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J.A. Apps and J.M. Neil

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*John A. Apps and John M. Neil**

Earth Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

August 1989

*Now with the United States Geological Survey
Federal Building, 2800 Cottage Way
Sacramento, California 95825

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Correlation of the Solubilities of Aluminum Hydroxides and Oxyhydroxides in Alkaline Solutions with the Thermodynamic Properties of $Al(OH)_4^-$.

John A. Apps and John M. Neil[1]

Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, California 94720

The solubilities of gibbsite, boehmite and diaspore in alkaline solutions between 20 and 350°C are evaluated and their thermodynamic properties reconciled. The thermodynamic properties of the aluminate ion, $Al(OH)_4^-$, are derived over the same temperature range and compared with predictions based on the revised Helgeson-Kirkham-Flowers equation of state. Preliminary thermodynamic properties of bayerite and $\Delta G^o_{f,298}$ for nordstrandite are also derived from solubility data in alkaline solutions. Log K_{s4} values for gibbsite, bayerite, boehmite and diaspore between 0 and 350°C, and thermodynamic data for $Al(OH)_4^-$ or AlO_2^-, are tabulated for use in distribution-of-species computer codes.

During the last decade, there has been an increasing interest in mathematically simulating the evolution of groundwaters. The purpose of such simulations is not only to reconcile observed with predicted groundwater compositions, but also to correlate the physical, mineralogical and isotopic changes of participating mineral and aqueous species with time, (1,2). Such modeling is required in a variety of programs for the deep burial of radioactive waste, toxic waste disposal, geothermal energy, and water resource management and conservation.

A complete description of any groundwater system necessitates consideration of reactions between rock forming minerals and the aqueous phase. This cannot be achieved without accurate thermodynamic properties of both the participating aluminosilicate minerals and aqueous aluminum species. Most computer codes used to calculate the distribution of species in the aqueous phase utilize the "reaction constant" approach as opposed to the "Gibbs free energy minimization" approach (3). In the former, aluminosilicate dissolution constants are usually written in terms of the aqueous aluminum species, Al^{+++}, which is related to other aqueous aluminum species by appropriate dissociation reactions.

[1]Current Address: United States Geological Survey, Federal Building, 2800 Cottage Way, Sacramento, California 95825.

The choice of Al^{+++} is unfortunate. The most recent CODATA compilation (4) gives $\Delta H^o_{f,298} = -128.68 \pm 0.36$ kcal.mol^{-1} and $S^o_{298} = -77.7 \pm 2.4$ cal.mol^{-1}.K^{-1} for Al^{+++}. These values are based in part on an earlier Russian analysis of calorimetric data and gibbsite solubility measurements (5). Some groundwater modelers (6,7) prefer Al^{+++} thermodynamic values determined by Hemingway et al. (8) where $\Delta H^o_{f,298} = -126.91 \pm 0.96$ kcal.mol^{-1} and $S^o_{298} = 73.6 \pm 3.6$ cal.mol^{-1}.K^{-1}. These are consistent with several gibbsite solubility measurements in dilute acid aqueous solutions (9–12) yielding similar log $*K_{s0,298}$ values near 8.11 (7,12) for the reaction

$$Al(OH)_3(\text{gibbsite}) + 3H^+ = Al^{+++} + 3H_2O$$

The CODATA thermodynamic properties for Al^{+++} are based in part on log $*K_{s0,298}$ = 7.95 ± 0.44 for gibbsite. Both are higher than those of two recent solubility studies using synthetic gibbsite that was treated to remove adhering foreign material, i.e., log $*K_{s0,298}$ = 7.55 ± 0.055 (13) and 7.74 ± 0.14 (14), respectively.

