T = 2327 K instead of 2318 K for α–Al_2O_3.

[d] Ho and Burn's recalculations[1] ofthe results of Fu[1] and Drowart[4] yield $\Delta_{at}H°$ = 367.0[1] and −364.6[4] kcal·mol^{-1} when converted to our new Al_2O_2 functions.

[e] Tungsten cell.

[f] Molybdenum cell.

Heat Capacity and Entropy

We adopt a square–planar structure of D_{2h} symmetry. The Al–O bond distance is taken as 1.8 Å, i.e., 0.1 Å longer than the predictions of ab initio[7] and MNDO[8] calculations and 0.07 Å longer than observed in Al_2O.[5] Similar predictions for Al_2O are I_A = 8.6080 × 10^{-39}, I_B = 14.5167 × 10^{-39} and I_C = 23.1247 × 10^{-39} g·cm^2.

Vibrational frequencies are estimated to be lower than values from MNDO calculations[8] but higher than Al_2F_2 values from ionic model calculations.[10] Matrix IR spectra gave a band near 496 cm^{-1} *that was assigned to D_{2h} Al_2O_2 in three studies*[11] but to cyclic AlO_2 in another.[12] A band at 686 cm^{-1}, once assigned to Al_2O_2,[13] was reassigned to Al(O_2)$_2$ by Finn[11] who also attributed bands at 490 and −1215 cm^{-1} to a C_{2v} form of Al_2O_2.

Evidence is contradictory on the most stable geometry. The square–planar form is 15 kcal·mol^{-1} more stable than linear AlOAlO according to ab initio calculations[7] but 27 kcal mol^{-1} less stable according to MNDO calculations.[8–9] Also possible is rhombic D_{2h} AlO_2Al with an O–O bond similar to that predicted by ab initio methods for LiO_2Li.[14] This geometry was not considered in the ab initio study[7] and showed no minimum in the MNDO study.[8] Better calculations are needed to resolve the question. Thermochemical and spectral evidence is inconclusive.[15] Uncertainties in the structure and vibrational frequencies cause an uncertainty of ≤3 cal·K^{-1}·mol^{-1} in $S°$ and −($G°$–$H°$)/T at 2000 K. Estimated values for the rhombic peroxide[6] are ~1 cal·K^{-1}·mol^{-1} lower at 2000 K but this difference could be plausibly reversed by use of lower frequencies.

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	−[$G°$−$H°(T_r)$]/T	$H°$−$H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0	INFINITE	−14.518	−391.307	−391.307	INFINITE
100	40.385	223.077	333.078	−11.000	−391.661	−395.241	206.453
200	56.664	256.193	286.829	−6.127	−393.303	−398.187	103.996
250	62.784	269.527	282.062	−3.134	−393.995	−399.325	83.434
298.15	67.164	280.980	280.980	0.	−394.551	−400.300	70.131
300	67.307	281.395	280.981	0.124	−394.571	−400.336	69.705
350	70 614	292.032	281.813	3.577	−395.065	−401.257	59.884
400	73.052	301.629	283.700	7.171	−395.511	−402.110	52.510
450	74.877	310.343	286.184	10.872	−395.935	−402.910	46.769
500	76.268	318.308	289.004	14.652	−396.355	−403.662	42.170
600	78.197	332.397	295.093	22.383	−397.255	−405.041	35.262
700	79.429	344.551	301.310	30.268	−398.319	−406.257	30.315
800	80.259	355.215	307.395	38.255	−399.630	−407.305	26.594
900	80.842	364.703	313.246	46.312	−401.261	−408.170	23.690
1000	81.266	373.244	318.825	54.418	−424.448	−407.314	21.276
1100	81.583	381.005	324.131	62.562	−426.164	−405.518	19.256
1200	81.827	388.114	329.171	70.733	−427.892	−403.565	17.567
1300	82.018	394.672	333.960	78.925	−429.632	−401.467	16.131
1400	82.171	400.756	338.517	87.135	−431.386	−399.235	14.896
1500	82.295	406.430	342.857	95.359	−433.154	−396.877	13.820
1600	82.396	411.744	346.998	103.593	−434.937	−394.400	12.876
1700	82.481	416.742	350.955	111.837	−436.735	−391.811	12.039
1800	82.552	421.459	354.742	120.089	−438.549	−389.117	11.292
1900	82.612	425.924	358.372	128.347	−440.380	−386.321	10.621
2000	82.663	430.162	361.857	136.611	−442.229	−383.428	10.014
2100	82.708	434.197	365.206	144.880	−444.096	−380.442	9.463
2200	82.746	438.045	368.430	153.152	−445.982	−377.366	8.960
2300	82.780	441.724	371.538	161.429	−447.886	−374.205	8.498
2400	82.810	445.248	374.536	169.708	−449.810	−370.961	8.074
2500	82.836	448.629	377.432	177.991	−451.752	−367.635	7.681
2600	82.859	451.878	380.234	186.275	−453.714	−364.232	7.318
2700	82.879	455.006	382.945	194.562	−455.694	−360.752	6.979
2800	82.898	458.020	385.573	202.851	−1045.495	−355.264	6.628
2900	82.915	460.929	388.122	211.142	−1045.321	−330.617	5.955
3000	82.930	463 741	390.596	219.434	−1045.166	−305.974	5.327
3100	82.943	466.460	392.999	227.728	−1045.027	−281.336	4.740
3200	82.955	469.094	395.336	236.023	−1044.907	−256.703	4.190
3300	82.967	471.646	397.610	244.319	−1044.803	−232.074	3.673
3400	82.977	474.123	399.825	252.616	−1044.715	−207.447	3.187
3500	82.986	476.529	401.982	260.914	−1044.645	−182.823	2.728
3600	82.995	478.867	404 085	269.213	−1044.590	−158.200	2.295
3700	83.003	481.141	406.137	277.513	−1044.552	−133.579	1.886
3800	83.010	483.354	408.140	285.814	−1044.531	−108.957	1.498
3900	83.017	485.511	410.097	294.115	−1044.526	−84.337	1.130
4000	83.023	487.613	412.008	302.417	−1044.538	−59.717	0.780
4100	83.029	489.663	413.877	310.720	−1044.567	−35.096	0.447
4200	83.034	491.664	415.706	319.023	−1044.615	−10.474	0.130
4300	83.039	493.618	417.495	327.327	−1044.681	14.149	−0.172
4400	83.044	495.527	419.247	335.631	−1044.767	38.774	−0.460
4500	83.049	497.393	420.963	343.935	−1044.869	63.400	−0.736
4600	83.053	499.218	422.644	352.240	−1044.998	88.029	−1.000
4700	83.056	501.004	424.293	360.546	−1045.150	112.662	−1.252
4800	83.060	502.753	425.909	368.852	−1045.327	137.298	−1.494
4900	83.063	504 466	427.495	377.158	−1045.529	161.939	−1.726
5000	83.067	506.144	429.051	385.464	−1045.763	186.583	−1.949
5100	83.070	507.789	430.579	393.771	−1046.028	211.233	−2.163
5200	83.073	509.402	432.079	402.078	−1046.326	235.887	−2.370
5300	83.075	510.984	433.553	410.386	−1046.661	260.549	−2.568
5400	83 078	512.537	435.001	418.693	−1047.036	285.217	−2.759
5500	83.080	514.062	436.425	427.001	−1047.453	309.891	−2.943
5600	83.082	515.559	437.825	435.309	−1047.915	334.575	−3.121
5700	83.085	517.029	439.202	443.618	−1048.425	359.266	−3.292
5800	83.087	518.474	440.556	451.926	−1048.981	383.968	−3.458
5900	83.088	519.895	441.889	460.235	−1049.597	408.677	−3.618
6000	83.090	521.291	443.200	468.544	−1050.227	433.396	−3.773

PREVIOUS· December 1979 (1 atm)   CURRENT December 1979 (1 bar)

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$S°(298.15\ K) = [289.7 \pm 16]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 564.0 \pm 60\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [567.414]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[560](1)	[320](1)	[460](1)
[370](1)	[180](1)	[600](1)

Ground State Quantum Weight: [2]
$\sigma = [4]$
Point Group: [D_{2h}]
Bond Distance: Al–O = [1.80] Å
Bond Angles: O–Al–O = [90]°; Al–O–Al = [90]°
Product of the Moments of Inertia: $I_A I_B I_C = [2.889607 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(0\ K)$ is calculated from that of Al_2O_2[1] using the appearance potential 9.9 ± 0.5 eV.[2-3] We assume that the appearance potential is equal to the ionization potential for $Al_2O_2(g) \rightarrow Al_2O_2(g) + e^-(g)$. Other reported appearance potentials include 10 ± 1[4-5] and 10 eV.[6]

$\Delta_f H°(298.15\ K)$ is obtained from $\Delta_f H°(Al_2O_2, 0\ K)$ by using $IP(Al_2O_2)$ with JANAF[1] enthalpies $H°(0\ K)-H°(298.15\ K)$ for $Al_2O_2(g)$, Al_2O_2 (g) and e (g). $\Delta_r H°(Al_2O_2 \rightarrow Al_2O_2^+ + e^-, 298.15\ K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[7] $\Delta_f H°(298.15\ K)$ should be changed by −1.481 kcal·mol⁻¹ if it is to be used in the convention that excludes the enthalpy of the electron. MNDO calculations[8] predicted $\Delta_f H°(Al_2O_2^+, 298.15\ K) = 78.7$ and $[\Delta_f H°(Al_2O_2^+, 298.15\ K) - \Delta_f H°(Al_2O_2, 298.15\ K)] = 186.7\ kcal \cdot mol^{-1}$ for the linear Al–O–Al–O ion and neutral molecule; our adopted values are larger by 43 and 57 kcal·mol⁻¹, respectively.

Heat Capacity and Entropy

The structure of $Al_2O_2^+$ is probably even more uncertain than that of Al_2O_2.[1] MNDO calculations[8] predict an Al–O–Al–O ion that is essentially linear, but a similar prediction for the neutral molecule is contradicted by ab initio calculations.[1] Pending resolution of this discrepancy, we arbitrarily adopt a square–planar structure like that adopted for Al_2O_2.[1] We assume the same bond distance as in Al_2O_2 since the changes on ionization are predicted to be small.[8] Vibrational frequencies are estimated to be slightly lower than those of Al_2O_2.[1] We assume the ground electronic state to be doublet, due to the odd number of electrons, and neglect excited states. The principal moments of inertia are: $I_A = 8.6079 \times 10^{-39}$, $I_B = 14.5167 \times 10^{-39}$ and $I_C = 23.1246 \times 10^{-39}\ g \cdot cm^2$.

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

	J·K⁻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	−14.975	564.004		
100	41.878	229.595	343.628	−11.403			
200	58.897	264.099	295.729	−6.326			
250	64.816	277.913	290.814	−3.225			
298.15	68.923	289.700	289.700	0.	567.414	552.810	−96.850
300	69.056	290.127	289.701	0.128	567.436	552.719	−96.237
350	72.091	301.013	290.554	3.660	568.061	550.218	−82.115
400	74.295	310.790	292.483	7.323	568.722	547.624	−71.512
450	75.927	319.640	295.017	11.080	569.395	544.946	−63.256
500	77.162	327.706	297.888	14.909	570.062	542.194	−56.643
600	78.860	341.937	304.076	22.717	571.318	536.500	−46.706
700	79.936	354.180	310.379	30.661	572.391	530.609	−39.594
800	80.657	364.904	316.539	38.692	573.203	524.581	−34.252
900	81.162	374.435	322.452	46.785	573.687	518.470	−30.091
1000	81.529	383.006	328.086	54.920	552.608	513.846	−26.841
1100	81.803	390.790	333.438	63.087	552.994	509.951	−24.216
1200	82.013	397.918	338.519	71.279	553.365	506.021	−22.027
1300	82.178	404.489	343.344	79.489	553.720	502.061	−20.173
1400	82.309	410.584	347.932	87.713	554.060	498.075	−18.583
1500	82.415	416.266	352.300	95.950	554.384	494.064	−17.205
1600	82.503	421.588	356.466	104.196	554.691	490.033	−15.998
1700	82.575	426.592	360.445	112.450	554.982	485.983	−14.932
1800	82.636	431.314	364.253	120.710	555.255	481.916	−13.985
1900	82.688	435.783	367.901	128.977	555.510	477.834	−13.137
2000	82.732	440.026	371.402	137.248	555.747	473.740	−12.373
2100	82.770	444.063	374.766	145.523	555.965	469.634	−11.682
2200	82.803	447.914	378.005	153.801	556.164	465.519	−11.053
2300	82.832	451.596	381.125	162.083	556.344	461.394	−10.479
2400	82.857	455.122	384.135	170.368	556.504	457.262	−9.952
2500	82.880	458.504	387.043	178.655	556.644	453.124	−9.468
2600	82.900	461.755	389.854	186.944	556.766	448.981	−9.020
2700	82.917	464.884	392.575	195.234	556.868	444.834	−8.606
2800	82.933	467.900	395.212	203.527	−30.851	442.619	−8.257
2900	82.947	470.811	397.769	211.821	−28.595	459.488	−8.276
3000	82.960	473.623	400.251	220.116	−26.358	476.280	−8.293
3100	82.972	476.343	402.662	228.413	−24.138	492.999	−8.307
3200	82.982	478.978	405.006	236.711	−21.936	509.645	−8.319
3300	82.992	481.531	407.286	245.010	−19.750	526.223	−8.329
3400	83.001	484.009	409.506	253.309	−17.582	542.735	−8.338
3500	83.009	486.415	411.670	261.610	−15.431	559.183	−8.345
3600	83.016	488.754	413.779	269.911	−13.295	575.571	−8.351
3700	83.023	491.028	415.836	278.213	−11.177	591.899	−8.356
3800	83.029	493.243	417.844	286.516	−9.075	608.171	−8.360
3900	83.035	495.399	419.805	294.819	−6.989	624.387	−8.363
4000	83.041	497.502	421.721	303.123	−4.921	640.549	−8.365
4100	83.046	499.552	423.595	311.427	−2.870	656.661	−8.366
4200	83.050	501.554	425.427	319.732	−0.837	672.722	−8.367
4300	83.054	503.508	427.220	328.037	1.177	688.736	−8.366
4400	83.059	505.417	428.976	336.343	3.170	704.702	−8.366
4500	83.062	507.284	430.695	344.649	5.148	720.623	−8.365
4600	83.066	509.110	432.380	352.955	7.100	736.500	−8.363
4700	83.069	510.896	434.032	361.262	9.028	752.336	−8.361
4800	83.072	512.645	435.651	369.569	10.931	768.131	−8.359
4900	83.075	514.358	437.240	377.876	12.808	783.887	−8.356
5000	83.078	516.036	438.799	386.184	14.654	799.605	−8.353
5100	83.080	517.681	440.330	394.492	16.469	815.286	−8.350
5200	83.083	519.295	441.833	402.800	18.250	830.931	−8.347
5300	83.085	520.877	443.310	411.108	19.994	846.543	−8.343
5400	83.087	522.430	444.761	419.417	21.699	862.122	−8.339
5500	83.089	523.955	446.187	427.726	23.362	877.670	−8.335
5600	83.091	525.452	447.589	436.035	24.980	893.189	−8.331
5700	83.093	526.923	448.968	444.344	26.549	908.678	−8.327
5800	83.095	528.368	450.324	452.653	28.072	924.141	−8.323
5900	83.096	529.788	451.659	460.963	29.536	939.576	−8.318
6000	83.098	531.185	452.973	469.273	30.986	954.985	−8.314

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

Aluminum Oxide, Alpha (α–Al_2O_3, Corundum) CRYSTAL (α) $M_r = 101.96128$ Aluminum Oxide, Alpha (Al_2O_3) Al_2O_3(cr)

$\Delta_f H°(0\ K) = -1663.6 \pm 1.2\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 50.950 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -1675.7 \pm 1.2\ kJ \cdot mol^{-1}$

$T_{fus} = 2327 \pm 6\ K$ $\Delta_{fus} H° = 111.1 \pm 4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°$ is from calorimetric heats of combustion measured by Mah[1] and Holley and Huber.[2] Early measurements of the heat of combustion of Al were seriously biased,[3] but the sources of bias were minimized in later studies. After conversion to the present atomic weight of Al these studies yield $\Delta_f H°$ values of -400.5 ± 0.25,[1] -400.5 ± 0.3,[2] -399.2 ± 0.3,[3] and -402 ± 2 or -400.6 ± 1.4[4] kcal·mol^{-1}.

