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Gibbs Energy of Aluminous Minerals

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Abstract. The discrepancy between the tabulated Gibbs Energies of Formation for Al_2SiO_5 and corundum relative to muscovite and kaolinite is considered to lie principally with the latter two minerals. New values for heat of formation of gibbsite [Gbs] will affect the tabulated ΔH_f^0, $\Delta G_{f(298,1)}^0$ for the other aluminous minerals which are referred to gibbsite as calorimetric aluminum reference. Gibbs Energy Difference Functions, calculated from phase equilibria in the system CaO—Al_2O_3—SiO_2—(H_2O—CO_2), can be used to estimate consistent ΔH_f^0, $\Delta G_{f(298,1)}^0$ values for aluminous minerals. A self consistent data set is presented referred to $\Delta G_{f(298,1)}^0$[Corundum] $= -378.08$ kcal mol^{-1}. Two independent values for $\Delta G_{f(298,1)}^0$[Anorthite] $= -961.52$ and -960.29 kcal, from a recalculation of the ΔH_f^0[Anor] based upon the revised $\Delta H_{f(298,1)}^0$[Gbs] $= -309.325$ kcal mol^{-1} and from measurement of silica activity on the anorthite-saturated part of the CaO—Al_2O_3—SiO_2 liquidus, respectively, are considered to show the magnitude of the discrepancy and are used in the calculations.

Introduction

The Gibbs Energy of formation values tabulated by Robie and Waldbaum (1968) for kaolinite and muscovite relative to Al_2SiO_5 polymorphs and corundum show discrepancies of about 7 kcal, when compared to values calculated from reversed equilibrium data (Zen 1969, 1972; Waldbaum, pers. comm. 1972; and others). Some workers have considered the error to be wholly with corundum (Chaterjee, 1972; Nicholls and Carmichael, 1972).

Recent redetermination of the heat of formation of gibbsite, by Gross *et al.* and Robie and Hemingway, suggest that the discrepancy in the Gibbs Energy values could lie with kaolinite and muscovite. This follows from the fact that gibbsite or $AlCl_3 \cdot 6H_2O$ were used as the aluminum reference in the calorimetric studies on these and other aluminous minerals.

The heats and Gibbs energies of formation of the aluminous minerals, tabulated by Robie and Waldbaum (1968) and Zen (1972), have been corrected with the revised value of $\Delta H_{f(298,1)}^0$[Gbs] and available entropy data. The revised values agree well with independent calculations using equilibria in the system CaO—Al_2O_3—SiO_2—(H_2O—CO_2), as previously suggested (Thompson, 1973b).

The standard enthalpies and Gibbs energies of formation, $\Delta H_{f(298,1}^0$ and $\Delta G_{f(298,1)}^0$, are referred to the standard state of the elements at 298.15 K and 1 bar, and have been abbreviated to ΔH_f^0 and ΔG_f^0.

Direct Revision of $\Delta H_{f(298,1)}^0$ for Aluminous Minerals Using a Revised Value for ΔH_f^0[Gbs]

Direct substitution of the revised value for ΔH_f^0[Gbs] $= -309.325$ kcal mol^{-1} (Hemingway and Robie, pers. comm. 1974; Gross *et al.*, pers. comm. 1972) into the "reaction schemes" used to determine ΔH_f^0 from heats of solution measurements by Barany, Kelley and coworkers, would make these values consistent with the revised ΔH_f^0 [Gbs]. It has been assumed that all reported *heats of solution measurements* (with the exception of $AlCl_3 \cdot 6H_2O$, see below) are correct as reported. In the recalculations presented here, the heats of formation of the reference substances were taken from Robie and Waldbaum (1968) in order that the recalculated values are wholly compatible with their reference states. This substitution has been made for various aluminous minerals and the revised ΔH_f^0, ΔG_f^0 are summarized in Table 1.

The recalculation of ΔH_f^0 [Anor], [Geh], [Mus], lawsonite, leonhardite, hexagonal anorthite, kaliophilite, eucryptite, α- and β-spodumene, $Na_{0.8}K_{0.2}AlSiO_4$ was straightforward in as much as the value for $\Delta H_f^0 [\mathrm{Gbs}] = -309.325$ kcal was substituted directly. The value for ΔH_f^0 [$CaAl_2SiO_6$] was recalculated with the revised value for ΔH_f^0 [Anor].

In recalculating ΔH_f^0 [Kao] it was assumed that the error lay in Coughlin's (1958) values for $AlCl_3 \cdot 6H_2O$ through the reaction

$$2\,Al(c) + (HCl \cdot 12.731\,H_2O)(l) = 2\,(AlCl_3 \cdot 6\,H_2O)(c) + 64.386\,H_2O(l) + 3\,H_2(g)$$

(Barany and Kelley, 1961, p. 5, reaction 6).

To correct their value, the revised value for ΔH_f^0 [Gbs] was substituted into their Eq. (8) resulting in a new value for their ΔH_7 (-208.761 ± 0.55 kcal). This value for ΔH_7 was combined with their value for ΔH_5 (31.140 ± 0.19 kcal) to obtain a new value for their ΔH_6 (-239.901 ± 0.45 kcal). This value for ΔH_6 was combined with their value for ΔH_{15} (31.410 ± 0.30 kcal) to give a new value for their ΔH_{16} (-208.491 ± 0.65 kcal). This leads to a value for $\Delta H_f^0 [\mathrm{Kao}] = -985.366 \pm 1.05\ \mathrm{kcal\ mol^{-1}}$.