Couturier et al. (15) found that log $*\beta_{4,298}$ for the reaction

$$Al^{+++} + 4H_2O = Al(OH)_4^- + 4H^+$$

derived from the earlier gibbsite solubility measurements (9,11,16) in dilute acid and basic aqueous solutions, was ≈−23.2 ± 0.2, which differs from the value of −22.20 derived from their own homogeneous aqueous solution measurements between 20 and 70°C. They concluded that either the gibbsite solubility measurements in acid media or those in basic media were incorrect. Using other evidence from natural systems, they determined that those in basic media were more reliable and accepted $\Delta H^o_{f,298} = -126.6$ kcal.mol^{-1} and $S^o_{298} = -77.0$ cal.mol^{-1}.K^{-1} for Al^{+++}.

It is clear that there is no consensus regarding the values assigned to the thermodynamic properties of Al^{+++}, and that present discrepancies in the recommended values are too large for any confidence to be placed in their use in groundwater modeling. Additional studies will be needed to close this issue. In contrast, there is a substantial and reconcilable literature for refinement of the thermodynamic properties of the aluminate ion, $Al(OH)_4^-$ or AlO_2^-. Many studies have been conducted on the solubilities of aluminum hydroxides in alkaline solutions, including gibbsite, whose thermodynamic properties have been well characterized by calorimetry. Much of this literature is in response to development of the Bayer process for refining bauxitic aluminum ores. The evaluation of aluminum hydroxide solubilities in alkaline solution is facilitated by relatively simple speciation. Although some questions have been raised as to the presence of polynuclear species in extremely concentrated aluminate solutions (17–20), sodium aluminate solutions generally contain only one mononuclear aluminum species, the aluminate ion. This contrasts with acid solutions where extensive hydrolysis of aluminum species occurs as a function of pH and temperature, and many real and imagined polynuclear hydroxy aluminum species have been identified (21–25).

There is therefore a strong argument in favor of defining aluminosilicate dissolution reactions in reaction constant codes in terms of the aluminate ion, because of the precision by which its thermodynamic properties might be determined in relation to well defined calorimetric standards, such as gibbsite and corundum. It is also preferable to describe aluminosilicate dissolution reactions in terms of the aluminate ion, because the need for recalculating the dissolution reaction constants for all aluminosilicate species can be avoided when refined properties for Al^{+++} become available. Finally, it should be noted that most groundwaters are neutral to slightly alkaline, where $Al(OH)_4^-$, rather than Al^{+++}

dominates in the absence of fluoride complexation.

In this paper, the procedures are summarized by which the solubilities of gibbsite, boehmite, and diapore in alkaline solution are evaluated and used to compute thermodynamic properties of boehmite and the aluminate ion. Published data are then used in conjunction with the derived properties of the aluminate ion given in this paper to calculate preliminary thermodynamic properties for bayerite, and the Gibbs free energy of formation of nordstrandite at 25°C. Aluminum hydroxide and oxyhydroxide, and corundum solubility reaction constants, and other data suitable for modifying the thermodynamic data bases in reaction constant computer codes are also tabulated. With this information, an investigator will be able to model more precisely neutral to alkaline groundwaters.

Readers who desire a complete tabulation of the data, a description of experimental methods used in acquiring previously unpublished data and a critical discussion regarding the accuracy of the data sets employed in the evaluation, should request a copy of (26) from the senior author.

Solubilities of Aluminum Hydroxides

The equilibration rates of aluminum hydroxide and oxhydroxides with the aqueous phase are greatly accelerated in strongly alkaline solutions and with increasing temperature (26). With care, and using a variety of techniques (26), it is possible to establish whether or not equilibration has been attained with respect to a given solid phase.

Available solubility measurements on gibbsite, boehmite and diaspore span a temperature range from 20-350°C thereby permitting, in principle, the calculation of the Gibbs free energy of formation, ΔG_f^o of $Al(OH)_4^-$, over that temperature range. To do this, however, also requires the heat capacity, $C_P^o(T)$, the entropy, S_{298}^o, and the enthalpy of formation, $\Delta H_{f,298}^o$, of the participating solid phases. These properties have been fully determined by calorimetric means only for gibbsite and corundum, although even the value of $\Delta H_{f,298}^o$ of the latter has been questioned (27). It is possible to compute $\Delta H_{f,298}^o$ for diaspore from corundum with available phase equilibria data (28–31), which, together with $C_P^o(T)$ and S_{298}^o from Perkins et al. (32), completely characterizes this phase. If the solubility of boehmite is reconciled with those of gibbsite and diaspore, the thermodynamic properties of boehmite can be refined and the consistency of the published properties of gibbsite and corundum can be tested. The thermodynamic data for the solid phases used in, and derived through this study, are summarized in Table I.