$\Delta_f H°$ is the value adopted by CODATA.[5] This direct calorimetric result has been criticized by various authors who proposed less negative $\Delta_f H°$ values, for example -393[6] and -397.1[7] kcal·mol^{1} based on emf and mineralogical data, respectively. Plausible explanations have been suggested[8, 9] for these different values. Moreover, the adopted $\Delta_f H°$ is confirmed by several direct and indirect measurements.

New direct confirmation includes $\Delta_f H° = -400.2 \pm 0.4$ and $\Delta_f H° < -399.9$ kcal·mol^{-1} obtained, respectively, from emf measurements[10] of $\Delta_f G°$(1030–1250 K) and from heat of combustion.[11] Indirect confirmation comes from data on reactions that link α–Al_2O_3 to other aluminum compounds. K_p data[12, 13] at high temperature yield $\Delta_f H° = -401.9 \pm 1.5$ kcal·mol^{-1} from $AlCl_3$(g) and -405.2 ± 1.5 from AlF_3(cr), although the latter value may be biased if aluminum oxyfluorides[14] were formed. $\Delta_f H°$ is confirmed to within 1.0 kcal·mol^{-1} by equilibria and calorimetry for independent reaction cycles involving each of the minerals mullite,[11] kaolinite[9] and gibbsite.[15] Data on many related minerals have been carefully evaluated by Haas *et al.*;[16] they found no inconsistency large enough to require a change in $\Delta_f H°$ of Al_2O_3.

Heat Capacity and Entropy

$C_p°$ is from the equations of Ditmars *et al.*[17, 19] for NBS Standard Reference Material 720 (α–Al_2O_3). These equations are based on NBS data: $C_p°$ of Chang[18] (8.6 to 371 K) and enthalpy data of Ditmars and Douglas[19] (323 to 1173 K) and Ditmars *et al.*[17] (1173 to 2257 K). We increase $C_p°$ slightly (by <0.2%) above 1700 K to avoid a rapidly rising extrapolation above T_{fus}. $C_p°$ from the equation[17, 19] has an upward inflection point near 2050 K that is not necessarily justified by the data.[17]

$S°(298.15\ K) = 12.177 \pm 0.02\ cal \cdot K^{-1} \cdot mol^{-1}$ is obtained from $C_p°$ based on $S°(9\ K) = 0.00053\ cal \cdot K^{-1} \cdot mol^{-1}$. CODATA[5] and Gurvich *et al.*[20] selected the slightly smaller values $S° = 12.17 \pm 0.02\ cal \cdot K^{-1} \cdot mol^{-1}$ and $H°(298.15\ K) - H°(0\ K) = 2.394 \pm 0.005\ kcal \cdot mol^{-1}$. We choose instead to be consistent with newly certified values for SRM 720.

Fusion Data and Sublimation Data

Refer to the liquid 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	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.020	−1663.608	−1663.608	INFINITE
100	12.855	4.295	101.230	−9 693	−1668.606	−1641.642	857.506
200	51.120	24.880	57.381	−6.500	−1673.383	−1612.656	421.183
298.15	79.015	50.950	50.950	0.	−1675.692	−1582.275	277 208
300	79.416	51.440	50.951	0.147	−1675.717	−1581.696	275.398
400	96.086	76.779	54.293	8.995	−1676.342	−1550.226	202.439
500	106.131	99.388	61.098	19.145	−1676.045	−1518.718	158.659
600	112.545	119.345	69.177	30.101	−1675.300	−1487.319	129.483
700	116.926	137.041	77.632	41.586	−1674.391	−1456.059	108.652
800	120.135	152.873	86.065	53.447	−1673.498	−1424.931	93.038
900	122.662	167.174	94.296	65.591	−1672.744	−1393.908	80.900
1000	124.771	180.210	102.245	77.965	−1693.394	−1361.437	71.114
1100	126.608	192.189	109.884	90.535	−1692.437	−1328.286	63.075
1200	128.252	203.277	117.211	103.280	−1691.366	−1295.228	56.380
1300	129.737	213.602	124.233	116.180	−1690.190	−1262.264	50.718
1400	131.081	223.267	130.965	129.222	−1688.918	−1229.393	45.869
1500	132.290	232.353	137.425	142.392	−1687.561	−1196.617	41.670
1600	133.361	240.925	143.628	155.675	−1686.128	−1163.934	37.999
1700	134.306	249.039	149.592	169.060	−1684.632	−1131.342	34.762
1800	135.143	256.740	155.333	182.533	−1683.082	−1098.841	31.888
1900	135.896	264.067	160.864	196.085	−1681.489	−1066.426	29.318
2000	136.608	271.056	166.201	209.710	−1679.858	−1034.096	27.008
2100	137.319	277.738	171.354	223.407	−1678.190	−1001.849	24.920
2200	138.030	284.143	176.336	237.174	−1676.485	−969.681	23.023
2300	138.741	290.294	181.158	251.013	−1674.743	−937.593	21.293
2327.000	138.934	291.914	182.434	254.761	--- ALPHA <--> LIQUID ---		
2400	139.453	296.214	185.829	264.922	−1672.963	−905.582	19.709
2500	140.206	301.922	190.360	278.905	−1671.142	−873.645	18.254
2600	140.959	307.435	194.757	292.963	−1669.279	−841.781	16.912
2700	141.754	312.770	199.030	307.098	−1667.369	−809.990	15.670
2800	142.591	317.940	203.185	321.315	−2253.212	−776.335	14.483
2900	143.511	322.960	207.229	335.620	−2249.002	−723.665	13.035
3000	144.474	327.841	211.168	350 019	−2244.729	−671.139	11.686

PREVIOUS: June 1975 CURRENT: December 1979

Aluminum Oxide, Delta (δ–Al_2O_3) CRYSTAL (δ) $M_r = 101.96128$ Aluminum Oxide, Delta (Al_2O_3) $Al_2O_3(cr)$

$\Delta_f H°(0\ K) = [-1653.9 \pm 4]\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = [50.6 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -1666.5 \pm 4\ kJ \cdot mol^{-1}$
$T_{fus} = [2308]\ K$ $\Delta_{fus} H° = [93.3]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of α–Al_2O_3[1] using $\Delta_r H°(978\ K) = -2.7 \pm 0.4\ kcal \cdot mol^{-1}$ for the irreversible process $\delta \rightarrow \alpha$. This yields $\Delta_r H°(298.15\ K) = -2.2\ kcal \cdot mol^{-1}$ based on our adopted functions. Yokokawa and Kleppa[2] determined $\Delta_r H°$ for the two crystalline forms from the difference in their heats of solution in an oxide melt at 978 K. DTA studies by Gani and McPherson[3] gave $\Delta_r H° = -2.8 \pm 0.5\ kcal \cdot mol^{-1}$. Assuming $T = -1400$ K, we derive $\Delta_r H°(298.15\ K) = -1.9\ kcal \cdot mol^{-1}$. This confirms the calometric result. Both samples of δ–Al_2O_3 had been obtained by rapid quenching from high temperature, one[2] from combustion of Al_4C_3 and the other[3] by a plasma method.

Heat Capacity and Entropy

$C_p°$ is assumed to be 3% larger than that of α–Al_2O_3[1] by comparison with the observed values for κ–Al_2O_3[1] and the adopted values for γ–Al_2O_3.[1] $S°$ is selected such that $\Delta_r G°(\kappa \rightarrow \delta) < 0$ below T_{fus} and $\Delta_r G°(\delta \rightarrow \alpha) < 0$ at $T \leq 2400$ K.

Marchidan *et al.*[4] measured enthalpy data (573–1177 K) for a sample designated only as TA–600 alumina. They attributed a transition at ~993 K (720°C) to the irreversible process $\eta \rightarrow \delta$. This temperature corresponds roughly to processes designated as either (γ or η) $\rightarrow \theta$ or $\gamma \rightarrow \delta$ by Lippens and Steggerda.[5] DTA data of Alevra *et al.*[6] showed an endotherm near 750 °C subsequent to the dehydration of hydroxide samples; however, TGA data indicated that the resulting alumina still retained considerable water at this temperature. The enthalpy data,[4] (1003–1177 K) are 4.7 ± 0.3% larger than those of α–Al_2O_3[1] and presumably correspond to an alumina containing a significant amount of water. The δ–Al_2O_3 used in $\Delta_f H°$ studies was presumably essentially anhydrous. Thus, we omit the enthalpy data[4] on the presumption that they are larger than those of our standard state which is anhydrous δ–Al_2O_3.

Phase Data

The stable crystalline form is corundum (α–alumina). Δ–alumina is one of several structurally related, metastable forms. These occur in "active alumina" and are much studied[5] due to their importance in adsorbents and catalysts. Lippens and Steggerda[5] summarized the classifications of metastable forms, their crystal stuctures and conditions of formaiton by dehydration. Mixtures of the closely related δ– and θ–aluminas are also formed by rapid cooling of droplets of molten alumina following their passage through a flame.[7] There is some controversy[5] over the X–ray data and unit–cell dimensions of δ–Al_2O_3 formed by the two methods. Recent data[8] for θ–Al_2O_3[5] suggest a similar controversy. Δ–alumina belongs to the "nearly anhydrous", high–temperature classification[5] based on the temperature of 600° to 900°C at which it forms during dehydration. The irreversible transitions $\delta \rightarrow \theta(+\alpha) \rightarrow \alpha$ are thermally activated at tempertures of 800°–1050 °C for the first step[5 6] and ~1200 °C for the final step.[5]

Fusion Data

The hypothetical melting point of metastable δ–phase is calculated as the temperature at which $\Delta_r G°(\delta \rightarrow l) = 0$. $\Delta_{fus} H°$ is the corresponding difference in $\Delta_f H°$.

References

[1] JANAF Thermochemical Tables: $Al_2O_3(cr, \alpha)$, $Al_2O_3(cr, \kappa)$, and $Al_2O_3(cr, \gamma)$, 12–31–79.
[2] T. Yokokawa and O. J. Kleppa, J. Phys. Chem. 68, 3246 (1964); J. Amer. Chem. Soc. 68, 3246 (1964).
[3] M. S. J. Gani and R. McPherson, Thermochim. Acta 7, 251 (1973).
[4] D. I. Marchidan, L. Pandele and A. Nicolescu, Rev. Roum. Chim. 17, 1493 (1972).
[5] B. C Lippens and J. J. Steggerda in "Physical and Chemical Aspects of Adsorbents and Catalysts," B. G. Linsen, Ed., Academic Press, New York, 171–211, (1970).
[6] V. Alevra, D. Ciomirtan and M. Ionescu, Rev. Roum. Chim. 17, 1379 (1972).
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[8] G. Yamaguchi, I. Yasui and W.–C. Chiu, Bull. Chem. Soc. Japan 43, 2487 (1970).