The same procedure was applied to Barany's (1962) data for analcime, giving $\Delta H^0_{f(298,1)} [\mathrm{Anc}] = -789.245\ \mathrm{kcal\ mol^{-1}}$, which using $\Delta S^0_{f(298,1)} = -174.673$ gives $\Delta G^0_{f(298,1)} [\mathrm{Anc}] = -737.166\ \mathrm{kcal\ mol^{-1}}$, compare Thompson (1973a). Recalculated values for halloysite, dickite and leucite, obtained in the same way, are shown in Table 1.

The recalculations result in a self-consistent set of ΔH_f^0 and ΔG_f^0 values for the aluminous minerals and correspond to *Set 1* of internally-consistent values presented by Zen (1972, p. 550). These revised values for ΔH_f^0 assume all heat of solution measurements by the original authors and, with the exception of gibbsite, all heats of formation of reference substances as tabulated by Robie and Waldbaum (1968), to be correct. Similarly the revised values of ΔG_f^0 assume correct values for ΔS_f^0, as calculated from Third Law entropies.

The revision of ΔH_f^0, ΔG_f^0 [Gbs] leads to revised values of ΔG_0 [Mus], [Kao] that are compatible with the tabulated ΔG_f^0 [Al_2SiO_5], [Cor] within their stated limits of precision (assuming correct values for ΔG_f^0 [quartz], [H_2O]). Remaining inconsistencies may reflect impurities of the samples used in the calorimetric measurements or imprecise entropy data. For example the muscovite sample used by Barany (1964) is clearly impure (86.88% $KAl_3Si_3O_{10}(OH)_2$, 6.33% SiO_2, 0.41% K_2O, 0.99% Na_2O, 0.79% MgO, 3.28% Fe_2O_3, 0.47% FeO, 0.85% H_2O, by weight) although a correction of -1.060 kcal was made to the mean heat of solution. The fact that the two kaolinite samples contained only 2% and 1.7%

Table 1. Dependence of ΔH_f^0, $\Delta G_{f(298,1)}^0$ for Thermochemically Investigated Aluminous Minerals upon $\Delta H_{f(298,1)}^0$ [Gbs]

Phase	Abbrev.	(Gibbsite data of Barany and Kelley)		(Gibbsite data of Hemingway and Robie, Gross et al.)		Reference
		$\Delta H_{f(298,1)}^0$ [a]	$\Delta G_{f(298,1)}^0$ [a]	$\Delta H_{f(298,1)}^0$ [b]	$\Delta G_{f(298,1)}^0$ [b]	
Gibbsite	[Gbs]	-306.380 ± 0.30	-273.486 ± 0.31	-309.325 ± 0.90	-276.431 ± 0.93	Barany and Kelley (1961)
Anorthite	[Anor]	-1009.300 ± 1.15	-955.626 ± 1.16	-1015.196 ± 1.25	-961.523 ± 1.27	Barany (1962)
Gehlenite	[Geh]	-952.740 ± 0.97	-904.432 ± 0.97	-958.636 ± 1.10	-910.328 ± 1.22	Barany (1963)
			-905.252 ± 1.05[c]		-911.146 ± 1.30[c]	
Muscovite	[Mus]	-1421.180 ± 1.30	-1330.103 ± 1.32	-1429.941 ± 1.37	-1338.865 ± 1.39	Barany (1964)
Kaolinite	[Kao]	-979.465 ± 0.95	-902.868 ± 0.96	-985.366 ± 1.05	-908.769 ± 1.07	Barany and Kelley (1961)
Lawsonite	[Law]	-1161.315 ± 1.09	-1076.910 ± 1.11	-1167.206 ± 1.14	-1082.280 ± 1.16	Barany (1962)
Leonhardite	[Leon]	-3397.535 ± 2.50	-3146.948 ± 2.70	-3409.317 ± 2.8	-3158.730 ± 2.85	Barany (1962)
Hexagonal Anorthite	[H-Anor]	-1004.410 ± 1.70	-949.958 ± 1.71	-1010.306 ± 1.85	-955.398 ± 1.87	Barany (1962)
Analcime	[Anc]	-786.341 ± 0.86	-734.262 ± 0.88	-789.245 ± 1.00	-737.166 ± 1.03	Barany (1962)
		Additional Revision of Data in Robie and Waldbaum (1968)				
Ca-Al pyroxene		-786.984 ± 0.66	-745.130 ± 0.71	-792.881 ± 0.72	-751.027 ± 0.74	
Kaliophilite		-503.926 ± 0.42	-476.230 ± 0.43	-506.870 ± 0.45	-479.174 ± 0.47	
Leucite		-721.650 ± 0.75	-681.642 ± 0.76	-724.600 ± 0.78	-684.592 ± 0.80	
Halloysite		-974.995 ± 0.90	-898.419 ± 0.91	-980.896 ± 0.98	-904.320 ± 1.01	
Dickite		-979.165 ± 0.90	-902.142 ± 0.91	-985.066 ± 0.98	-908.043 ± 1.01	
Eucryptite		-505.126 ± 0.55		-508.070 ± 0.62		
α-Spodumene		-727.735 ± 0.82		-730.68 ± 0.87		
β-Spodumene		-720.995 ± 0.81		-723.94 ± 0.86		
$Na_{0.8}K_{0.2}AlSiO_4$		-500.993 ± 0.45		-504.028 ± 0.51		

[a] Values as tabulated by Robie and Waldbaum (1968), in kcal mol^{-1}.