Aluminum hydroxides are assumed to dissolve according to the following reactions:

$$Al(OH)_3 + OH^- = Al(OH)_4^- \qquad K_{s4} = \frac{[Al(OH)_4^-]}{[Al(OH)_3]\,[OH^-]} \tag{1}$$

and

$$AlOOH + OH^- + H_2O = Al(OH)_4^- \qquad K_{s4} = \frac{[Al(OH)_4^-]}{[AlOOH]\,[OH^-]\,[H_2O]} \qquad (2)$$

where [ ] denote activities. Solubility data from the investigations listed on Figures. 1-4 (11,12,38–66) were evaluated using the EQ3 distribution of species code (67) and log K_{s4} computed. The results were plotted graphically against computed ionic strength, I, and extrapolated empirically to I = 0. The empirical extrapolation procedure was necessary because the electrolyte model was used outside its range of validity, and because no better models were or are available for evaluation of high ionic strength alkaline aluminate solutions. The resulting log $K_{s4}(I = 0)$ values for the respective hydroxides are plotted against the reciprocal of absolute temperature in Figures 1–4.

Discrepancies between the data sets were reconciled as discussed in (26). The increasing scatter in K_{s4} for gibbsite with falling temperature is attributed primarily to contamination of Bayer process gibbsite with bayerite or other surface reactive precipitates, and is discussed further below. Those measurements which are believed to approach most closely the true solubility of gibbsite are reported by by Kittrick (11) and Russell et al. (45).

Calculation of the Thermodynamic Properties

Boehmite, AlOOH. Log K_T^o for the univariant reactions: gibbsite = boehmite + $H_2O(l)$, and boehmite = diaspore, were calculated from the differences in log K_{s4} for the respective aluminum hydroxides at discrete temperatures, and where the solubility determinations overlapped. Log K_f^o for boehmite was then calculated using calculated values of log K_f^o for gibbsite, diaspore and water. The log K_f^o data for boehmite were regressed in conjunction with the Maier-Kelley heat capacity function determined by Mukaibo et al. (34), and the respective values of $\Delta G^o_{f,298}$, $\Delta H^o_{f,298}$ and S^o_{298} derived for boehmite, as given in Table I. The most notable feature of these properties, is that S^o_{298} = 8.99 ± 1.03 cal.mol^{-1}.K^{-1}. This differs substantially from 11.58 ± 0.05 cal.mol^{-1}.K^{-1}, determined for an aluminum monohydrate by Shomate and Cook (68), and often erroneously assigned to boehmite.

The Aluminate Ion, $Al(OH)_4^-$. Calculation of $\Delta\bar{G}_f^o$ or log $\bar{K}_f^o$ of the aluminate ion from gibbsite, boehmite and diaspore in alkaline solutions using equations (1) or (2) requires the corresponding standard state partial molal properties of the hydroxyl ion, OH^-. These may be determined from the dissociation constant for water, K_w if it is accurately known over the range of temperatures and pressures investigated. The experimental measurements of diaspore solubility, reported here, extend to 350°C on the aqueous phase saturation surface, but experimental determinations of K_w by Sweeton et al. (69) attain only 300°C. An electrolyte model is therefore needed to extrapolate K_w another 50°C. The recently revised version of the Helgeson, Kirkham, Flowers (H.K.F.) equation of state by Tanger and Helgeson (70) was used to perform this extrapolation.