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	81.385	50.626	50.626	0.	−1666.487	−1572.974	275.579
300	81.799	51.131	50.628	0.151	−1666.507	−1572.394	273.778
400	98.968	77.231	54.070	9.264	−1666.867	−1540.932	201.225
500	109.315	100.518	61.079	19.719	−1666.266	−1509.504	157.697
600	115.922	121.073	69.400	31.004	−1665.192	−1478.248	128.693
700	120.434	139.300	78.109	42.834	−1663.938	−1447.188	107.991
800	123.739	155.608	86.795	55.050	−1662.689	−1416.311	92.476
900	126.342	170.338	95.273	67.558	−1661.571	−1385.582	80.417
1000	128.514	183.764	103.460	80.304	−1681.850	−1353.447	70.697
1100	130.406	196.103	111.329	93.251	−1680.516	−1320.670	62.713
1200	132.100	207.524	118.875	106.378	−1679.063	−1288.021	56.066
1300	133.630	218.159	126.108	119.666	−1677.500	−1255.496	50.446
1400	135.013	228.113	133.042	133.099	−1675.837	−1223.096	45.634
1500	136.258	237.471	139.696	146.664	−1674.084	−1190.819	41.468
1600	137.362	246.301	146.085	160.346	−1672.253	−1158.660	37.826
1700	138.336	254.658	152.228	174.132	−1670.355	−1126.618	34.617
1800	139.197	262.590	158.141	188.009	−1668.402	−1094.690	31.767
1900	139.973	270.137	163.838	201.968	−1666.402	−1062.872	29.220
2000	140.706	277.336	169.335	216.002	−1664.362	−1031.160	26.931
2100	141.438	284.218	174.643	230.109	−1662.283	−999.550	24.862
2200	142.171	290.815	179.774	244.289	−1660.165	−968.040	22.984
2300	142.904	297.151	184.741	258.543	−1658.008	−936.629	21.272
2400	143.636	303.248	189.552	272.870	−1655.810	−905.312	19.704
2500	144.412	309.128	194.219	287.272	−1653.570	−874.087	18.263
2600	145.188	314.806	198.748	301.752	−1651.285	−842.953	16.935
2700	146.007	320.301	203.149	316.311	−1648.952	−811.907	15.707
2800	146.868	325.626	207.428	330.954	−2234.367	−779.013	14.533
2900	147.817	330.797	211.594	345.688	−2229.729	−727.118	13.097
3000	148.808	335.824	215.651	360.519	−2225.023	−675.384	11.759

PREVIOUS: June 1975 CURRENT December 1979

Aluminum Oxide, Gamma (γ–Al$_2$O$_3$) **CRYSTAL (γ)** **M_r = 101.96128** **Aluminum Oxide, Gamma (Al$_2$O$_3$)** **Al$_2$O$_3$(cr)**

$\Delta_f H°(0\ \mathrm{K}) = [-1644.3 \pm 6.3]\ \mathrm{kJ \cdot mol^{-1}}$
$S°(298.15\ \mathrm{K}) = [52.3 \pm 8]\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ $\Delta_f H°(298.15\ \mathrm{K}) = -1656.9 \pm 6.3\ \mathrm{kJ \cdot mol^{-1}}$
$T_{fus} = [2289]\ \mathrm{K}$ $\Delta_{fus} H° = [78.49]\ \mathrm{kJ \cdot mol^{-1}}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of α–Al$_2$O$_3$[1] using $\Delta_r H°(978\ \mathrm{K}) = -5.3\ \mathrm{kcal \cdot mol^{-1}}$ for the irreversible process $\gamma \to \alpha$. Yokokawa and Kleppa[2] determined $\Delta_r H°$ for the two crystalline forms from the difference in their heats of solution in an oxide melt at 978 K. This yields $\Delta_r H°(298.15\ \mathrm{K}) = -4.5\ \mathrm{kcal \cdot mol^{-1}}$ based on our adopted functions. DTA studies by Gani and McPherson[3] gave $\Delta_r H°(\gamma \to \alpha) = -5.8 \pm 1.6\ \mathrm{kcal \cdot mol^{-1}}$. Assuming $T = -1400$ K, we derive $\Delta_r H°(298.15\ \mathrm{K}) = -4.4\ \mathrm{kcal\ mol^{-1}}$ which confirms the calorimetric result.[2] Yamada *et al.*[4] used dynamic, adiabatic calorimetry to measure $\Delta_r H°(773\ \mathrm{K}) = 12.6 \pm 1.1\ \mathrm{kcal \cdot mol^{-1}}$ for Al$_2$O$_3$H$_2$O(cr, boehmite) $\to$ Al$_2$O$_3$(γ) + H$_2$O(g). Enthalpies from[4 1] convert this to $\Delta_r H°(298.15\ \mathrm{K}) = 17.54 \pm 1.3\ \mathrm{kcal \cdot mol^{-1}}$, yielding $\Delta_f H°(\gamma$–Al$_2$O$_3$, 298.15 K$) = -398.1 \pm 1.5$ or $-396.7 \pm 2\ \mathrm{kcal \cdot mol^{-1}}$ based on new or old values for $\Delta_f H°$(boehmite, 298.15 K)) $= -473.4 \pm 0.4$ [5] or -472.0[6] $\mathrm{kcal \cdot mol^{-1}}$.

We adopt $\Delta_f H°(\gamma$, 298.15 K$) = -396.0 \pm 1.5\ \mathrm{kcal \cdot mol^{-1}}$ and $\Delta_r H°(\gamma \to \alpha$, 298.15 K$) = -4.5\ \mathrm{kcal \cdot mol^{-1}}$. These values derive[2] from the highest ignition temperature prior to the appearance of a more stable phase (κ– or α–Al$_2$O$_3$) in the sample. This standard state should involve maximum attainable crystal development and minimum residual water. γ–alumina shows much variability depending on its thermal history. Lower ignition temperatures gave values of $\Delta_r H°(\gamma \to \alpha)$ more negative by as much as 2.5 kcal·mol^{-1}.[2] Other reported values of $\Delta_r H°(\gamma \to \alpha)$, including -4.5 to -7.5,[3] -7.7,[7] -9.1,[8] -11.0[9] and -7.8[10] kcal·mol^{-1}, tend to be skewed toward more negative values. These values correspond to less stable samples, presumably with more residual water and less well developed crystal structure This is consistent with $\Delta_r H°(298.15\ \mathrm{K}) = -388 \pm 2\ \mathrm{kcal \cdot mol^{-1}}$ observed[4] for ρ'–Al$_2$O$_3$ which is nearly amorphous.

Heat Capacity and Entropy

$C_p°$ is assumed to be 4.7% larger than that of α–Al$_2$O$_3$.[1] Structural and related characteristics[11] suggest that $C_p°(\gamma) > C_p°(\kappa)$ which in turn is ~2.2% larger[1 4] than $C_p°(\alpha)$. Our estimate is derived from Marchidan *et al.*[12] who measured enthalpies (1003–1177 K) which are 4.7 ± 0.3% larger than those of α–Al$_2$O$_3$. $S°$ is estimated such that $\Delta_r G°(\gamma \to \alpha) < 0$ at $T \leq 2400$ K. This is consistent with observed stability relationships.[11,2]

Marchidan *et al.*[12] measured enthalpy data (573–1177 K) for a sample designated only as TA–600 alumina. They attributed a transition at ~993 K to the irreversible process $\eta \to \delta$. Comtemporary studies[11] from the same institution lead us to presume that the TA–600 sample retained a significant amount of water even above the transition. The "low–temperature" forms γ and η are difficult to distinquish;[11] they retain more water[11 13] than the "high–temperature" forms. This may explain the unusual enthalpy data attributed[12] to η–Al$_2$O$_3$, these deviate from α–Al$_2$O$_3$ by + 12.4% at 573 to 620 K and then decrease linearly to +3.8% at 991 K. These data do not seem suitable for standard–state γ–Al$_2$O$_3$ having minimum water content and maximum crystal development. We adopt instead the constant deviation of +4.7% found at higher temperature. Differential enthalpy analysis[8] gave an enthalpy 2% larger than α–Al$_2$O$_3$ at 1290 K, but the error is large (±4% in enthalpy) and no information is given on the sample history The observed $\Delta_r H(\gamma \to \alpha) = -9.1\ \mathrm{kcal \cdot mol^{-1}}$ [8] suggests the sample differed from our desired standard state.

The adopted entropy may be compared with the value $\Delta S°(\alpha \to \gamma) = 1.56\ \mathrm{cal \cdot K^{-1} \cdot mol^{-1}}$ estimated by Borer and Gunthard[14] for the "defect" spinel structure of γ–Al$_2$O$_3$. This yields $S°(\gamma$, 298.15 K$)) = 13.7$ or $14.3\ \mathrm{cal \cdot K^{-1}\ mol^{-1}}$ assuming $C_p°(\gamma)/C_p°(\alpha) = 1.00$ or 1.047, respectively. The authors' assumption[14] concerning the structure of γ–Al$_2$O$_3$[11] is overly simplified.

Phase Data

The stable crystalline form is corundum (α–alumina). γ–alumina is one of several structurally related, metastable forms. These occur in "active alumina" and are much studied[11] due to their importance in adsorbents and catalysts. Lippens and Steggerda[11] summarized the classifications of metastable forms, their crystal structures and conditions of formation by dehydration. "Low–temperature" forms γ and η have similar X–ray diffraction patterns. Their nomenclature is confused in the literature. The term γ–Al$_2$O$_3$ has been applied to either form and as a generic term for all low temperature forms. γ and η are often poorly crystallized and difficult to distinquish.[11] They retain various amounts of water[11 13] depending on their thermal history. The low–temperature forms are obtained by dehydrating temperatures not exceeding 600 °C and change irreversibly to "high–temperature" forms (δ, θ or κ) at 600° to 900 °C.[11 13 2]

Fusion Data

The hypothetical melting point of metastable γ–phase is calculated as the temperature at which $\Delta_r G°(\gamma \to \mathrm{l}) = 0$. $\Delta_{fus} H°$ is the corresponding difference in $\Delta_f H°$.

References

[1] JANAF Thermochemical Tables: Al$_2$O$_3$(cr, α), Al$_2$O$_3$(cr, δ) and Al$_2$O$_3$(cr, κ); 12–31–79; H$_2$O(g), 3–31–79.
[2] T. Yokokawa and O J. Kleppa, J Phys. Chem. 68, 3246 (1964).
[3] M. S. J. Gani and R. McPherson, Thermochim. Acta 7, 251 (1973).
[4] K. Yamada, T. Fukunaga, Y. Takahashi and T. Mukaibo, Denki Kagaku 41, 290 and 287 (1973).
[5] J. L. Haas, G. R Robinson and B. S. Hemingway, J Phys. Chem. Ref. Data 10, 575 (1981).
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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	82.729	52.300	52.300	0.	−1656.864	−1563.850	273.980
300	83.149	52.813	52.302	0.153	−1656.882	−1563.273	272.190
400	100.602	79.343	55.800	9.417	−1657.091	−1532.001	200.059
500	111.120	103.015	62.925	20.045	−1656.317	−1500.804	156.788
600	117.835	123.909	71.384	31.515	−1655.057	−1469.815	127.959
700	122.422	142.438	80.236	43.541	−1653.608	−1439.054	107.384
800	125.782	159 014	89.066	55.959	−1652.158	−1408.504	91.966
900	128.427	173.987	97.683	68.674	−1650.833	−1378.128	79.985
1000	130.635	187.635	106.006	81.629	−1670.901	−1346.370	70.327
1100	132.558	200.178	114.005	94.790	−1669.354	−1313.990	62.396
1200	134.280	211.787	121.675	108.134	−1667.684	−1281.757	55.793
1300	135.835	222.597	129.028	121.641	−1665.902	−1249.668	50.212
1400	137.241	232.716	136.076	135.296	−1664.017	−1217.720	45.434
1500	138.507	242.229	142.839	149.084	−1662.040	−1185.911	41.297
1600	139.629	251.204	149.334	162.992	−1659.983	−1154.236	37.682
1700	140.619	259.700	155.579	177.006	−1657.858	−1122.691	34.496
1800	141.495	267.762	161.589	191.112	−1655.675	−1091.274	31.668
1900	142.283	275.434	167.381	205.301	−1653.445	−1059.979	29 141
2000	143.028	282.751	172.968	219.567	−1651.174	−1028.802	26.870
2100	143.773	289.747	178.363	233.907	−1648.862	−997.740	24.817
2200	144.518	296 453	183.580	248.321	−1646.510	−966.788	22.954
2300	145.262	302.893	188.628	262.810	−1644.117	−935.946	21.256
2400	146.007	309.091	193.519	277.374	−1641.683	−905.209	19.701
2500	146.796	315.068	198.262	292.014	−1639.206	−874.573	18.273
2600	147.584	320.840	202.866	306.732	−1636.681	−844.037	16.957
2700	148.416	326.426	207.340	321.532	−1634.108	−813.599	15.740
2800	149.292	331.839	211.690	336.417	−2219.282	−781.322	14.576
2900	150.256	337.094	215.924	351.394	−2214.400	−730.053	13.150
3000	151.264	342.205	220.049	366.469	−2209.450	−678.952	11.822

PREVIOUS June 1975 CURRENT December 1979

Aluminum Oxide, Gamma (Al$_2$O$_3$) **Al$_2$O$_3$(cr)**

Aluminum Oxide, Kappa (κ–Al_2O_3) CRYSTAL(κ) $M_r = 101.96128$ Aluminum Oxide, Kappa (Al_2O_3) Al_2O_3(cr)

$\Delta_f H°(0\ K) = [-1650.0 \pm 4]\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = [53.6 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -1662.3 \pm 4\ kJ \cdot mol^{-1}$
$T_{fus} = [2312]\ K$ $\Delta_{fus} H° = [91.2]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of α–Al_2O_3[1] using $\Delta_r H°(978\ K) = -3.6\ kcal\ mol^{-1}$ for the irreversible process κ → α. This yields $\Delta_r H°(298.15\ K) = -3.2\ kcal \cdot mol^{-1}$ based on our adopted functions. Yokokawa and Kleppa[2] determined $\Delta_r H°$ for the two crystalline forms from the difference in their heats of solution in an oxide melt at 978 K. Yamada *et al*[3] derived $\Delta_r H°(298.15\ K) = -397 \pm 1\ kcal \cdot mol^{-1}$ from the same data.

Heat Capacity and Entropy

$C_p°$(380 to 1110 K) was measured by Takahashi *et al.*[4] using a dynamic, adiabatic calorimeter with an open-type container for the sample. Reproducibility of the data was reported to be within ±1.5% up to 1100 K. We represent the observed data by a $C_p°$ curve which is 2.2% larger than that of α–Al_2O_3.[1] Deviations from the adopted curve exceed 1.0% for only 3 of the 39 points:[4] i.e., −1.6% (400 K), +1.4% (993.8 K) and +1.3% (1070.8 K). Takahashi *et al.*[4] prepared their κ–Al_2O_3 by dehydration of tohdite ($Al_2O_3$1/5 H_2O) at 840 °C under a vacuum of 10^{-5} torr.

$S°$ is selected arbitrarily so that $\Delta_r G°(κ \to α) = 0$ near 2400 K. This is consistent with the view that κ–phase is unstable with respect to α–phase at all temperatures below T_{fus}.

Phase Data

The stable crystalline form is corundum (α–alumina). Kappa–alumina is one of several structurally related, metastable forms. These occur in "active alumina" and are much studied[5] due to their importance in adsorbents and catalysts. Lippens and Steggerda[5] summarized the classifications of metastable forms, their crystal structures and conditions of formation by dehydration. Okumiya *et al.*[6] recently published an extensive study on the formation and structural relations of κ–Al_2O_3 and its precursors κ'–Al_2O_3 and tohdite. κ–alumina belongs to the "nearly anhydrous", high-temperature classification[5] based on its formation temperture of 900° to 1000 °C (somewhat lower in vacuo). The irreversible transition κ → α is thermally activated at ~1200 °C.[2,5] Thermochemical studies cited in this table presume that the samples of κ–Al_2O_3 were essentially anhydrous.

Fusion Data

The hypothetical melting point of metastable κ–phase is calculated as the temperature at which $\Delta_r G°(κ \to l) = 0$. $\Delta_{fus} H°$ is the corresponding difference in $\Delta_f H°$.