[b] Calculated by inserting H_f^0[Gbs] into calorimetric scheme of reference work to compute H_f^0[phase] and using reference data (for oxides etc.) from Robie and Waldbaum (1968). The same $\Delta S_{f,s}$ values were used in the recalculation (Zen, 1972), based upon Third Law Entropies tabulated by Robie and Waldbaum (1968).

[c] Revised according to S^0[Geh] $= 50.15$ cal deg^{-1} mol^{-1}, proposed by Waldbaum (1973).

total impurities, demonstrates that since the discrepancy exists for both muscovite and kaolinite, the cause must lie elsewhere.

Evaluation of Gibbs Energies from Difference Functions

Various reversed experimental equilibrium data have been used to calculate Gibbs Energy Difference Functions for phases involved in the various reactions (see Thompson, 1973a). The procedure follows that outlined by Apps (1968) and Zen (1969, 1972). Where available high-temperature entropy data have been used to calculate $\Delta S^0_{f,S(T)}$ (see Robie, 1965). In the absence of this data $\Delta S_{f,s(298)}$ has been used (see Zen, 1972, p. 530). The values are shown as footnotes in Tables 2–4 to facilitate any necessary revision.

The treatment of standard errors follows that of Zen (1972, p. 531). Where not given by the author, precision limits of ±10° C and ±200 bars for hydrothermal apparatus studies, and ±25° C and ±2 kbar for solid-media apparatus studies, have been assumed.

Molar volumes are taken from Robie and Waldbaum (1968), entropies of formation are taken from Zen (1972) and values of $G^*[H_2O]$ are taken from Fisher and Zen (1971). Other data sources are indicated in the tables. A revised $S^0[\mathrm{Geh}] = 50.15\ \mathrm{cal\ K^{-1}}$, proposed by Waldbaum (1973), has been used to recalculate $\Delta G^0_f[\mathrm{Geh}]$.

The System Al_2O_3—SiO_2

Of the many studies in the system Al_2O_3—H_2O very few have achieved equilibrium and even fewer have produced satisfactory reversals.

It is possible to use the data of Haas (1972) for the diaspore-corundum reaction

$$2\,\mathrm{AlO(OH)}\,(\mathrm{diaspore}) = \mathrm{Al_2O_3}\,(\mathrm{corundum}) + \mathrm{H_2O} \qquad (1)$$

to obtain a value of $\Delta G^0_f[\mathrm{Diasp}] = -220.453 \pm 0.5\ \mathrm{kcal\ mol^{-1}}$, relative to $\Delta G^0_f[\mathrm{Cor}] = -378.082\ \mathrm{kcal\ mol^{-1}}$.

If we *assume* that the data of Kennedy (1959) and Torkar and Worel (1957) reflect stable equilibrium then their data for the gibbsite-diaspore reaction (2)

$$\mathrm{Al(OH)_3}\,(\mathrm{gibbsite}) = \mathrm{AlO(OH)}\,(\mathrm{diaspore}) + \mathrm{H_2O} \qquad (2)$$

may be used to calculate $\Delta G^0_f[\mathrm{Gbs}]$. Values of -277.43 and $-277.95\ \mathrm{kcal mol^{-1}}$, respectively, were obtained relative to $\Delta G^0_f[\mathrm{Diasp}] = -220.453 \pm 0.5\ \mathrm{kcal\ mol^{-1}}$. The data used are shown in Table 2. These values, although based upon uncertain data, compare favorably with $\Delta G^0_f[\mathrm{Gbs}] = -276.431\ \mathrm{kcal\ mol^{-1}}$ from the recent thermochemical values from Hemingway and Robie and Gross *et al.*

From aqueous solubility studies Parks (1972) estimates $\Delta G^0_f[\mathrm{Gbs}] = -275.3 \pm 0.2\ \mathrm{kcal\ mol^{-1}}$, relative to $\Delta G^0_f[\mathrm{Cor}] = -378.2$ and $\Delta G^0_f[\mathrm{Al^{3+}}] = -116.0$, $\mathrm{kcal mol^{-1}}$.

The System Al_2O_3—SiO_2—H_2O

The discrepancy between $\Delta G^0_f[\mathrm{Kao}]$ and $\Delta G^0_f[\mathrm{And}]$ was demonstrated by Zen (1969) from a consideration of Gibbs energy values calculated from experimental

Table 2. Gibbs energy difference functions for reactions in the system Al_2O_3—H_2O

Diaspore-corundum equilibria (1)

$L \equiv 2\Delta G_f^0[\mathrm{Diasp}]^a - \Delta G_f^0[\mathrm{Cor}] = \Delta V_s \Delta P - \Delta S_{f,s} \Delta T + G^*_{H_2O}$