Table I. Summary of thermodynamic properties of gibbsite, boehmite, diaspore, and corundum

Mineral	Formula	$C^o_{P,298}$	Maier-Kelley Function[a] parameters			S^o_{298}	$\Delta H^o_{f,298}$	$\Delta G^o_{f,298}$	$\log K^o_{f,298}$
		$cal.mol^{-1}.K^{-1}$	a	$b \times 10^3$	$c \times 10^{-5}$	$cal.mol^{-1}.K^{-1}$	$kcal.mol^{-1}$	$kcal.mol^{-1}$	–
Bayerite[c]	$Al(OH)_3$	22.246	8.65	45.6	0.0	18.97±1.43[d]	−307.83±0.31[d]	−275.57±0.32[d]	202.00±0.24[d]
Gibbsite	$Al(OH)_3$	22.246	8.65[b]	45.6[b]	0.0[b]	16.36±0.03[f]	−309.06±0.28[f]	−276.02±0.29[f]	202.33±0.21[f]
Nordstrandite	$Al(OH)_3$	–	–	–	–	–	–	−275.83±0.31[d]	202.18±0.23[d]
Boehmite	AlOOH	15.696	12.905[e]	20.700[e]	−3.005[e]	8.99±1.03[d]	−237.89±0.31[d]	−219.29±0.30[d]	160.74±0.22[d]
Diaspore	AlOOH	12.771	12.149[g]	13.273[g]	−2.965[g]	8.45±0.02[g]	−238.83±0.16[h]	−220.08±0.16[h]	161.32±0.12[h]
Corundum	Al_2O_3	19.006	21.742[f]	11.065[f]	−5.365[f]	12.18±0.03[f]	−400.50±0.31[f]	−378.16±0.32[f]	277.20±0.23[f]

Uncertanties are = 2σ when based upon a statistical evaluation. Note that the uncertainties in ΔH^o_{298}, ΔG^o_{298} and $\log K^o_{298}$ of the aluminum hydroxides and oxyhydroxides with respect to corundum and liquid water are between 2 and 5 times smaller than those of the corresponding properties with respect to the elements.

[a] $C^o_P = a + bT + cT^{-2}$.

[b] Kelley (33).

[c] Heat capacity assumed to be the same as that of gibbsite.

[d] This paper and Apps et al. (26).

[e] Mukaibo et al. (34).

[f] Calculated from Hemingway and Robie (35), Hemingway et al. (36), Robie et al. (37)

[g] Calculated from Perkins et al. (32).

[h] Calculated using phase equilibria data by Haas (30) as reported by Helgeson et al. (27).

Calculation of log $\overline{K}_f^o$, and $\overline{\Delta G}_{f,T}^o$ for $Al(OH)_4^-$ was conducted in two steps; an initial regression of selected experimental values of log K_{s4} for gibbsite, boehmite and diaspore between 20°C and 350°C, followed by calculation of log $\overline{K}_{f,T}^o$, and $\overline{\Delta G}_{f,T}^o$ for $Al(OH)_4^-$ at 25°C intervals between 0°C and 350°C. These results are presented in Table II. $\overline{C}_{P,298}^o$, $\overline{S}_{298}^o$ and $\overline{\Delta H}_{f,298}^o$ for $Al(OH)_4^-$ may be calculated from $\overline{\Delta G}_f^o$ variation with temperature, but are very sensitive to experimental error. This calculation was performed between 20° and 70°C assuming that $\overline{C}_P^o$ remains constant over that temperature interval, and the resulting values incorporated in Table III. $\overline{C}_P^o$ = +21.08 ± 1.65 cal.mol^{-1}.K^{-1}, which is in good agreement with the 23.06 cal.mol^{-1}.K^{-1} value obtained by Hovey et al. (71) using calorimetry. The procedures recommended by Shock and Helgeson (72), were used to calculate the revised H.K.F. equation of state parameters for AlO_2^-, which are summarized in Table III. The predicted values of log $\overline{K}_{f,T}^o$ for $Al(OH)_4^-$ using this equation of state, are in excellent agreement with those obtained from solubility measurements, the maximum deviation being 0.07 at 250°C, (Table II). The H.K.F. equation of state prediction may be slightly more precise; however, differences are essentially within the limits of experimental error.