References

[1] JANAF Thermochemical Tables Al_2O_3(cr, α), 12–31–79.
[2] T. Yokokawa and O. J. Kleppa, J. Phys. Chem. 68, 3246 (1964).
[3] K. Yamada, T. Fukunaga, Y. Takahashi and T. Mukaibo, Denki Kagaku 41, 290 (1973).
[4] Y. Takahashi, K. Yamada, T Fukunaga and T. Mukaibo, Denki Kagaku 41, 287 (1973).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	80.753	53.555	53.555	0.	−1662.303	−1569.663	274 998
300	81.164	54.056	53.557	0 150	−1662.325	−1569 088	273.203
400	98.199	79.953	56.972	9 192	−1662 755	−1537.909	200.830
500	108.466	103 059	63.926	19.566	−1662.235	−1506.744	157.408
600	115.021	123.455	72.183	30.763	−1661.249	−1475.734	128.474
700	119 498	141.540	80.824	42.501	−1660.087	−1444.905	107.820
800	122.778	157.721	89.443	54.622	−1658.933	−1414.245	92.341
900	125.361	172.337	97.855	67.034	−1657.912	−1383.722	80.309
1000	127.516	185.659	105.979	79.680	−1678.290	−1351.782	70 610
1100	129.393	197 902	113.786	92.527	−1677.056	−1319.189	62.643
1200	131.074	209.234	121.274	105.552	−1675.705	−1286.715	56.009
1300	132.592	219 786	128.451	118.736	−1674.245	−1254.358	50.401
1400	133.964	229.663	135.331	132.065	−1672.687	−1222.116	45.598
1500	135.200	238.949	141.933	145.525	−1671.039	−1189.990	41.439
1600	136.295	247.710	148.272	159.100	−1669.314	−1157.976	37.804
1700	137.261	256.003	154.368	172.779	−1667.524	−1126.072	34.600
1800	138.116	263 873	160.235	186.549	−1665.678	−1094.275	31.755
1900	138.886	271.361	165.888	200.399	−1663.787	−1062.582	29.212
2000	139.613	278.504	171.342	214.324	−1661.856	−1030.989	26.927
2100	140.340	285.333	176.608	228.322	−1659 886	−999.494	24 861
2200	141.067	291.878	181.700	242.392	−1657.878	−968.093	22.985
2300	141.794	298.165	186.628	256.535	−1655.832	−936.785	21.275
2400	142.521	304.215	191.402	270.751	−1653.746	−905.567	19.709
2500	143.290	310.049	196.032	285.041	−1651.617	−874.437	18.270
2600	144.060	315.683	200.526	299.408	−1649.445	−843.392	16 944
2700	144.873	321.135	204.893	313.855	−1647.225	−812.432	15 717
2800	145.728	326.419	209.139	328.384	−2232.754	−779.619	14.544
2900	146.668	331.549	213.272	343.003	−2228.230	−727.802	13.109
3000	147.652	336.538	217.298	357.719	−2223.639	−676.141	11.773

PREVIOUS: June 1975 CURRENT: December 1979

Aluminum Oxide (Al_2O_3) LIQUID M_r = 101.96128 Aluminum Oxide (Al_2O_3) $Al_2O_3(l)$

$S°(298.15 K) = [67.298]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15 K) = [-1620.567]\ kJ·mol^{-1}$

$T_{fus} = 2327 \pm 6 K$ $\Delta_{fus}H° = 111.1 \pm 4.2\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of the crystal by adding the enthalpy of fusion and the difference in enthalpy, $H°(2327 K)-H°(298.15 K)$, between the crystal and liquid.

Heat Capacity and Entropy

Enthalpy data for the liquid include those of Shpil'rain *et al.*,[1,2] (2326 to 3104 K), Sheindlin *et al.*,[3] (2350 to 2800 K), Kantor *et al.*[4,5] (2337 to 2480 K), and approximate values of West and Ishihara[6] (2345 to 2495 K). The latest study[1,2] is the most extensive. It satisfactorily resolves the discrepancy in $C_p°$ which was reported earlier to be 47.7[3] or 34.6[4] cal·K⁻¹·mol⁻¹. The new data[1,2] yield 46.0 cal·K⁻¹·mol⁻¹, assuming $C_p°$ is independent of temperature. Although Shpil'rain *et al.*[1,2] derived a $C_p°$ which decreases linearly with increasing temperature, this does not significantly improve the fit of the enthalpy data. The apparent value of the temperature coefficient of $C_p°$ is very data dependent; it changes sign on omission of the point at 2326 K (2323 K, IPTS–48).

We adopt $C_p° = 46.0$ cal·K⁻¹·mol⁻¹. Compared to our adopted functions, the enthalpy data deviate by < ± 1.0%,[1,2] −0.9 to −0.1%[3] (equation), +2.4 to +0.2%[4,5] and +2 to +5%.[6] We assume a glass transition at 1350 K, below which $C_p°$ is taken to be the same as for Al_2O_3(cr, α). The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

$T_{fus} = 2054 \pm 6°C$ was recommended by Schneider[7] as the result of a cooperative measurement of the melting point by nine groups in seven countries. We adopt this value. It is confirmed by several recent studies (e.g.8–10); however, Nelson *et al.*[11] suggested the possibility that T_{fus} may be somewhat different in an oxygen atmosphere than in inert gases or vacuum.

$\Delta_{fus}H°$ is the difference at T_{fus} between the adopted enthalpy fits of Al_2O_3(l) and Al_2O_3(α). Reported calorimetric values of $\Delta_{fus}H°$ include 25.7 ± 1.3,[1,2] 25.9,[3] and 28.3 ± 0.6[4,5] kcal·mol⁻¹.

Sublimation and Vaporization Data

Vaporization of Al_2O_3(α) and Al_2O_3(l) has been studied by several methods.[12-22] Additional references are cited by Farber *et al.*[14] and Burns.[16] Vaporization is sometimes considered to be congruent but the vapor composition is complex.[14,16] Atomic species predominate below T_{fus}, but molecular species (e.g., AlO and Al_2O) become increasingly important at higher temperatures. For the crystal the average vaporization coefficient is α < 0.3.[12,14-16] The rate of evaporation increases discontinuously during melting by radiative heating; this has been attributed to a change in α[16] or to a change in absorbance and emittance.[19] Other work[11] suggests that the radiative properties change on melting. Container materials such as Mo or W cause changes in the partial pressures of O, Al and the molecular species observed in effusion studies;[14,16,21] these effects can be predicted with a model developed by Banon *et al.*[20] Partial pressures reported[14,22] for all observed vapor species yield an overall O/Al ratio of ~1.1 instead of the value 1.5 required for congruent vaporization; however, these data do not yield a definite conclusion about congruency due to their relatively large uncertainties.

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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⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	79.015	67.298	67.298	0.	−1620.567	−1532.025	268.404
300	79.416	67.788	67.299	0.147	−1620.592	−1531.475	266.654
400	96.086	93.127	70.641	8.995	−1621.217	−1501.641	196.094
500	106.131	115 736	77.446	19.145	−1620.920	−1471.768	153.755
600	112.545	135.693	85.525	30.101	−1620.175	−1442.003	125.538
700	116.926	153.389	93.980	41.586	−1619.266	−1412.378	105.393
800	120.135	169.222	102.413	53.447	−1618.373	−1382.885	90.293
900	122.662	183.522	110.644	65.591	−1617.619	−1353.496	78.555
1000	124 771	196.558	118.593	77.965	−1638.269	−1322.660	69.089
1100	126.608	208.537	126.233	90.535	−1637.312	−1291.144	61.311
1200	128.252	219.625	133.559	103.280	−1636.241	−1259.721	54.834
1300	129.737	229.951	140.581	116.180	−1635.065	−1228.392	49.357
1350 000	130.424	234.860	143.983	122.684	——— GLASS <––> LIQUID ———		
1350.000	192.464	234.860	143.983	122.684	TRANSITION		
1400	192.464	241.859	147.354	132.308	−1630.708	−1197.213	44.669
1500	192 464	255.138	154 102	151.554	−1623.274	−1166.509	40.621
1600	192.464	267.559	160.809	170.800	−1615.878	−1136.299	37.096
1700	192.464	279.227	167.435	190.047	−1608.520	−1106.551	34.000
1800	192.464	290.228	173.954	209.293	−1601.197	−1077.235	31.261
1900	192.464	300.634	180.350	228.540	−1593.910	−1048.325	28.820
2000	192.464	310.507	186.613	247.786	−1586.658	−1019.797	26.634
2100	192.464	319.897	192.739	267.032	−1579.440	−991.632	24.665
2200	192.464	328.850	198.724	286.279	−1572.256	−963.809	22.884
2300	192.464	337.406	204.569	305.525	−1565.106	−936.313	21.264
2327.000	192.464	339.652	206.123	310.722	––– ALPHA <––> LIQUID –––		
2400	192.464	345.597	210.275	324.772	−1557.989	−909.127	19.787
2500	192.464	353.454	215.846	344.018	−1550.905	−882.237	18.433
2600	192.464	361 002	221.285	363.264	−1543.853	−855.629	17.190
2700	192.464	368.266	226.595	382.511	−1536.832	−829.292	16.044
2800	192.464	375.265	231.781	401.757	−2117.645	−801.279	14.948
2900	192.464	382.019	236.845	421.004	−2108.494	−754.429	13.589
3000	192.464	388.544	241.794	440.250	−2099.372	−707.892	12.325
3100	192.464	394.855	246.630	459.496	−2090.279	−661.658	11.149
3200	192.464	400.965	251.358	478.743	−2081.214	−615.720	10.051
3300	192.464	406.888	255.982	497.989	−2072.175	−570.063	9.023
3400	192.464	412.633	260.505	517.236	−2063.163	−524.679	8.061
3500	192.464	418.212	264.932	536.482	−2054.176	−479.561	7.157
3600	192.464	423.634	269.265	555.728	−2045.214	−434.699	6.307
3700	192.464	428.908	273.509	574.975	−2036.276	−390.086	5.507
3800	192.464	434 040	277.666	594.221	−2027.363	−345.712	4.752
3900	192.464	439.040	281.740	613.468	−2018.474	−301.574	4.039
4000	192.464	443.912	285.734	632.714	−2009.610	−257.664	3.365

PREVIOUS: June 1975 CURRENT: December 1979

Aluminum Oxide (Al_2O_3) $Al_2O_3(l)$

Aluminum Oxide (Al_2O_3) CRYSTAL(α)-LIQUID M_r = 101.96128 Aluminum Oxide (Al_2O_3) Al_2O_3(cr,l)

0	to 2327 K	crystal, alpha (corundum)
above	2327 K	liquid

Refer to the individual tables for details.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.020	−1663.608	−1663.608	INFINITE
100	12.855	4.295	101.230	−9.693	−1668.606	−1641.642	857.506
200	51 120	24.880	57.381	−6.500	−1673.383	−1612.656	421.183
298.15	79.015	50.950	50.950	0.	−1675.692	−1582.275	277.208
300	79.416	51 440	50.951	0.147	−1675.717	−1581.696	275.398
400	96.086	76.779	54.293	8.995	−1676.342	−1550.226	202.439
500	106.131	99.388	61.098	19.145	−1676.045	−1518.718	158.659
600	112.545	119.345	69.177	30.101	−1675.300	−1487.319	129.483
700	116.926	137.041	77.632	41.586	−1674.391	−1456.059	108.652
800	120.135	152.873	86.065	53.447	−1673.498	−1424.931	93.038
900	122.662	167.174	94.296	65.591	−1672.744	−1393.908	80.900
1000	124.771	180.210	102.245	77.965	−1693.394	−1361.437	71.114
1100	126.608	192.189	109.884	90.535	−1692.437	−1328.286	63.075
1200	128.252	203.277	117.211	103.280	−1691.366	−1295.228	56.380
1300	129.737	213.602	124.233	116.180	−1690.190	−1262.264	50.718
1400	131.081	223.267	130.965	129.222	−1688.918	−1229.393	45.869
1500	132.290	232.353	137.425	142.392	−1687.561	−1196.617	41.670
1600	133.361	240.925	143.628	155.675	−1686.128	−1163.934	37.999
1700	134.306	249.039	149.592	169.060	−1684.632	−1131.342	34.762
1800	135.143	256.740	155.333	182.533	−1683.082	−1098.841	31.888
1900	135.896	264.067	160.864	196.085	−1681.489	−1066.426	29.318
2000	136.608	271.056	166.201	209.710	−1679.858	−1034.096	27.008
2100	137.319	277.738	171.354	223.407	−1678.190	−1001.849	24.920
2200	138.030	284.143	176.336	237.174	−1676.485	−969.681	23.023
2300	138.741	290.294	181.158	251.013	−1674.743	−937.593	21.293
2327.000	138.934	291.914	182.434	254.761	ALPHA <––> LIQUID		
2327.000	192.464	339.652	182.434	365.847	TRANSITION		
2400	192.464	345.597	187.307	379.896	−1557.989	−909.127	19.787
2500	192.464	353.454	193.796	399.143	−1550.905	−882.237	18.433
2600	192.464	361.002	200.083	418.389	−1543.853	−855.629	17.190
2700	192.464	368.266	206.179	437.636	−1536.832	−829.292	16.044
2800	192.464	375.265	212.093	456.882	−2117.645	−801.279	14.948
2900	192.464	382.019	217.837	476.128	−2108.494	−754.429	13.589
3000	192.464	388.544	223.419	495.375	−2099.372	−707.892	12.325
3100	192.464	394.855	228.848	514.621	−2090.279	−661.658	11.149
3200	192.464	400.965	234.132	533.868	−2081.214	−615.719	10.051
3300	192.464	406.888	239.277	553.114	−2072.175	−570.063	9.023
3400	192.464	412.633	244.292	572.360	−2063.162	−524.679	8.061
3500	192.464	418.212	249.182	591.607	−2054.176	−479.561	7.157
3600	192.464	423.634	253.953	610.853	−2045.213	−434.699	6.307
3700	192.464	428.908	258.610	630.100	−2036.276	−390.086	5.507
3800	192.464	434.040	263.160	649.346	−2027.363	−345.712	4.752
3900	192.464	439.040	267.606	668.592	−2018.474	−301.574	4.039
4000	192.464	443.912	271.953	687.839	−2009.609	−257.664	3.365

PREVIOUS. CURRENT December 1979

Aluminum Silicate, Andalusite (Al_2SiO_5) CRYSTAL M_r = 162.04558 Aluminum Silicate, Andalusite (Al_2SiO_5) $Al_2O_5Si_1(cr)$

$\Delta_fH°(0\ K) = -2575.16 \pm 2.1\ kJ\cdot mol^{-1}$

$S°(298.15\ K) = 93.22 \pm 0.4\ J\cdot K^{-1}\cdot mol^{-1}$ $\Delta_fH°(298.15\ K) = -2592.07 \pm kJ\cdot mol^{-1}$

Enthalpy of Formation

The heat of the reaction $Al_2O_3(cr, \alpha) + SiO_2(quartz) \rightarrow Al_2SiO_5$ (andalusite) has been determined at 968 K by Holm and Kleppa[1, 2] to be $-1.99 \pm 0.17\ kcal\cdot mol^{-1}$. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to $\Delta_rH°(298.15\ K) = -1.42\ kcal\cdot mol^{-1}$ which is used to calculate the adopted value for the enthalpy of formation.