P kbar	T^0 C	$G^*_{H_2O}$	L kcal mol^{-1}	Reference
1.75	398 ± 5	−42898	−62.242 ± 0.45	Haas (1972)
2.4	409 ± 5	−41831	−61.788 ± 0.45	Haas (1972)
3.5	420 ± 5	−40750	−61.633 ± 0.45	Haas (1972)
4.8	428 ± 8	−39874	−61.831 ± 0.90	Haas (1972)
7.0	458 ± 10	−37695	−61.450 ± 1.05	Haas (1972)
		average	−61.789 ± 0.85	Haas (1972)

Gibbsite-diaspore equilibria (2)

$M \equiv \Delta G_f^0[\mathrm{Gbs}] - \Delta G_f^0[\mathrm{Diasp}] = \Delta V_s \Delta P - \Delta S_{f,s} \Delta T + G^*_{H_2O}$

P kbar	T^0 C	$G^*_{H_2O}$	M kcal mol^{-1}	Reference
10	176 + 6 − 14	−46776	−57.343 + 0.95 − 1.35	Kennedy (1959)
0.1	162 ± 10	−51560	−58.145 ± 0.75	Torkar and Worel (1957)

[a] ΔG_f^0[phase] refers to $\Delta G_{f(98,1)}^0$[phase]

Reaction (1) $\Delta V_s = +0.23772$ cal bar^{-1} $\Delta S_{f,s} = +51.02$ cal deg-mol^{-1}.

(2) $\Delta V_s = -0.3393$ cal bar^{-1} $\Delta S_{f,s} = +47.82$ cal deg-mol^{-1}.

studies on the kaolinite-pyrophyllite-quartz reaction

$$Al_2Si_2O_5(OH)_4 + 2\,SiO_2 = Al_2Si_4O_{10}(OH)_2 + H_2O \qquad (3)$$

and the pyrophyllite-andalusite-quartz reaction

$$Al_2Si_4O_{10}(OH)_2 = Al_2SiO_5 + 3\,SiO_2 + H_2O. \qquad (4)$$

It is therefore necessary to compare values of $\Delta G_f^0[Al_2SiO_5]$ and $\Delta G_f^0[Al_2O_3]$ obtained from reversed equilibria not involving kaolinite, pyrophyllite (or muscovite, paragonite), and independently of the aluminosilicate-corundum-quartz reaction

$$Al_2SiO_5 = Al_2O_3 + SiO_2. \qquad (5)$$

The System CaO—Al_2O_3—SiO_2—H_2O—(CO_2)

Several sets of experimental data have been used to evaluate Gibbs Energy Difference Functions for phases in the system CaO—Al_2O_3—SiO_2—(H_2O—CO_2). The data sources and values used are presented in Tables 3 and 4.

Values of $\Delta G_f^0[Al_2SiO_5]$, [Cor] were not evaluated directly since some of the tabulated Gibbs energy values for the calcium-aluminosilicates are obtained from ΔH_f^0 data which use gibbsite as the aluminum reference in the original work (gehlenite, anorthite).

Although the heats of solution determinations on gehlenite by Barany (1963) were made upon synthetic material, the tabulated ΔG_f^0[Geh] depends, in addition, upon entropy data derived from heat capacity determinations by Weller and

Table 3. Free energy difference functions for reactions involving Al_2SiO_5 or Corundum

Calcite-andalusite-anorthite-quartz-CO_2 equilibria (6)

$A \equiv \Delta G_f^0[\text{And}]^{a} - \Delta G_f^0[\text{Anor}] = -\Delta G_f^0[\text{Cal}] - \Delta G_f^0[\text{Q}] + \Delta V_s \Delta P - \Delta S_{f,s} \Delta T + G_{CO_2}$

P kbar	T^0 C[b]	G_{CO_2}	A kcal mol^{-1}	Reference
2.0	440 ± 10	−83459[c]	+373.11 ± 1.45	Thompson (1971; unpub.)
0.5	410 ± 15	−86862[c]	+370.92 ± 1.67	Thompson (1971; unpub.)
2.0	460 ± 15	−83297[c]	+372.43 ± 1.42	Nitsch (unpub; pers. comm.)
		average	+372.15 ± 1.55	

Anorthite-grossular-kyanite-quartz equilibria (7)

$B \equiv \Delta G_f^0[\text{Gr}] + 2\Delta G_f^0[\text{Ky}] - 3\Delta G_f^0[\text{Anor}] = -\Delta G_f^0[\text{Q}] + \Delta V_s \Delta P - \Delta S_{f,s} \Delta T$

P kbar	T^0 C		B kcal mol^{-1}	Reference
28.5–28.6	1300		+201.02 ± 0.62	Hays (1967)
30.4–32.2	1400		+199.73 ± 1.80	Hays (1967)
29.5–32.0	1350		+202.67 ± 1.75	Hariya and Kennedy (1968)
24.0–25.5	1150		+202.68 ± 1.72	Hariya and Kennedy (1968)
		average	+201.45 ± 1.60	

Zoisite-Al_2SiO_5-anorthite-quartz-H_2O equilibria (8)

$C \equiv \Delta G_f^0[Al_2SiO_5] + 2\Delta G_f^0[\text{Zo}] - 4\Delta G_f^0[\text{Anor}] = -\Delta G_f^0[\text{Q}] + \Delta V_s \Delta P - \Delta S_{f,s} \Delta T + G^*_{H_2O}$