Table II. Log $\overline{K}_f^o(Al(OH)_4^-)$ and $\Delta\overline{G}_f^o(Al(OH)_4^-)$ between 0 and 350°C Along the Saturation Surface of Water

T,°C	P, bars	$\Delta\overline{G}_f^o(Al(OH)_4^-)$, kcal.mol^{-1}	log $\overline{K}_f^o(Al(OH)_4^-)$		
			This work	Predicted by the H.K.F. Equation of State	Difference
0	0.006	−315.667	252.556	252.580	−0.02
25	0.032	−311.862	228.590	228.609	−0.02
50	0.123	−308.020	208.307	208.322	−0.01
60	0.199	−306.476	201.042	201.055	−0.01
75	0.386	−304.158	190.925	190.932	0.00
100	1.013	−300.281	175.863	175.858	0.00
125	2.320	−296.380	162.679	162.662	+0.02
150	4.957	−292.446	151.036	151.013	+0.03
175	8.918	−288.471	140.672	140.637	+0.04
200	15.536	−284.460	131.387	131.333	+0.06
225	25.478	−280.375	123.001	122.940	+0.06
250	39.735	−276.202	115.380	115.314	+0.07
275	59.425	−271.901	108.403	108.339	+0.06
300	85.832	−267.428	101.969	101.910	+0.06
325	120.447	−262.676	95.971	95.926	–[a]
350	165.212	−257.436	90.283	90.251	–[a]

[a]This work is not independent of the H.K.F. Equation of State above 300°C.

Bayerite, $Al(OH)_3$. Bayerite occurs very rarely in nature (26), but is easily synthesized. Little is known regarding its thermodynamic properties. Some heats of decomposition have been measured in relation to gibbsite (73–76). One HF calorimetry study (77) and

Table III. Summary of thermodynamic properties of the aluminate ion

Formula	$\bar{C}^{o}_{P,298}$ cal.mol^{-1}.K^{-1}	$\bar{S}^{o}_{298}$ cal.mol^{-1}.K^{-1}	$\Delta\bar{H}^{o}_{f,298}$ kcal.mol^{-1}	$\Delta\bar{G}^{o}_{f,298}$ kcal.mol^{-1}	$\log \bar{K}^{o}_{f,298}$ –	$\bar{V}^{o}$ cm^{3}.mol^{-1}
$Al(OH)_4^-$	+21.08±1.65	+29.59±1.03	−357.56±0.31	−311.88±0.33	+228.61±0.24	+46.3±0.3[a]
AlO_2^-	−14.89	−3.81	−220.93	−198.51	+145.51	+10.2

Uncertainties are 2σ when based upon a statistical evaluation.

[a] Hovey et al. (71).

H.K.F. Equation of State Parameters for AlO_2^-

$a_1 \times 10^1$ cal.mol^{-1}.bar^{-1}	$a_2 \times 10^{-2}$ cal.mol^{-1}	a_3 cal.K.mol^{-1}.bar^{-1}	$a_4 \times 10^{-4}$ cal.K.mol^{-1}	c_1 cal.mol^{-1}.K^{-1}	$c_2 \times 10^{-4}$ cal.K.mol^{-1}	$\omega \times 10^5$ cal.mol^{-1}
3.1586	3.0566	−2.1559	−2.9054	13.331	−6.075	1.6866

several alkaline solubility measurements (45,57–63,65) have also been made. Apps et al. (26) evaluated these measurements as a function of temperature between 20 and 100°C, making the approximation that $C^{o}_{P,T}$ of bayerite is the same as that of gibbsite. A plot of log K_{s4} for bayerite versus reciprocal temperature, using the H.K.F. equation of state is given in Figure 4. Comparison of the difference in $\Delta H^{o}_{f,298}$ between gibbsite and bayerite, derived from calorimetric studies (77) with that determined from solubility measurements is excellent, i.e., 1.24 ± 0.11 kcal.mol^{-1}, versus +1.20 ± 0.26 kcal.mol^{-1}, lending credence to the validity of the solubility measurements.