The above value is in serious disagreement with the solution data of Neumann;[3] this work, however, has recently been questioned by several workers. Flood *et al.*[4] suggested that $\Delta_rH°$ was between 0 and $-10\ kcal\cdot mol^{-1}$. Pankratz *et al.*[5] conclude that $\Delta_rH°$ should lie between 0 and $-6\ kcal\cdot mol^{-1}$. Waldbaum[6] calculated $\Delta_rH° = -1.108\ kcal\cdot mol^{-1}$ from high temperature–high pressure equilibria. These latter values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.9 to 296.2 K by Todd.[7] The entropy is based on $S°(51\ K) = 0.62\ cal\cdot K^{-1}\cdot mol^{-1}$. The high temperature enthalpy has been measured to 1600 K by Pankratz *et al.*[5] The low and high temperature data were joined smoothly together by means of a Shomate function plot.[8] Since all the aluminum and silicon atoms occupy differently coordinated sites, there is no possibility of any residual entropy of mixing in this polymorph.

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

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	$\log K_f$
0	0.	0.	INFINITE	−17.093	−2575.159	−2575 159	INFINITE
100	30.323	13.563	174.899	−16.134	−2582.696	−2538.944	1326.209
200	84.605	51.844	103.323	−10.296	−2588.917	−2492.553	650.988
298.15	122.755	93.221	93.221	0.	−2592.072	−2444.482	428.263
300	123.320	93.982	93.223	0.228	−2592.107	−2443.567	425.463
400	149.565	133.277	98.402	13.950	−2592.950	−2393.872	312.608
500	165.368	168.473	108.968	29.752	−2592.338	−2344.152	244.892
600	174.515	199.471	121.524	46.768	−2591.068	−2294.628	199.765
700	181.067	226.884	134.656	64.560	−2589.556	−2245.340	167.549
800	186.121	251.401	147.744	82.926	−2588.003	−2196.273	143.402
900	190.351	273.572	160.512	101.754	−2586.532	−2147.396	124.632
1000	194.041	293.822	172.845	120.977	−2606.407	−2097.155	109.544
1100	197.380	312.475	184.702	140.550	−2604.612	−2046.314	97.171
1200	200.481	329.783	196.080	160.444	−2602.639	−1995.646	86.868
1300	203.414	345.947	206.993	180.640	−2600.491	−1945.149	78.157
1400	206.225	361.125	217.466	201.122	−2598.175	−1894.824	70 697
1500	208.949	375.446	227.525	221.882	−2595.693	−1844.671	64.237
1600	211.602	389.016	237.198	242.910	−2593.049	−1794.688	58.591
1700	214.200	401.923	246.511	264.200	−2640.423	−1744.428	53.600
1800	216.756	414.238	255.489	285.748	−2637.235	−1691.815	49.095
1900	219.283	426.026	264.157	307.550	−2633.851	−1639.382	45.070
2000	221.781	437.337	272.535	329.604	−2630.273	−1587.133	41.452
2100	224.258	448.218	280.644	351.906	−2626.505	−1535.068	38.183
2200	226.714	458.707	288.500	374.455	−2622.546	−1483.186	35.215
2300	229.149	468.839	296.122	397.248	−2618.399	−1431.490	32.510
2400	231.563	478.642	303.524	420.284	−2614.066	−1379 978	30.034
2500	233.957	488.144	310.720	443.560	−2609.546	−1328.650	27.761
2600	236.329	497.366	317.722	467.075	−2604.842	−1277.506	25.665
2700	238.680	506.329	324.542	490.825	−2599.954	−1226.546	23.729
2800	241.011	515.052	331.191	514.810	−3182.686	−1173.836	21.898
2900	243.321	523.550	337.678	539.027	−3175.242	−1102.224	19.853
3000	245.609	531.837	344.013	563.473	−3167.617	−1030.869	17.949

PREVIOUS. September 1966 CURRENT: September 1967

Aluminum Silicate, Kyanite (Al_2SiO_5) CRYSTAL M_r = 162.04558 Aluminum Silicate, Kyanite (Al_2SiO_5) $Al_2O_5Si_1(cr)$

$\Delta_f H°(0\ K) = -2576.37 \pm 2.1\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 83.815 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -2594.33 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The heat of the reaction $Al_2O_3(cr, \alpha) + SiO_2(quartz) \rightarrow Al_2SiO_5(cr, kyanite)$ has been determined at 968 K by Holm and Kleppa[1,2] to be $-2.37 \pm 0.15\ kcal \cdot mol^{-1}$. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to $\Delta_r H°(298.15\ K) = -1.96\ kcal \cdot mol^{-1}$, which is used to calculate the adopted value for the heat of formation of kyanite.

The above value is in serious disagreement with the solution data of Neumann.[3] This work, however, has recently been questioned by several workers. Flood and Knapp[4] suggested that $\Delta_r H°$ was between 0 and $-10\ kcal \cdot mol^{-1}$. Pankratz Kelley[5] conclude that $\Delta_r H°$ should lie between 0 and $-6\ kcal \cdot mol^{-1}$. From phase equilibria, Haskell and DeVries[6] obtained $\Delta_r H° = -2 \pm 7\ kcal \cdot mol^{-1}$. Waldbaum[7] calculated $\Delta_r H° = -0.622\ kcal \cdot mol^{-1}$ from high temperature–high pressure equilibria. These latter values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.8 to 296.3 K by Todd.[8] The entropy is based on $S°(51\ K) = 0.33\ cal \cdot K^{-1} \cdot mol^{-1}$. The high temperature enthalpy has been measured to 1500K by Pankratz and Kelley.[5] The low and high temperature data were joined smoothly together by means of a Shomate function plot.[9] The high temperature heat capacity has been measured between 100° and 1200°C by Leonidov, Barskii and Khitarov.[10] The values reported are in excellent agreement with the adopted functions. Since the aluminum atoms and the silicon atoms occupy different types of sites there is no possibility of any residual entropy of mixing in this polymorph.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.045	−2576.370	−2576.370	INFINITE
100	23.695	8.935	162.808	−15.387	−2584.209	−2539.995	1326.757
200	80.977	43.273	93.769	−10.099	−2590.980	−2492.902	651.079
298.15	121.751	83.815	83.815	0.	−2594.331	−2443.937	428.168
300	122.306	84.570	83.817	0.226	−2594.368	−2443.004	425.365
400	148.277	123.509	88.949	13.824	−2595.336	−2392.351	312.409
500	165.498	158.566	99.433	29.567	−2594.783	−2341.644	244 630
600	176.230	189.745	111.939	46.684	−2593.412	−2291.137	199.461
700	183.238	217.463	125.072	64.674	−2591.701	−2240.890	167.217
800	188.280	242.271	138.199	83.258	−2589.930	−2190.896	143.051
900	192.359	264.685	151.027	102.292	−2588.254	−2141.119	124.267
1000	196.213	285.154	163.431	121.723	−2607.920	−2090.000	109.170
1100	199.761	304.023	175.366	141.523	−2605.899	−2038.304	96 791
1200	203.167	321.554	186.826	161.673	−2603.669	−1986.801	86.483
1300	206.100	337.933	197.827	182.138	−2601.253	−1935.492	77.769
1400	208.861	353.308	208.389	202.887	−2598.670	−1884.376	70.307
1500	211.451	367.806	218.538	223.902	−2595.932	−1833.450	63.846
1600	214.129	381.538	228.300	245.181	−2593.037	−1782.711	58.200
1700	216.727	394.598	237.701	266.724	−2640.158	−1731.712	53.209
1800	219.302	407.059	246.766	288.526	−2636.716	−1678.373	48.705
1900	221.853	418.984	255.519	310.584	−2633.077	−1625.229	44.681
2000	224.380	430.428	263.980	332.896	−2629.241	−1572.283	41.064
2100	226.855	441.436	272.170	355.458	−2625.212	−1519.533	37.796
2200	229.321	452.046	280.107	378.267	−2620.994	−1466.979	34.831
2300	231.776	462.294	287.806	401.322	−2616.585	−1414.623	32.127
2400	234.221	472.210	295.284	424.622	−2611.987	−1362.462	29.653
2500	236.655	481.821	302.554	448.165	−2607.200	−1310.496	27.381
2600	239.079	491.150	309.630	471.952	−2602.224	−1258.725	25.288
2700	241.493	500.218	316.521	495.981	−2597.058	−1207.149	23.354
2800	243.896	509.044	323.240	520.251	−3179.505	−1153.832	21.525
2900	246.289	517.644	329.796	544.760	−3171.768	−1081.625	19.482
3000	248.672	526.034	336.198	569.508	−3163.841	−1009.684	17.580

PREVIOUS: September 1966 CURRENT: September 1967

Aluminum Silicate, Sillimanite (Al_2SiO_5) CRYSTAL M_r = 162.04558 Aluminum Silicate, Sillimanite (Al_2SiO_5) $Al_2O_5Si_1(cr)$

$\Delta_fH°(0\ K) = -2572.52 \pm 2.1\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 96.179 \pm 0.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = -2589.10 \pm 2.1\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The heat of the reaction $Al_2O_3(cr, \alpha) + SiO_2(quartz) \rightarrow Al_2SiO_5(sillimanite)$ has been determined at 968 K by Holm and Kleppa[1,2] to be $-1.51 \pm 0.15\ kcal{\cdot}mol^{-1}$. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to $\Delta_fH°(298.15\ K) = -0.71\ kcal{\cdot}mol^{-1}$ which is used to calculate the adopted value for the enthalpy of formation.

The above value is in serious disagreement with the solution data of Neumann;[3] this work, however, has recently been questioned by several workers. Flood and Knapp[4] suggested that $\Delta_rH°$ was between 0 and $-10\ kcal{\cdot}mol^{-1}$. Pankratz and Kelley[5] conclude that $\Delta_rH°$ should lie between 0 and $-6\ kcal{\cdot}mol^{-1}$. Waldbaum[6] calculated $\Delta_rH° = -0\ 356\ kcal{\cdot}mol^{-1}$ from high temperature–high pressure equilibria. These latter values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.4 to 296.5 K by Todd.[7] The entropy is based on $S°(51\ K) = 0.73\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. The high temperature enthalpy has been measured to 1500 K by Pankratz and Kelley.[5] The low and high temperature data were joined smoothly together by means of a Shomate function plot.[8] The crystal structure of sillimanite indicates that there is no mixing of the tetra-coordinated aluminum and silicon atoms.[9] Thus there should be no residual entropy at 0 K.

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

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−17.424	−2572.519	−2572.519	INFINITE
100	32.277	15.099	178.603	−16.350	−2579.942	−2536.344	1324.850
200	85.773	54.593	106.303	−10.342	−2585.993	−2490.179	650.368
298.15	122.215	96.179	96.179	0.	−2589.101	−2442.394	427.897
300	122.769	96.937	96.182	0.227	−2589.137	−2441.483	425.100
400	147.478	135.871	101.322	13.820	−2590.110	−2392.070	312.372
500	163.197	170.578	111.773	29.402	−2589 718	−2342.584	244.728
600	173.025	201.248	124.183	46.239	−2588.627	−2293.253	199.645
700	179.757	228.445	137.172	63.891	−2587.254	−2244.131	167.459
800	184.996	252.798	150.130	82.135	−2585.824	−2195.211	143.333
900	189.510	274.853	162.782	100.864	−2584.452	−2146.468	124.578
1000	193.535	295.031	175.012	120.019	−2604.393	−2096.351	109.502
1100	197.158	313.647	186.780	139.554	−2602.637	−2045.629	97.139
1200	200.765	330.958	198.082	159.451	−2600.661	−1995.078	86.843
1300	204.292	347.168	208.933	179.706	−2598.455	−1944.701	78 139
1400	207.577	362.429	219.357	200.300	−2596.027	−1894.501	70.685
1500	210.777	376.860	229.381	221.218	−2593.386	−1844.484	64.231
1600	213.911	390.563	239.030	242.453	−2590.535	−1794.649	58.589
1700	216.999	403.624	248.331	263.999	−2637.654	−1744.552	53.604
1800	220.045	416.114	257.308	285.852	−2634.161	−1692 117	49.104
1900	223.062	428.092	265.983	308.007	−2630.424	−1639 881	45.083
2000	226.053	439.610	274.378	330.463	−2626.444	−1587 849	41.470
2100	229.013	450.711	282.512	353.216	−2622.224	−1536.022	38.206
2200	231.964	461.432	290.403	376.265	−2617.765	−1484.400	35.244
2300	234.906	471.809	298.066	399.609	−2613.068	−1432.989	32.544
2400	237.840	481.868	305.516	423.246	−2608.133	−1381.787	30.074
2500	240.764	491.637	312.766	447.176	−2602.959	−1330.795	27.805
2600	243.680	501.136	319.829	471.399	−2597.547	−1280.014	25.716
2700	246.586	510.387	326.716	495.912	−2591.897	−1229.446	23.785
2800	249.484	519 408	333.438	520.716	−3173.809	−1177.155	21.960
2900	252.373	528.213	340.003	545.809	−3165.489	−1105.994	19.921
3000	255.253	536.817	346.420	571.190	−3156.929	−1035.121	18.023

PREVIOUS: September 1966 CURRENT: September 1967

Aluminum Sulfide (Al_2S_3) CRYSTAL M_r = 150.14308 Aluminum Sulfide (Al_2S_3) Al_2S_3(cr)

$\Delta_f H°(0\ K) = -647.35 \pm 3.8\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 116.85 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -651.03 \pm 3.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted value for $\Delta_f H°(298.15\ K)$ is taken from the recent solution calorimetric studies of Ko *et al.*[1] The discrepancy between this value and other measured values is quite large. Korshunov[2] and Kapustinskii and Golutvin[3] determined values of $\Delta_f H°(298.15\ K) = -121.5 \pm 0.4\ kcal \cdot mol^{-1}$ and $-172.9 \pm 4.3\ kcal \cdot mol^{-1}$, respectively, by direct combination of the elements. Sabatier[4] measured a value of $-75.0\ kcal \cdot mol^{-1}$ for the reaction $Al_2S_3(cr) + 3H_2O(l) \rightarrow Al_2O_3 3H_2O(cr) + H_2S(g)$. The heat of formation of Al_2S_3 based on this heat has been widely quoted[1, 5] as $-140.5\ kcal \cdot mol^{-1}$ which is an apparent misinterpretation. Sabatier gives a value of $\Delta_f H°(298.15\ K) = -124.4\ kcal \cdot mol^{-1}$ based on heats of formation for the other materials as accepted at that time Our reanalysis of Sabatier's data using currently accepted heats of formation[6, 7] yields $\Delta_f H°(298.15\ K) = -148.0\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The adopted $C_p°$ data are based on the low temperature $C_p°$ measurements (12–312 K) of Ho *et al.*[1] and the high temperature enthalpy measurements (403–852 K) of Ferrante and McCune.[8] We have not reanalyzed these results except to extrapolate them to higher temperature. The entropy is based on $S°(15\ K) = 0.046\ cal \cdot K^{-1} \cdot mol^{-1}$.