P kbar	T^0 C	$G^*_{H_2O}$	C [Sill] kcal mol^{-1}	C [Ky]	Reference
7.2	550 ± 15 ?	−34441	+138.03 ± 1.85	+137.40 ± 86	Newton (1966)
8.9	650 ± ?	−30148	+136.65 ± 1.45	+135.99 ± 1.45	Newton (1966)
12.7	760 ± ?	−22950[d]		+139.76 ± 0.87	Boettcher (1970)
		average	+137.36 ± 1.65	+137.71 ± 1.42	

Grossular-corundum-anorthite-gehlenite equilibria (9)

$D \equiv \Delta Gf[\text{Gr}] + \Delta Gf[\text{Cor}] - \Delta Gf[\text{Anor}] - \Delta Gf[\text{Geh}] = \Delta V_s \Delta P - \Delta S_{f,s} \Delta T$

P kbar	T° C	D kcal mol^{-1}	Reference
1	770 ± 15	−20.28 ± 0.55	Boettcher (1970)

[a] ΔG_f^0[phase] refers to $\Delta G_{f(298,1)}^0$[phase].

[b] For $P_{\text{total}} = P_{H_2O} + P_{CO_2}$ where $X_{CO_2} = 0.5$.

[c] Calculated from Robie (1966, p. 458) and assuming ideal mixing for $X_{CO_2} = 0.5$.

[d] Extrapolated from Fisher and Zen (1971).

The following values were used with above calculations:

Reaction (6)	$\Delta V_s = -0.2477$ cal bar^{-1}	$\Delta S_{f,s}$ (298)	$= +44.507$ cal deg-mol^{-1}
		(700)	+42.15
(7)	+1.5823	(298)	+37.738
		(1600)	+38.21
		(1700)	+39.58
		(1600)	+38.21
		(1400)	+36.56
(8) [Ky]	+1.5155	(298)	+83.12
[Sill]	+1.3767	(298)	+80.16
(9)	+0.9597	(298)	+25.97
		(1000)	+28.51

ΔG_f^0[Cal], ΔG_f^0[Q] taken from Robie and Waldbaum (1968).

Table 4. Free energy difference functions for additional reactions in the System $CaO—Al_2O_3—SiO_2—(H_2O)$

Grossular-quartz-anorthite-wollastonite equilibria (10)

$$E \equiv \Delta G_f^0[\mathrm{Gr}]^a - \Delta G_f^0[\mathrm{Anor}] = 2\Delta G_f^0[\mathrm{Wo}] - \Delta G_f^0[\mathrm{Q}] + \Delta V_s\,\Delta P - \Delta S_{f,s}\,\Delta T$$

P kbar	T° C		E [Wo, Pswo]	E [Wo]	Reference
			kcal mol^{-1}		
3.0	635 ± 15		−545.55 ± 0.45	− 545.55 ± 0.45	Boettcher (1970)
17.1–18.6	1200		−548.42 ± 1.15	−545.903 ± 1.10	Hay (1967)
11.5–16.1	1100		−548.59 ± 2.10	−545.848 ± 2.05	Hays (1967)
		average	−547.52 ± 1.25	−545.767 ± 1.25	

Grossular-anorthite-gehlenite-wollastonite equilibria (11)

$$F \equiv 2\Delta G_f^0[\mathrm{Gr}] - \Delta G_f^0[\mathrm{Anor}] - \Delta G_f^0[\mathrm{Geh}] = 3\Delta G_f^0[\mathrm{Wo}] + \Delta V_s\,\Delta P - \Delta S_{f,s}\,\Delta T$$

P kbar	T° C		F [Wo, Pswo]	F [Wo]	Reference
1.0	840 ± 20		−1145.64 ± 0.95	−1145.64 ± 0.95	Boettcher (1970)
7.4 ± 9.9	1200		−1150.87 ± 1.72	−1147.10 ± 1.62	Hays (1967)
9.4–11.0	1250		−1151.02 ± 1.58	−1147.63 ± 1.57	Hays (1967)
		average	−1149.17 ± 1.55	−1146.41 ± 1.52	

Zoisite-quartz-anorthite-grossular-H_2O equilibria (12)

$$I \equiv 4\Delta G_f^0[\mathrm{Zo}] - 5\Delta G_f^0[\mathrm{Anor}] - \Delta G_f^0[\mathrm{Gr}] = -\Delta G_f^0[\mathrm{Q}] + \Delta V_s\,\Delta P - \Delta S_{f,s}\,\Delta T + 2G^*_{\mathrm{H_2O}}$$

P kbar	T° C	G^*H_2O	I kcal mol^{-1}	Reference
2	500 ± 15	−38870	+ 69.466 ± 2.10	Newton (1966)
4	595 ± 15	−34538	+ 69.526 ± 2.05	Boettcher (1970)
5.3	650 ± 10	−31906	+ 70.064 ± 1.35	Boettcher (1970)
		average	+ 69.685 ± 1.60	

Prehnite-zoisite-grossular-quartz-H_2O equilibria (13)

$$J \equiv 5\Delta G_f^0[\mathrm{Pr}] - 2\Delta G_f^0[\mathrm{Zo}] - 2\Delta G_f^0[\mathrm{Gr}] = 3\Delta G_f^0[\mathrm{Q}] + \Delta V_s\,\Delta P - \Delta S_{f,s}\,\Delta T + 4G^*_{\mathrm{H_2O}}$$