Bayerite is a frequent but unsuspected contaminant in Bayer process gibbsite (78–80). This material is often used in experimental determinations of gibbsite solubility in dilute acid and alkaline solutions (11–14,38,65,81) leading with rare exceptions (13,14) to misleading interpretations of gibbsite solubility. Bayerite is only slightly more soluble than gibbsite between 20 and 100°C. A comparison of Figure 1 with Figure 4, suggests that many of the plotted gibbsite measurements in Figure 2 may be similarly affected by bayerite contamination. This is supported by many observations in the literature (79,82-86). Several reported solubility measurements on bayerite and gibbsite included in Figure 4, fall well above those values accepted in this paper as correct. While it is not possible to infer in all cases, the causes of the discrepancies, it is probable that equilibrium was measured with respect either to finely crystalline particles with a significant surface free energy contribution to the solubility, or to surface contamination. When combined with the short duration of the experiments, a temperature near 25°C, and the dilute nature of some of the alkaline solutions, it would not be surprising to find that equilibrium was not attained with respect to coarsely crystalline bayerite or gibbsite.

Other Gibbsite Polymorphs. Apart from bayerite, two other gibbsite polymorphs have also been observed in nature. The most common is nordstrandite, first reported to occur naturally in 1962 (87,88), but subsequently found in four distinctive low temperature, i.e. less than 100°C, environments (26,89,90). A summary of reported occurrences is given by Apps et al. (26). Both laboratory (91) and field evidence (92) suggest that nordstrandite solubility at earth surface temperatures falls between those of bayerite and gibbsite. Apps et al. (26) attempted to quantify the nordstrandite solubility at 25°C by taking into account small contributions to Gibbs free energy due to the variable surface areas of nordstrandite coexisting with gibbsite and bayerite. This lead to a calculated $\Delta G^{o}_{f,298}$ = -275.83 ± 0.31 kcal.mol^{-1} for nordstrandite.

Another recently discovered polymorph is doyleite (93). Chao et al. (93) believe that other polymorphs may also occur depending on the stacking order of the $Al(OH)_3$ sheets, e.g., see (94). A notable feature is the small differences in Gibbs free energy separating the gibbsite, bayerite and nordstrandite polymorphs at 25°C. Their persistence in nature may consequently be governed by their particle size, by slight differences in environmental conditions, or by slow reaction kinetics.

Application of Thermodynamic Data to Modeling

Table IV summarizes log K_{s4} values for aluminum hydroxides and oxyhydroxides, and corundum between 0 and 350°C. They were calculated using the modified H.K.F. equation of state (70) together with the data given in Tables I and II. These values are suitable for incorporation into distribution of species codes such as EQ3 (67), provided that $Al(OH)_4^-$ (or AlO_2^-) is made a basis species. Calculation of dissolution constants for other

aluminosilicates can be made using the Gibbs free energy data for $Al(OH)_4^-$ or AlO_2^- provided in Table II.

Table IV. Log K_{s4} for Aluminum Hydroxides and Oxyhydroxides, and Corundum taken along the Water Saturation Surface

T,°C	Log K_{s4}				
	Gibbsite	Bayerite	Boehmite	Diaspore	0.5 Corundum
0	−1.679	−1.263	−1.462	−2.108	+0.127
25	−1.276	−0.943	−1.240	−1.821	+0.119
50	−0.889	−0.626	−1.022	−1.548	+0.138
60	−0.740	−0.502	−0.937	−1.445	+0.149
100	−0.184	−0.032	−0.623	−1.059	+0.210
150	+0.433	+0.499	−0.279	−0.638	+0.298
200			+0.018	−0.269	+0.391
250			+0.276	+0.057	+0.481
300			+0.500	+0.348	+0.568
350			+0.689	+0.604	+0.642