Phase Data

This table is for the hexagonal phase of Al_2S_3 usually designated as the α phase.[8] Other phases known to exist at higher temperatures are the rhombohedral (γ) and face centered cubic phases. Ferrante and McCune[8] observed an extra enthalpy effect at 878.5 K which they confirmed to be partial conversion to the metastable γ phase via X-ray diffraction. They further showed via X-ray techniques that conversion to the γ phase is essentially complete after heating in the 1320–1500 K range. They were unable to measure the enthalpy of the γ phase since conversion to the γ phase appears to be slow and rapid quenching in the drop calorimeter leads to mixed phases. The α–γ transition temperature was reported as 1273 K[9] and melting points of 1403 K[10] and 1373 K[9] were reported.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.634	−647.350	−647.350	INFINITE
100	48.677	30.970	197.042	−16.607	−648.360	−646.303	337.594
200	87.571	78.115	126.026	−9.582	−649.864	−643.647	168.103
298.15	105.064	116.847	116.847	0.	−651.030	−640.335	112.184
300	105.282	117 497	116.849	0.195	−651.052	−640.269	111.481
400	114.947	149.264	121.114	11.260	−658 794	−636.244	83.085
500	120.365	175.538	129.449	23.045	−664.059	−630.029	65.819
600	124.135	197.832	139.035	35.278	−668.050	−622.827	54.222
700	127.127	217.199	148.848	47.846	−671.218	−615.032	45.894
800	129.700	234.346	158.484	60.690	−673.970	−606.814	39.621
900	132.039	249.760	167.784	73.778	−835.933	−595.021	34.534
1000	134.051	263.777	176.693	87.084	−856.026	−566.794	29.606
1100	135.825	276.639	185.202	100.580	−854.495	−537.943	25.545
1200	137.327	288.523	193.323	114.240	−852.846	−509.238	22.167
1300	138.566	299.566	201.076	128.037	−851.107	−480:674	19.314
1400	139.536	309.872	208.483	141.944	−849.304	−452.247	16.874
1500	140.235	319.524	215.568	155.935	−847.463	−423.949	14.763

PREVIOUS: CURRENT: December 1979

Chiolite ($Na_5Al_3F_{14}$) CRYSTAL $M_r = 461.871112$ Chiolite ($Na_5Al_3F_{14}$) $Al_3F_{14}Na_5(cr)$

$S°(298.15\ K) = 483.54 \pm 0.8\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 1010 \pm 2\ K$

$\Delta_fH°(0\ K) = -7554.7 \pm 16\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15) = -7581.4 \pm 16\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 228.9 \pm 8\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Our adopted value of the heat of formation, $\Delta_fH°(Na_5Al_3F_{14}$, cr, 298.15 K) = -1812.0 ± 4 kcal·mol⁻¹ is based on the emf work of Dewing.[1] Dewing used solid–electrolyte emf cells of the type Al/Na_3AlF_6, $Na_5Al_3F_{14}/Na$ $/Na_5Al_3F_{14}$, AlF_3/Al to determine the free energies for the reaction 5 NaF(cr) + 3 AlF_3(cr) = $Na_5Al_3F_{14}$(cr) over the range 844–996 K. Based on Dewing's[1] reported $\Delta_rG°$ values (20 points), we evaluate $\Delta_rH°$(298.15 K) = -36.58 ± 0.36 kcal·mol⁻¹ and -39.97 ± 0.42 kcal·mol⁻¹ by the 2nd and 3rd law methods, respectively. From the 3rd law value, we calculate $\Delta_fH°(Na_5Al_3F_{14}$, cr, 298.15 K) = -1811.95 ± 2.1 kcal·mol⁻¹. There has been some confusion over the exact reaction to which Dewing's $\Delta_rG°$ values apply. Both Dewing[1] and Stuve and Ferrante[2] applied the reported $\Delta_rG°$ values to the erroneous reaction 3 Na_3AlF_6(cr) = $Na_5Al_3F_{14}$(cr) + 4 NaF(cr). Our adopted heat of formation is 58 kcal·mol⁻¹ less stable than their reported values.[1, 2]

Holm[3] estimated $\Delta_rH°$(910 K) = -2.7 ± 1.2 kcal·mol⁻¹ for the reaction 5/8 NaF(cr) + 3/8 AlF_3(cr) = 1/8 $Na_5Al_3F_{14}$(cr). Converting to a molar basis, we obtain $\Delta_rH°$(910 K) = -21.6 ± 10 kcal·mol⁻¹ for the reaction 5 NaF(cr) + 3 AlF_3(cr) = $Na_5Al_3F_{14}$(cr). Using JANAF enthalpies[4] and auxiliary data from,[4 5] we obtain $\Delta_fH°(Na_5Al_3F_{14}$, cr, 298.15 K) = -1791.7 ± 12 kcal·mol⁻¹.

Grjotheim *et al.*[6] studied the vapor pressures over the solid systems $Na_5Al_3F_{14}/AlF_3$ and $Na_5Al_3F_{14}/Na_3AlF_6$ by the weight–loss effusion method. Their results are in good agreement with the mass–spectrometric observations of Sidorov *et al.*[7] on similar systems. Results have been sumamrized by Grjotheim *et al.*[6] who obtained $\Delta_rH°$(910 K) = 60.65 ± 1.5 kcal·mol⁻¹ for the reaction 1/5 $Na_5Al_3F_{14}$(cr) + 2/5 AlF_3(cr) = $NaAlF_4$(g). Using JANAF enthalpies[4] and $\Delta_fH°$(298.15 K) values from,[4,5] we obtain $\Delta_fH°(Na_5Al_3F_{14}$, cr, 298 15 K) = -1831.0 ± 20 kcal·mol⁻¹. Similarly, Grjotheim *et al.*[6] obtained $\Delta_rH°$(910 K) = 59.74 ± 2.0 kcal·mol⁻¹ and recalculated $\Delta_rH°$(910 K) = 60.4 ± 2 kcal·mol⁻¹ from the data of Sidorov *et al.*[7] for the reaction 1/2 $Na_5Al_3F_{14}$(cr) = 1/2 Na_3AlF_6(cr) + $NaAlF_4$(g). Using the same auxiliary data as above, we obtain $\Delta_fH°(Na_5Al_3F_{14}$, cr, 298.15 K) = -1808.3 ± 10 kcal·mol⁻¹ from[6] and $\Delta_fH°(Na_5Al_3F_{14}$, cr, 298.15 K) = -1809.6 ± 10 kcal·mol⁻¹ from.[7] These results are in very good agreement with the recalculated value from Dewing.[1]

Heat Capacity and Entropy

Low–temperature heat capacities of chiolite were determined by Stuve and Ferrante[2] by adiabatic calorimetry over the range 5.83–315.75 K. A slight bump was noted in the heat capacity curve between 140 and 175 K. $S°$(298.15 K) = 115.57 ± 0.2 cal·K⁻¹·mol⁻¹ is based on $S°$(5 K) = 0.022 cal·K⁻¹·mol⁻¹ obtained by extrapolating the function C_p/T versus T^2.[2] $H°$(298.15 K)–$H°$(0 K) = 19.338 kcal·mol⁻¹.

High temperature enthalpies were measured by Stuve and Ferrante[2] (402.8–991.5 K) and by Holm[3] (677.0–931.7 K). The data of Holm are consistently higher (2.3 ± 0.3 kcal, corresponding to 3–4%) than the data of Stuve and Ferrante and show more scatter. This positive bias ascribed to the calorimeter of Holm was also evident in a study on cryolite (see the Na_3AlF_6, cr, β table). We adopt heat capacities for chiolite based on the drop calorimetry work of Stuve and ferante.[2]

Fusion Data

Chiolite is the mineral name for $Na_5Al_3F_{14}$ (corresponds to 5 NaF + 3 AlF_3). The crystals are tetragonal, space group P_4/mnc.[8] Chiolite melts incongruently at 1010 K[1,3,6] to a combination of cryolite and AlF_3. The value of $\Delta_{fus}H°$ for this process is calculated as the difference between the enthalpies of the crystal and liquid at 1010 K.

References

[1] E. W. Dewing, Met. Trans. 2, 2211 (1970).
[2] J. M. Stuve and M. J. Ferrante, U.S. Bur. Mines RI 8442, 8 pp. (1980).
[3] J. L. Holm, High Temp. Sci. 6, 16 (1974).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−80.910	−7554.692	−7554.692	INFINITE
100	214.723	142.800	861.276	−71.848	−7574.128	−7455.146	3894.169
200	370.912	317.691	522.895	−41.041	−7581.508	−7325.950	1913.342
298.15	454.006	483.545	483.545	0.	−7581.408	−7200.348	1261.471
300	455.094	486.357	483.554	0.841	−7581.368	−7197.984	1253.280
400	499.570	623.823	501.993	48.732	−7591.644	−7069.564	923.190
500	525.092	738.188	538.126	100 031	−7587.309	−6939.508	724.965
600	542.665	835.534	579.783	153.451	−7581.492	−6810.474	592.904
700	556.472	920.245	622.500	208.421	−7574.685	−6682.498	498 654
800	568.606	995.357	664.500	264.686	−7567.175	−6555.548	428.033
900	579.484	1062.962	705.080	322.094	−7559.205	−6429.570	373.163
1000	589.944	1124.591	743.994	380.597	−7582.715	−6302.216	329.194
1010.000	590.781	1130.465	747.792	386.500	--- CRYSTAL <--> LIQUID ---		
1100	600.319	1181.296	781.205	440.100	−7573.318	−6174.615	293.208
1200	610.864	1233.983	816.767	500.660	−8047.057	−6035.700	262.727
1300	621.324	1283.291	850.776	562.269	−8031.751	−5868.701	235.807
1400	631 784	1329.719	883.344	624.925	−8015.548	−5702.916	212.778
1500	642.244	1373.664	914.580	688.626	−7998.439	−5538.319	192.861

PREVIOUS: CURRENT: December 1979

Chiolite ($Na_5Al_3F_{14}$) $Al_3F_{14}Na_5(cr)$

Chiolite ($Na_5Al_3F_{14}$) LIQUID $M_r = 461.871112$ Chiolite ($Na_5Al_3F_{14}$) $Al_3F_{14}Na_5(l)$

$S°(298.15\ K) = [532.124]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 1010 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-7497.408]\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 228.9 \pm 8\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Na_5Al_3F_{14}$, l, 298.15 K) is calculated from $\Delta_f H°(Na_5Al_3F_{14}$, cr, 298.15 K) by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1010\ K)–H°(298.15\ K)$, between the crystal and liquid.

Hong and Kleppa[2] measured the enthalpies of mixing for the reaction 5/8 NaF(l) + 3/8 AlF (cr) = 1/8 $Na_5Al_3F_{14}(l)$ as $\Delta_r H°(298.15\ K) = -0.591\ kcal{\cdot}mol^{-1}$. Converting to a molar basis, we obtain $\Delta_r H°(1298\ K) = -4.725\ kcal{\cdot}mol^{-1}$ for the reaction 5 NaF(l) + 3 AlF_3(cr) = $Na_5Al_3F_{14}(l)$, using JANAF data[1] for the enthalpies of formation from JANAF[1] and NBS,[3] we obtain $\Delta_f H°(Na_5Al_3F_{14}$, l, 298.15 K) = $-1793.5 \pm 10\ kcal{\cdot}mol^{-1}$.

Hong and Kleppa[4] also measured the enthalpy of mixing for the reaction 5/9 $Na_3AlF_6(l)$ + 4/9 $AlF_3(cr)$ = 1/3 $Na_5Al_3F_{14}(l)$ as $\Delta_r H°(1298\ K) = 4.49\ kcal{\cdot}mol^{-1}$. Converting to a molar basis, we obtain $\Delta_r H°(1298\ K) = 40.40\ kcal{\cdot}mol^{-1}$ for the reaction 5 $Na_3AlF_6(l)$ + 4 $AlF_3(cr)$ = 3 $Na_5Al_3F_{14}(l)$. Using enthalpies from JANAF[1] and enthalpies of formation from JANAF[1] and NBS,[3] we obtain $\Delta_f H°(Na_5Al_3F_{14}$, l, 298.15 K) = $-1794.1 \pm 10\ kcal{\cdot}mol^{-1}$. These results are in good agreement with adopted enthalpy of formation.

Heat Capacity and Entropy

High temperature enthalpies were measured by drop calorimetry by Holm,[5] (1046.6–1172.9 K). Our analysis of his experimental data leads to a constant heat capacity of $232.76\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. We have corrected his experimental enthalpies for what we believe to be a positive bias by subtracting 2.3 $kcal{\cdot}mol^{-1}$ from his measured data. Our adopted enthalpies can be represented by the equation $H°(T)–H°(298.15\ K) = -88{,}000 + 232.76\ T\ cal{\cdot}mol^{-1}$ (1010–1200 K). A hypothetical glass transition is assumed at 650 K. The $C_p°$ values above 1172.9 K are obtained by linear extrapolation. The entropy, 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.

References

[1] JANAF Thermochemical Tables: $Na_5Al_3F_{14}$(cr) and Na_3AlF_6(l), 12–30–79; AlF_3(cr), 9–30–79.
[2] K. C. Hong and U. J. Kleppa, J. Phys. Chem. 82, 176 (1978).
[3] U. S. Nat. Bur. Stand. IR 75–968, (1976).
[4] K. C. Hong and U. J. Kleppa, High Temp. Sci. 8, 299 (1976).
[5] J. L. Holm, High Temp. Sci. 6, 16 (1974).