P kbar	T° C	G^*H_2O	J kcal mol^{-1}	Reference
3.0	403 ± 15	−41692	−847.720 ± 0.75	Liou (1971)
4.0	399 ± 10	−41200	−847.833 ± 1.45	Liou (1971)
5.0	393 ± 5	−41000	−848.802 ± 0.75	Liou (1971)
		average	−848.119 ± 0.95	

Prehnite-anorthite-wollastonite-H_2O equilibria (14)

$$K \equiv \Delta G_f^0[\mathrm{Pr}] - \Delta G_f^0[\mathrm{Anor}] = \Delta G_f^0[\mathrm{Wo}] + \Delta V_s\,\Delta P - \Delta S_{f,s}\,\Delta T + G^*_{\mathrm{H_2O}}$$

P kbar	T° C	G^*H_2O	K kcal mol^{-1}	Reference
1.0	440 ± 5	−41483	−434.239 ± 0.42	Liou (1971)
2.0	465 ± 5	−40032	−434.145 ± 0.42	Liou (1971)
3.0	495 ± 5	−38452	−434.193 ± 0.42	Liou (1971)
4.0	520 ± 5	−37064	−434.161 ± 0.42	Liou (1971)
5.0	550 ± 5	−35521	−434.247 ± 0.42	Liou (1971)
		average	−434.197 ± 0.42	

[a] ΔG_f^0[phase] refers to $\Delta G^0_{f(298,1)}$[phase].

(Table 4 continued)

The following values were used with above calculations:

Reaction (10)	$\Delta V_s = +0.7807$ cal bar^{-1}	$\Delta S_{f,s}$	(298) =	+ 20.072 cal deg-mol^{-1}
			(900)	+ 19.53
			(1500)	+ 22.41
			(1400)	+ 20.30
(11)	$+1.4392$		(298)	+ 39.251
			(1100)	+ 44.35
			(1500)	+ 44.70
			(1500)	+ 44.70
(12)	$+1.8017$		(298)	+ 128.51
(13)	-2.7048		(298)	+ 155.82
(14)	-0.0057		(298)	+ 54.06

ΔG_f^0 [Q], ΔG_f^0 [Wo] taken from Robie and Waldbaum (1968).

Kelley (1963). For samples of unspecified structural state, significant configurational entropy contributions may exist (Waldbaum, 1973).

The tabulated ΔH_f^0, ΔG_f^0 [Anor] were obtained from heat of solution measurements made by Barany (1962) on a sample prepared by dehydrating natural lawsonite (at 1050° C for 30 hours) containing significant impurities (especially 1.56% Fe_2O_3). An impurity correction of -2.120 kcal was made by Barany.

The value tabulated by Robie and Waldbaum (1968) for ΔG_f^0 [Gr] is circularly dependent upon ΔG_f^0 [Ky]. [Anor], [Q] since this value was calculated by Hays (1967) from his experimental data. The values calculated by Zen (1972) for ΔG_f^0 [Zo], [Pr] are likewise dependent upon the values tabulated by Robie and Waldbaum (1968) for ΔG_f^0 [Anor], [Gr], [Wo], [Q].

In the evaluation of the Gibbs Energy Difference Functions in Tables 3 and 4 it has been assumed that the tabulated ΔH_f^0, ΔG_f^0 values for wollastonite (Benz and Wagner, 1961; Torgeson and Sahama, 1948) and quartz (Good, 1962; Wise *et al.*, 1963) are accurate.

If the Difference Functions were exact solutions they could be solved simultaneously. Multiple linear regression procedures, using differential weighting based upon precision limits and numbers of data points, gave a set of regressed compatible mean values which may be simultaneously solved for each ΔG_f^0 [phase]. This simultaneous solution of regressed Difference Functions provides ΔG_f^0 [phase] data which are not linked to the calorimetric values for $\Delta G_{f(298,1)}^0$ [phase]. While this has considerable advantage in that possible errors in calorimetric data are by-passed it has significant disadvantages of poor precision, accumulated error and, most important, results in data which are uncoupled from the elemental reference states.

The first column, of the two sets of regressed data in Table 5, shows regressed Difference Functions weighted only by $1/\sigma$, where σ is the estimated average precision. The second column shows a "filtered solution" which, in addition to an n/σ weighting (n is number of data points) has also been weighted to those ΔG_f^0 whose values have been calorimetrically measured (ΔG_f^0 [Anor], [Geh]).

The Difference Functions could be evaluated using the regressed values in Table 5 and "tying" the data to the revised ΔG_f^0 [Anor], [Geh] presented in

Table 5. Regressed mean values of Gibbs Energy Difference Functions

Difference Function as linear equations in $\Delta G^0_{f\,(298,1)}$ [phase]	Set 1		Set 2	
	a (kcal)	*b* (kcal)	*a* (kcal)	*b* (kcal)
A ≡ [And] − [Anor]	+ 372	+ 372.1	+ 373.03	+ 372.30
B ≡ [Gr] −2 [Ky] −3 [Anor]	+ 203.8	+ 201.9	+ 202.76	+ 202.04
C ≡ [Ky] + 2 [Zo] − 4 [Anor]	+ 137.3	+ 136.3	+ 136.82	+ 136.06
D ≡ [Gr] + [Cor] − [Anor] − [Geh]	− 20.47	− 20.89	− 20.82	− 22.17
E ≡ [Gr] − [Anor]	− 544.7	− 544.6		
F ≡ 2 [Gr] − [Anor] − [Geh]	−1145	−1144	−1144.5	−1144.9
I ≡ 4 [Zo] − 5 [Anor] − [Gr]	+ 70.78	+ 70.68	+ 70.88	+ 70.08
J ≡ 5 [Pr] − 2 [Zo] − 2 [Gr]	− 847.5	− 847.7	− 847.67	− 847.92
K ≡ [Pr] − [Anor]	− 434.8	− 434.8	− 434.63	− 434.27
[Ky] − [Cor]	− 205.6	− 205.6	− 205.78	− 206.65
[And] − [Ky]			−0.537	−0.417

In each set, column *a* refers to weighting the data as $1/\sigma$, column *b* refers to weighting by n/σ, where σ is 2 standard errors on Difference Function and n is number of data points.

In Set 1 only 7 of the 10 equations are linearly independent and while this does not affect the regressed mean values it does not allow the correct solution of the simultaneous linear equations for each ΔG^0_f [phase]. Set 2 is an attempt to reduce the number of dependent equations but actually contains only 7 independent equations.

A comparison of the regressed Difference Functions with the average functions in Tables 3 and 4 allows a choice to be made between the most consistent experimental data. In the cases where widepressure ranges are indicated from the experimental results, these mean values allow significant interpolation.

Table 1. However some of the Difference Functions show large discrepancies compared to the regressed mean values, even for equilibria that were originally considered to be well reversed. One of the major problems in using this approach concerns the use of tabulated and estimated entropy data, especially in extrapolation to high temperature. If sufficient data were available, linear Difference Functions could be factored into enthalpy and entropy terms, perhaps enabling distinction of the largest uncertainties. A further independent test of ΔG^0_f values determined from Difference Functions is needed before ΔG^0_f data tied to revised values of ΔG^0_f [Anor], [Geh], can be justified.

Evaluation of $\Delta G^0_{f(298,1)}$ [Anor], [Geh] from Liquidus Studies

Kay and Taylor's (1960) measurements of silica activity of liquids in the CaO—Al_2O_3—SiO_2 system gave $\Delta G^0_f = -21.750$ kcal at 1823 K (1550° C) for the reaction

$$CaO \cdot Al_2O_3(s) + 2\,SiO_2(s) = CaAl_2Si_2O_8(s).$$

Parker *et al.* (1971) give a value of $\Delta G^0_{f(298,1)}[CaO \cdot Al_2O_3] = -527.9$ kcal mol^{-1}, from which $\Delta G^0_{f(1823,1)} = -384.170$ was calculated using $\Delta S^0_{f,298} = -94.247$ cal deg^{-1}mol^{-1} and the approximation

$$\Delta G_{f(T,1)} = \Delta G_{f(298,1)} + \Delta T\, \Delta S_{f(298,1)}.$$

Using Robie and Waldbaum's (1968) values for $\Delta G^0_{f(1823,1}$ [cristobalite] $= -139.861$, a value of $\Delta G^0_{f(1823,1)}$ [Anor] $= -685.632$ leading to $\Delta G^0_{f(298,1)}$ [Anor] $= -960.295$ kcal mol^{-1} (with $\Delta S^0_{f,298}$ [Anor] $= -180.02$ cal deg^{-1} mol^{-1}) was obtained.

Using Coughlin's (1956) value of $\Delta G^0_{f(298,1)}$ [$CaO \cdot Al_2O_3$] $= 526.124$ kcal mol^{-1}, a value of $\Delta G^0_{f(298,1)}$ [Anor] $= -958.38$ kcal mol^{-1}, was obtained.

Kay and Taylor (1960) give $\Delta G^0_f = 8.000$ kcal at 1543 K (1270° C) for the reaction

$$CaSiO_3(s) + CaAl_2Si_2O_8(s) = Ca_2Al_2SiO_7(s) + 2\,SiO_2(\text{liquid}).$$

Using their data for silica activity and $\Delta G^0_{f(1543,1)}$ [PsWo] $= -286.562$ kcal mol^{-1} from Robie and Waldbaum (1968) (from oxides $= -21.322$ kcal mol^{-1}) we obtain

$$\Delta G^0_{f(1543,1)}[\text{Geh}] - \Delta G^0_{f(1543,1)}[\text{Anor}] = -13.322 \text{ kcal}.$$

Using the value of $\Delta G^0_{f(298,1)}$ [Anor] $= -960.295$ kcal, obtained from their data and correcting to 1543 K, we obtain $\Delta G^0_{f(298,1)}$ [Geh] $= -908.89$ kcal mol^{-1} (using $\Delta S^0_{f,298}$ [Geh] $= -159.276$ cal deg^{-1} mol^{-1}).

Although no real accuracy may be assigned to these calculated values for $\Delta G^0_{f(298,1)}$ [Anor], [Geh] it is considered that precision would be in the range ± 1.6 kcal mol^{-1}. These values are obviously more negative than the tabulated values but some 1 kcal more positive than the values obtained by directly inserting the ΔG^0 [Gbs] from Gross *et al.* into the calorimetric schemes (Table 1).