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

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	454.006	532.124	532.124	0.	−7497.408	−7130.832	1249.292
300	455.094	534.935	532.132	0.841	−7497.367	−7128.557	1241.192
400	499.570	672.402	550.572	48.732	−7507.644	−7004.995	914.759
500	525.092	786.767	586.704	100.031	−7503.309	−6879.797	718.727
600	542.665	884.124	628.363	153.456	−7497.486	−6755.621	588.129
650.000	549.778	927.848	649.737	180.772	GLASS <--> LIQUID		
650.000	973.868	927.848	649.737	180.772	TRANSITION		
700	973.868	1000.020	672.212	229.465	−7469.641	−6633.296	494.983
800	973.868	1130.062	721.496	326.852	−7421.008	−6517.144	425.526
900	973.868	1244.767	773.390	424.239	−7373.059	−6407.048	371.855
1000	973.868	1347.374	825.748	521.626	−7357.686	−6299.969	329.077
1010.000	973.868	1357.064	830.961	531.365	--- CRYSTAL <--> LIQUID ---		
1100	973.868	1440.193	877.455	619.013	−7310.405	−6196.490	294.247
1200	973.868	1524.931	927.932	716.399	−7747.317	−6085.098	264.877
1300	973.868	1602.882	976.893	813.786	−7696.233	−5948.652	239.020
1400	973.868	1675.053	1024.216	911.173	−7645.300	−5816.135	217.003
1500	973.868	1742.243	1069.870	1008.560	−7594.505	−5687.253	198.048
1600	973.868	1805.095	1113.879	1105.947	−7543.838	−5561.756	181.573
1700	973.868	1864.136	1156.293	1203.333	−7493.288	−5439 424	167.133
1800	973.868	1919.800	1197.178	1300.720	−7442.840	−5320.064	154.384
1900	973.868	1972.455	1236.609	1398.107	−7392.479	−5203.508	143.054
2000	973.868	2022.408	1274 661	1495.494	−7342.185	−5089.599	132.927
2100	973.868	2069.923	1311.408	1592.880	−7291.938	−4978.207	123.826
2200	973.868	2115.227	1346.924	1690.267	−7241.715	−4869.206	115.610
2300	973.868	2158.517	1381.276	1787.654	−7191.493	−4762.488	108.160
2400	973.868	2199.965	1414.531	1885.041	−7141.249	−4657.956	101.378
2500	973.868	2239.720	1446.749	1982.428	−7090.962	−4555.519	95.182
2600	973.868	2277.916	1477.987	2079.814	−7040.610	−4455.095	89.504
2700	973.868	2314.670	1508.299	2177.201	−6990.174	−4356 609	84.284
2800	973.868	2350.087	1537.734	2274.588	−7821.342	−4257.091	79.417
2900	973.868	2384.261	1566.339	2371.975	−7767.406	−4130.747	74.403
3000	973.868	2417.277	1594.157	2469.362	−7713.346	−4006.267	69.755

PREVIOUS: CURRENT: December 1979

Chiolite ($Na_5Al_3F_{14}$) CRYSTAL-LIQUID

0 to 1010 K crystal
above 1010 K liquid

Refer to the individual tables for details.

Adopted enthalpy equations used to prepare this tabulation:

$Na_5Al_3F_{14}$(cr)
$H_T - H_{298} = 17.894 \times 10^5/T - -43{,}416 + 122.461\ T + 10.158 \times 10^{-3}\ T^2$ cal·mol^{-1} (298.15–1010 K)

$Na_5Al_3F_{14}$(l)
$H_T - H_{298} = -88{,}000 + 232.76\ T$ cal mol $^{-1}$ (1010–1200 K)

$M_r = 461.871112$ Chiolite ($Na_5Al_3F_{14}$) $Al_3F_{14}Na_5$(cr,l)

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−80.910	−7554 692	−7554.692	INFINITE
100	214.723	142.800	861.276	−71.848	−7574.128	−7455.146	3894.169
200	370.912	317.691	522.895	−41.041	−7581.508	−7325.950	1913.342
298.15	454.006	483.545	483.545	0.	−7581.408	−7200.348	1261.471
300	455.094	486.357	483.554	0.841	−7581.368	−7197 984	1253.280
400	499.570	623.823	501.993	48.732	−7591.644	−7069.564	923.190
500	525.092	738.188	538.126	100.031	−7587.309	−6939.508	724.965
600	542.665	835.534	579.783	153.451	−7581.492	−6810.474	592.904
700	556.472	920.245	622.500	208.421	−7574.685	−6682.498	498 654
800	568.606	995.357	664.500	264.686	−7567.175	−6555.548	428.033
900	579.484	1062.962	705.080	322.094	−7559.205	−6429.570	373.163
1000	589.944	1124.591	743.994	380.597	−7582.715	−6302.216	329.194
1010.000	590.781	1130.465	747.792	386.500	CRYSTAL <--> LIQUID		
1010.000	973.868	1357.064	747.792	615.365		TRANSITION	
1100	973.868	1440.193	801.090	703.013	−7310.405	−6196.490	294.247
1200	973.868	1524.931	857.931	800.400	−7747.317	−6085.097	264.877
1300	973.868	1602.882	912.277	897.787	−7696.233	−5948.652	239.020
1400	973.868	1675.053	964.215	995.174	−7645.299	−5816.135	217.003
1500	973.868	1742.243	1013.870	1092.560	−7594.504	−5687.253	198.048
1600	973.868	1805.095	1061.378	1189.947	−7543.838	−5561.756	181.573
1700	973.868	1864 136	1106.880	1287.334	−7493.287	−5439.424	167.133
1800	973.868	1919.800	1150.511	1384.721	−7442.840	−5320 064	154.384
1900	973 868	1972.455	1192.398	1482.108	−7392.479	−5203.507	143.054
2000	973 868	2022.408	1232.660	1579.494	−7342.185	−5089.598	132.927
2100	973.868	2069.923	1271.408	1676.881	−7291.937	−4978.206	123.826
2200	973.868	2115.227	1308.742	1774.268	−7241.714	−4869.206	115.610
2300	973.868	2158.517	1344.754	1871.655	−7191.493	−4762.488	108.159
2400	973.868	2199.965	1379.531	1969.042	−7141.249	−4657.956	101.378
2500	973.868	2239.720	1413.149	2066.428	−7090.962	−4555.518	95.182
2600	973.868	2277.916	1445.679	2163.815	−7040.610	−4455.094	89.504
2700	973.868	2314.670	1477.188	2261.202	−6990.174	−4356.609	84.284
2800	973.868	2350.087	1507.734	2358.589	−7821.342	−4257.090	79.417
2900	973.868	2384.261	1537.373	2455.975	−7767.406	−4130.747	74.403
3000	973.868	2417.277	1566.156	2553.362	−7713.346	−4006.267	69.755

PREVIOUS.

CURRENT: December 1979

Beryllium Aluminum Oxide ($BeAl_6O_{10}$) CRYSTAL $M_r = 330.89542$ Beryllium Aluminum Oxide ($BeAl_6O_{10}$) $Al_6Be_1O_{10}(cr)$

$S°(298.15\ K) = 175.55 \pm 0.3\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{fus} = 2186 \pm 10\ K$

$\Delta_f H°(0\ K) = -5585.7 \pm 5\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -5624.1 \pm 5\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = [402]\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Al_6BeO_{10}$, cr, 298.15 K) is calculated from $\Delta_r H°(298.15\ K) = 2.71 \pm 0.45\ kcal\cdot mol^{-1}$ for BeO(cr, α) + 3 Al_2O_3(cr, α) → Al_6BeO_{10}(cr) using current value of $\Delta_f H°$ for the reactants.[1] $\Delta_r H°$ is based on the value 2.9 ± 0.45 $kcal\cdot mol^{-1}$ at 968 K determined by Holm and Kleppa[2] from the difference in heats of solution of the three components in an oxide melt.

For comparison with the above reaction, we derive $\Delta_r H°(298.15\ K) = 0.6\ kcal\cdot mol^{-1}$ from $\Delta_r G°(1800\ K) = -3.95\ kcal\cdot mol^{-1}$ based on equilibrium data. Young[3] used water vapor as a carrier gas to determine the transport of BeO, presumably as $Be(OH)_2$, in equilibrium with BeO(cr) and Al_6BeO_{10}(cr) The difference between the two equilibria gives the above reaction. We compare at 1800 K, near the upper limit of the data, where the experimental method is most sensitive. The resulting difference in $\Delta_r H°(298.15\ K)$ is $-2.1\ kcal\cdot mol^{-1}$, roughly twice the uncertainty claimed for $\Delta_r G°$.[3]

Heat Capacity and Entropy

$C_p°$ and the derived properties below 298.15 K are taken from calorimetric data (15–380 K) of Furukawa and Saba.[4] The entropy is based on $S°(15\ K) = 0.011\ cal\cdot K^{-1}\cdot mol^{-1}$. The heat capacity is extrapolated above 1200 K by comparison with current values[1] for $BeAl_2O_4$(cr), Al_2O_3(cr, α), and BeO(cr, α).

Holm and Kleppa[2] combined their $\Delta_r H°$ for formation from the oxides with the corresponding $\Delta_r G°$ from Young[3] in order to calculate $\Delta_r S°$. Based on the present functions and Young's result at 1800 K, we calculate an entropy which is 1.2 $cal\cdot K^{-1}\cdot mol^{-1}$ larger than the adopted calorimetric value. To explain the difference, Holm and Kleppa[2] proposed Be–Al disorder in the crystal, which might provide extra entropy up to 2.76 $cal\cdot K^{-1}\cdot mol^{-1}$. Crystal structure data were recently published [6], but they do not appear to be sufficient to test the hypothesis of disorder. Although we believe that the discrepancy is within the uncertainty of the equilibrium data, further information is desirable.

Fusion Data

Refer to the liquid table for details.

References

[1] JANAF Thermochemical Tables: BeO(cr, α), 6–30–71; Al_2O_3(cr, α) and $BeAl_2O_4$(cr), 6–30–77.
[2] J. L. Holm and O. J. Kleppa, Acta Chem. Scand. **20**, 2568 (1966).
[3] W. A. Young, J. Phys. Chem. **64**, 1003 (1960).
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[5] D. A. Ditmars and T. B. Douglas, J. Res. Nat. Bur. Stand. **71A**, 97 (1967).
[6] L. A. Harris and H. L. Yakel, J. Amer. Ceram. Soc. **53**, 359 (1970).

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

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−34.112	−5585.659	−5585.659	INFINITE
100	47.049	16.606	345.259	−32.865	−5601.878	−5512.643	2879.509
200	172.929	87.939	197.142	−21.840	−5616.797	−5417.092	1414.799
298.15	265.186	175.552	175.552	0.	−5624.133	−5317.254	931.561
300	266.546	177.197	175.557	0.492	−5624.212	−5315.350	925.485
400	324.268	262.481	186.792	30.275	−5626.175	−5211.985	680.616
500	358.527	338.838	209.722	64.558	−5625.087	−5108.521	533.684
600	380.560	406.278	236.976	101.581	−5622.541	−5005.431	435.762
700	396.083	466.167	265.522	140.452	−5619.419	−4902.822	365.853
800	407.827	519.854	294.016	180.671	−5616.267	−4800.669	313.452
900	417.249	568.451	321.852	221.939	−5613.464	−4698.893	272.717
1000	425.178	612.834	348.763	264.071	−5674.818	−4592.838	239.905
1100	431.998	653.685	374.651	306.937	−5671.319	−4484.805	212.966
1200	437 939	691.532	399.500	350.439	−5667 470	−4377.108	190.531
1300	443.295	726.800	423.336	394.503	−5663.316	−4269.745	171.560
1400	448.316	759.835	446.204	439.084	−5658.886	−4162.711	155.313
1500	453.336	790.936	468.159	484.165	−5654.182	−4056.005	141.243
1600	458.566	820.358	489.260	529.756	−5663.723	−3949.095	128.925
1700	464.215	848.326	509.566	575.892	−5657.995	−3842.104	118.053
1800	470.282	875.028	529.133	622.612	−5651.825	−3735.464	108.400
1900	476.976	900.632	548.016	669.969	−5645.155	−3629.179	99.773
2000	484.298	925.281	566.267	718.028	−5637.922	−3523.259	92.018
2100	492.248	949.100	583.933	766.850	−5630.062	−3417.716	85.011
2186.000	499.586	969.001	598.692	809.495	--- CRYSTAL <--> LIQUID ---		
2200	500.825	972.195	601.059	816.498	−5621.511	−3312.561	78.650
2300	510.030	994 658	617.686	867.036	−5612.205	−3207.816	72.852
2400	519.862	1016.570	633.851	918.525	−5602.079	−3103.493	67.546
2500	530.322	1038.002	649.590	971.029	−5591.070	−2999.608	62.673
2600	541.410	1059.015	664.934	1024.610	−5579.112	−2896.182	58.185
2700	553.125	1079.666	679.914	1079.332	−5566.140	−2793.234	54.038
2800	565.468	1100.003	694.554	1135.256	−7606.453	−2678.757	49.973
2900	578.438	1120.071	708.882	1192.446	−7583.620	−2503.171	45.087
3000	592.036	1139.908	722.920	1250.965	−7559.563	−2328.388	40.541

PREVIOUS· CURRENT: June 1972

Beryllium Aluminum Oxide ($BeAl_6O_{10}$) LIQUID $M_r = 330.89542$

$S°(298.15\ K) = [314.903]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-5299.312]\ kJ \cdot mol^{-1}$
$T_{fus} = 2186 \pm 10\ K$ $\Delta_{fus} H° = [402]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Al_6BeO_{10}, l, 298.15\ K)$ is calculated from $\Delta_f H°(Al_6BeO_{10}, cr, 298\ 15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(2186\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is assumed to be 136 $cal \cdot K^{-1} \cdot mol^{-1}$, corresponding to 8 $cal \cdot K^{-1}$ g–atom^{-1}, by analogy with current tables[1] for $BeAl_2O_4(l)$ and $Al_2O_3(l)$. Below the assumed glass transition at 1400 K, $C_p°$ is taken to be the same as that of the crystal. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus}, adjusted to IPTS–68, is from the phase study of Lang *et al* [2] $\Delta_{fus} H°$ is estimated as being slightly smaller than the sum of $\Delta_{fus} H°$ for the component oxides.[1] Data for $BeAl_2O_4$ are consistent with this approach.

References

[1] JANAF Thermochemical Tables: BeO(l), 6–30–71; $Al_2O_3(l)$ and $BeAl_2O_4(l)$, 6–30–72.
[2] S. M. Lang, C L. Fillmore, and L. H. Maxwell, J. Res. Nat. Bur. Stand. 48, 298 (1952).

Beryllium Aluminum Oxide ($BeAl_6O_{10}$) $Al_6Be_1O_{10}(l)$

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	265.186	314.903	314.903	0.	−5299.312	−5033.981	881.933
300	266.546	316.548	314.908	0.492	−5299.391	−5032.335	876.207
400	324.268	401.832	326.143	30.275	−5301.355	−4942.905	645.477
500	358.527	478.189	349.073	64.558	−5300.266	−4853.375	507.029
600	380.560	545.629	376.328	101.581	−5297.720	−4764.221	414.762
700	396 083	605.518	404.873	140.452	−5294.599	−4675.547	348.894
800	407.827	659.205	433.367	180.671	−5291.446	−4587.329	299.522
900	417.249	707.802	461.203	221.939	−5288.643	−4499.488	261.143
1000	425.178	752.185	488 114	264.071	−5349.998	−4407.369	230.217
1100	431.998	793.036	514.002	306.937	−5346.498	−4313.271	204.820
1200	437.939	830.883	538.851	350.439	−5342.649	−4219.509	183 670
1300	443.295	866.151	562.687	394.503	−5338.496	−4126.080	165.788
1400	448.316	899.188	585.555	439.087	−5334.063	−4032.982	150.472
1400.010	448.316	899.191	585.557	439.091	GLASS <- -> LIQUID		
1400.010	569.024	899.191	585.557	439.091	TRANSITION		
1500	569.024	938.446	607.787	495.988	−5317.538	−3940.627	137.225
1600	569.024	975.170	629.614	552.890	−5315.768	−3848.840	125.652
1700	569.024	1009.667	650.965	609.793	−5299.273	−3757.662	115.459
1800	569.024	1042.191	671.805	666.695	−5282.920	−3667.453	106.427
1900	569.024	1072.957	692.116	723.598	−5266.706	−3578.147	98.370
2000	569.024	1102.144	711.894	780.500	−5250.630	−3489.692	91.141
2100	569.024	1129.907	731.144	837.402	−5234.689	−3402.038	84.621
2186.000	569.024	1152.745	747.284	886.338	--- CRYSTAL <- -> LIQUID ---		
2200	569.024	1156.378	749.876	894.305	−5218.884	−3315.136	78.711
2300	569.024	1181.672	768.104	951.207	−5203.212	−3228.956	73.332
2400	569.024	1205.889	785.844	1008.110	−5187.674	−3143.454	68.415
2500	569.024	1229.118	803.113	1065.012	−5172.266	−3058.595	63.906
2600	569.024	1251 436	819.930	1121.914	−5156.987	−2974.350	59.755
2700	569.024	1272.911	836.312	1178.817	−5141.834	−2890.689	55.924
2800	569.024	1293.605	852.277	1235.719	−7181.169	−2795.558	52.152
2900	569.024	1313.573	867.841	1292.622	−7158.624	−2639.331	47.539
3000	569.024	1332.863	883.022	1349.524	−7136.183	−2483.875	43.248
3100	569.024	1351.522	897.836	1406.426	−7113.842	−2329.164	39.246
3200	569.024	1369.587	912.297	1463.329	−7091.601	−2175.178	35.506
3300	569.024	1387.097	926.421	1520.231	−7069.458	−2021.884	32.004
3400	569.024	1404.084	940.221	1577.134	−7047.412	−1869.255	28.718
3500	569.024	1420.579	953.711	1634.036	−7025.465	−1717.278	25.629
3600	569.024	1436.609	966.904	1690.938	−7003.614	−1565.924	22.721
3700	569 024	1452.199	979.810	1747.841	−6981.861	−1415.179	19.979
3800	569.024	1467.374	992.442	1804.743	−6960.207	−1265.014	17.389
3900	569.024	1482.155	1004.810	1861.646	−6938.652	−1115.420	14.939
4000	569.024	1496.561	1016.924	1918.548	−6917.201	−966.382	12.620

PREVIOUS. CURRENT June 1972

Beryllium Aluminum Oxide ($BeAl_6O_{10}$) CRYSTAL–LIQUID M_r = 330.89542 Beryllium Aluminum Oxide ($BeAl_6O_{10}$) $Al_6Be_1O_{10}$(cr,l)

0 to	2186 K	crystal
above	2186 K	liquid

Refer to the individual tables for details.

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

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−34.112	−5585.659	−5585.659	INFINITE
100	47.049	16.606	345.259	−32.865	−5601.878	−5512.643	2879.509
200	172.929	87.939	197.142	−21.840	−5616.797	−5417.092	1414.799
298.15	265.186	175.552	175.552	0.	−5624.133	−5317.254	931.561
300	266.546	177.197	175.557	0.492	−5624.212	−5315.350	925.485
400	324.268	262.481	186.792	30.275	−5626.175	−5211.985	680.616
500	358.527	338.838	209.722	64.558	−5625.087	−5108.521	533.684
600	380.560	406.278	236.976	101.581	−5622.541	−5005.431	435.762
700	396.083	466.167	265.522	140.452	−5619.419	−4902.822	365.853
800	407.827	519.854	294.016	180.671	−5616.267	−4800.669	313.452
900	417.249	568.451	321.852	221.939	−5613.464	−4698.893	272.717
1000	425.178	612.834	348.763	264.071	−5674.818	−4592.838	239.905
1100	431.998	653.685	374.651	306.937	−5671.319	−4484.805	212.966
1200	437.939	691.532	399.500	350.439	−5667.470	−4377.108	190.531
1300	443.295	726.800	423.336	394.503	−5663.316	−4269 745	171.560
1400	448.316	759.835	446.204	439.084	−5658.886	−4162.711	155.313
1500	453.336	790.936	468.159	484.165	−5654.182	−4056 005	141.243
1600	458.566	820.358	489.260	529.756	−5663.723	−3949.095	128.925
1700	464.215	848.326	509.566	575.892	−5657 995	−3842.104	118.053
1800	470.282	875.028	529 133	622.612	−5651.825	−3735.464	108.400
1900	476.976	900.632	548.016	669.969	−5645 155	−3629.179	99.773
2000	484.298	925.281	566.267	718.028	−5637 922	−3523.259	92.018
2100	492.248	949.100	583.933	766.850	−5630 062	−3417.716	85.011
2186.000	499.586	969.001	598.692	809.495	CRYSTAL <--> LIQUID TRANSITION		
2186 000	569 024	1152.745	598.692	1211.159			
2200	569 024	1156.378	602.230	1219.126	−5218.884	−3315.136	78.711
2300	569.024	1181.672	626.877	1276.028	−5203.212	−3228.956	73.332
2400	569.024	1205.889	650.502	1332.930	−5187.673	−3143 454	68.415
2500	569.024	1229.118	673.185	1389.833	−5172.266	−3058.595	63.906
2600	569.024	1251.436	694.999	1446.735	−5156.987	−2974.350	59.755
2700	569.024	1272.911	716.008	1503.638	−5141.834	−2890 689	55.924
2800	569.024	1293.605	736.269	1560.540	−7181.169	−2795.558	52.152
2900	569.024	1313.573	755.834	1617.442	−7158.624	−2639.331	47.539
3000	569.024	1332.863	774.748	1674.345	−7136.183	−2483.874	43.248
3100	569.024	1351.522	793.055	1731.247	−7113 842	−2329.163	39.246
3200	569.024	1369.587	810.791	1788.150	−7091.601	−2175.178	35.506
3300	569.024	1387.097	827.991	1845.052	−7069.458	−2021.884	32.004
3400	569.024	1404.084	844.686	1901.954	−7047.412	−1869.255	28.718
3500	569.024	1420.579	860.905	1958.857	−7025.465	−1717.278	25.629
3600	569.024	1436.609	876.676	2015.759	−7003.614	−1565.924	22.721
3700	569.024	1452.199	892.021	2072.662	−6981.861	−1415.179	19.979
3800	569.024	1467.374	906.963	2129.564	−6960.207	−1265.014	17.389
3900	569.024	1482.155	921.523	2186.466	−6938.652	−1115 420	14.939
4000	569.024	1496.561	935.719	2243.369	−6917.201	−966.382	12.620

PREVIOUS: CURRENT: June 1972

Aluminum Silicate, Mullite ($Al_6Si_2O_{13}$) CRYSTAL M_r = 26.05244

$\Delta_f H°(0\ K) = -6775.17 \pm 6.3\ kJ{\cdot}mol^{-1}$

$S°(298.15\ K) = 274.9 \pm 12\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = -6819.21 \pm 6.3\ kJ{\cdot}mol^{-1}$

$T_{fus} = 2123 \pm 15\ K$

Enthalpy of Formation

The heat of the reaction 3 Al_2O_3(cr, α) + 2 SiO_2(quartz) → $Al_6Si_2O_{13}$(cr) has been determined at 968 K by Holm and Kleppa[1, 2] to be +5.44 ± 0.35 kcal·mol^{-1}. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to $\Delta_f H°(298.15\ K) = 6.77\ kcal{\cdot}mol^{-1}$, which is used to calculate the adopted value for the enthalpy of formation.

Heat Capacity and Entropy

The low temperature heat capacity and high temperature enthalpy of mullite have been measured by Pankratz *et al.*[3] The low temperature investigations extended from 53.5 K to 296.4 K; the Debye–Einstein equation 3D(182/T) + 15E(350/T) + 10E(502/T) + 15E(897/T) represented the data from 53.5 to 114.6 K within 1.4 percent and gave a smooth extrapolation to zero. From this equation, the entropy at 51 K was found to be 2.17 cal·K^{-1}·mol^{-1} as opposed to the value 1.96 cal·K^{-1}·mol^{-1} found by Pankratz *et al.*[5] However, since it is known that mullite has some of its Al atoms on Si sites, there will be configurational entropy remaining at 0 K. This is borne out by the free energy determinations of Rein and Chipman[4] and Kay and Taylor,[5] who obtain $\Delta_f G°(1823\ K) = -5.7 \pm 0.1\ kcal{\cdot}mol^{-1}$ for the formation from oxide. If the entropies and enthalpies reported by Pankratz *et al* are used with the heat of formation, they yield $\Delta_f G°(1823\ K) = +2.9\ kcal{\cdot}mol^{-1}$. Holm and Kleppa[1,2] calcualte that random mixing of tetra–coordinated aluminum and silicon atoms could produce 7 cal·K^{-1}·mol^{-1} residual entropy. We have added 4.7 cal·K^{-1}·mol^{-1} in order to match the measured $\Delta_f G°(1823\ K)$.

A review of the enthalpy determination indicated that the values might easily be 2 percent low if as little as 4 percent of kyanite remained unchanged in the sample used for measurement. Since X–ray could not detect this amount, it is not an unreasonable assumption Accordingly, we have checked the effect of increasing the heat capacity above 298.15 K by 2 percent; this then gives $\Delta_f G°(1823\ K) = -2.10\ kcal{\cdot}mol^{-1}$. In order to bring this within reasonable agreement with the observations, a residual configurational entropy of 2 cal·K^{-1} mol^{-1} would be needed. Thus the uncertainty in the residual entropy is of the order of 2 cal·K^{-1}·mol^{-1} due to possible uncertainty in the high temperature heat capacity.

Fusion Data

The congruent melting point of mullite was reported by Aramaki and Roy.[6]

References

[1] J. L. Holm and O. J. Kleppa, J. Phys. Chem. 70, 1690 (1966).
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Aluminum Silicate, Mullite ($Al_6Si_2O_{13}$) $Al_6O_{13}Si_2$(cr)

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

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−46.072	−6775.166	−6775.166	INFINITE
100	85.264	60.703	493.090	−43.239	−6794.649	−6683.111	3490.899
200	225.957	164.662	301.776	−27.423	−6810.923	−6564.686	1714.520
298.15	325.641	274.889	274.889	0.	−6819.209	−6441.793	1128.575
300	327.031	276.907	274.895	0.604	−6819.302	−6439.451	1121.208
400	390.744	380.251	288.552	36.680	−6821.830	−6312.326	824.305
500	431.998	472.124	316.267	77.929	−6820.816	−6185.013	646.144
600	459.822	553.470	349.157	122.588	−6817.859	−6058.108	527.405
700	479.486	625.893	383.614	169.595	−6813.987	−5931.782	442.635
800	494.130	690.919	418.033	218.309	−6809.866	−5806.035	379.095
900	504.800	749.756	451.675	268.273	−6806.008	−5680.793	329.705
1000	513.377	803.395	484.205	319.190	−6866.308	−5551.389	289.975
1100	519.705	852.625	515.491	370.848	−6861.822	−5420.111	257.380
1200	525.618	898.102	545.504	423.117	−6857.067	−5289.254	230.235
1300	531.115	940.394	574.273	475.957	−6852.049	−5158.805	207.283
1400	536.198	979.942	601.852	529.326	−6846.783	−5028.752	187.625
1500	540 866	1017 097	628.309	583.183	−6841.293	−4899.084	170.601
1600	544.325	1052.115	653.713	637.443	−6835.652	−4769.787	155.718
1700	547.766	1085.217	678.131	692.047	−6930.264	−4639.951	142.568
1800	551.188	1116.624	701.626	746.995	−6923.960	−4505.410	130.744
1900	554.593	1146.516	724.261	802.285	−6917.466	−4371.222	120.173
2000	557 978	1175.049	746.093	857.913	−6910 783	−4237.380	110.669
2100	561.098	1202.348	767.174	913.866	−6903.926	−4103.878	102.078
2200	564.323	1228.525	787.554	970.136	−6896.898	−3970.703	94.276
2300	567.653	1253.683	807.277	1026.734	−6889.690	−3837.857	87.160
2400	571.089	1277.914	826.385	1083.670	−6882.287	−3705.329	80.644
2500	574.631	1301.299	844.916	1140.956	−6874.678	−3573.111	74.656
2600	578.277	1323.907	862.907	1198.600	−6866.849	−3441.202	69.135
2700	582.030	1345.801	880.388	1256.615	−6858.786	−3309.596	64.028
2800	585.887	1367.038	897.391	1315.010	−8613.882	−3172.488	59.183
2900	589.850	1387.666	913.943	1373.796	−8598.737	−2978.424	53.647
3000	593.919	1407.731	930.070	1432.983	−8583.318	−2784.880	48.489

PREVIOUS September 1966 CURRENT: September 1967

Aluminum Silicate, Mullite ($Al_6Si_2O_{13}$) $Al_6O_{13}Si_2$(cr)

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