Consistent Values for $G^0_{f(298,1)}$ for Aluminous Minerals

A consistent set of Gibbs Energy data for aluminous minerals was obtained using the revised ΔH^0_f data based upon the new ΔH^0_f [Gbs] and regressed Gibbs Energy Difference Functions. The suggestion by Essene *et al.* (1972) that $\Delta G^0_{(298,1)} = +0.8 \pm 0.4$ kcal for the kyanite-corundum-quartz reaction (5) was incorporated in Table 5. The data of Holdaway (1971) was used to calculate $\Delta G^0_{f(298,1)}$ [And-Ky].

Table 6. A consistent set of $\Delta G^0_{f\,(298,1)}$ values for aluminous minerals (kcal mol^{-1})

Corundum	− 378.08	Anorthite	− 961.5	
Andalusite	− 584.13	Gehlenite	− 910.3	(−911.1)[a]
Kyanite	− 584.00	$CaAl_2SiO_6$	− 751	
Sillimanite	− 583.60	Grossular	−1509	
Gibbsite	− 276.43	Zoisite	−1562	
Diaspore	− 219.9	Prehnite	−1395	
Kaolinite	− 908.7	Laumontite	−1603	
Pyrophyllite	−1259.1	Wairakite	−1483	
Muscovite	−1338.8	Lawsonite	−1082.3	
Paragonite	−1328.6			
Analcime	− 737.16			

[a] For different entropy values, see Table 1.

Although some of the values are probably known with better precision they have been rounded off (particularly those that have been calculated relative to anorthite). For these values the precision is probably no better than ±2.5 kcal, in view of possible impurities and uncertain structural state of the calorimetric anorthite sample (see text). No estimate of accuracy is made.

These $\Delta G^0_{f(298,1)}$ values, shown in Table 6, are "tied" to the Robie and Waldbaum (1968) values for ΔG^0_f [Cor], [Al_2SiO_5].

There is no real reason to suppose that the value obtained by Mah (1958) for ΔH^0_f [Cor] $= -400.4 \pm 0.3$ kcal mol^{-1}, from oxygen combustion of Al metal, is in serious error (see the commentary by Kubaschewski *et al.*, 1967, p. 94). Waldbaum (1971) noted that if the aluminum were incompletely burned or γ—Al_2O_3 formed then the ΔH^0_f [Cor] should be *more negative* than the tabulated value, opposing the sign of the discrepancy noted by Zen (1969, 1972). The tabulated ΔG^0_f [Al_2SiO_5] are derived from calculations by Waldbaum (1965) using experimental data on aluminosilicate equilibria and sillimanite-mullite-quartz equilibria, heat capacity data from Todd (1950) and Pankratz and Kelley (1964), and oxide-melt calorimetric data of Holm and Kleppa (1966). These ΔG^0_f [Al_2SiO_5], calculated relative to $\Delta H^0_{f(298,1)}$ [Cor] $= -400.4$ kcal mol^{-1} and $S^0_{f(298,1)} = 12.18$ cal K^{-1}, should not be in serious error despite the discrepancies in the Holm and Kleppa kyanite-sillimanite data as shown by Anderson and Kleppa (1969), Shearer and Kleppa (1973).

Possible Causes of the Discrepancy in $\Delta G^0_{f(298,1)}$ for Aluminous Minerals

The error in ΔH^0 [Gbs] does not appear to lie with measurement of the heat of solution of gibbsite, and may suggest inaccuracies in the heat of solution of Al metal or $AlCl_3 \cdot 6H_2O$ or ΔH^0_f of the latter. A further discrepancy is found in the values for the *inferred* heat of solution of Al_2O_3, which cannot be determined directly because of its insolubility, in 20% HF or in 20% HCl—5% HF acid solutions [compare Kelley (1962), Troitzsch (1935, reference in Sommerfeld, 1967) and Kracek *et al.* (1952)]. A recalculation of Sommerfeld's (1967) heat of solution measurements, in 20% HCl—5% HF acid solutions, yields the values

	$\Delta H^0_{f(298,1)}$ kcal mol^{-1}	$\Delta G^0_{f(298,1)}$ kcal mol^{-1}
Muscovite	−1430.165	−1339.08
Anorthite	−1017.59	−963.917
Zoisite	−1663.837	−1568.578

The values for ΔH^0_f, ΔG^0_f [Mus], [Anor] are in close agreement with the revised data in Table 1. The difference between this ΔG^0_f [Zo] and that in Table 6 may be related to Sommerfeld's use of calcite in the zoisite-acid dissolution or to his large impurity corrections. Use of his tabulated *uncorrected* data (Sommerfeld, 1967, Table 2, column 3) would considerably reduce the ΔH^0_f, ΔG^0_f [Zo] values shown above.

Other discrepancies in the present recalculated values are likely and will only be solved by improved thermochemical data, especially since many of the direct revisions in Table 1 are based upon ΔH^0_f [Gbs] $= -13.3 \pm 0.7$ kcal, relative to α—Al_2O_3 and liquid H_2O, and currently tabulated entropy data.

The internal consistency of the revised data in Tables 1 and 6 suggest that tabulated ΔH^0_f, $\Delta G^0_{f(298,1)}$ values for Al^{3+} and other aqueous aluminum complexes should be reexamined (compare Ulbrich and Merino, 1974).

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