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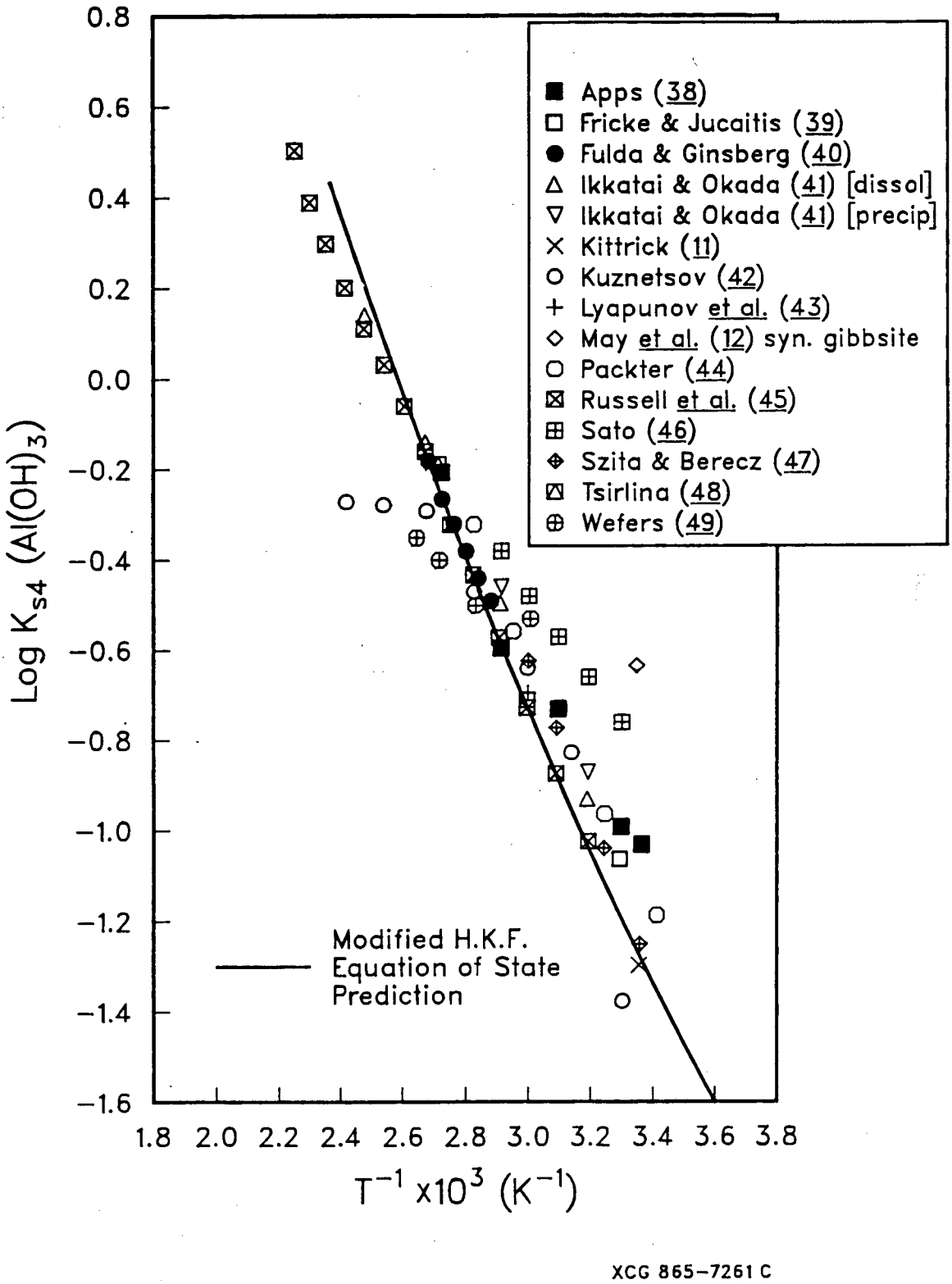

Figure 1. Plot of log $K_{s4}(Al(OH)_3)$ versus the reciprocal of absolute temperature, in which solubility measurements attributed to gibbsite are compared. The experimental precision of the solubility measurements produces a maximum 2σ uncertainty of $\leq \pm$ 0.1 in log K_{S4} and $\leq \pm$ 4K in temperature.

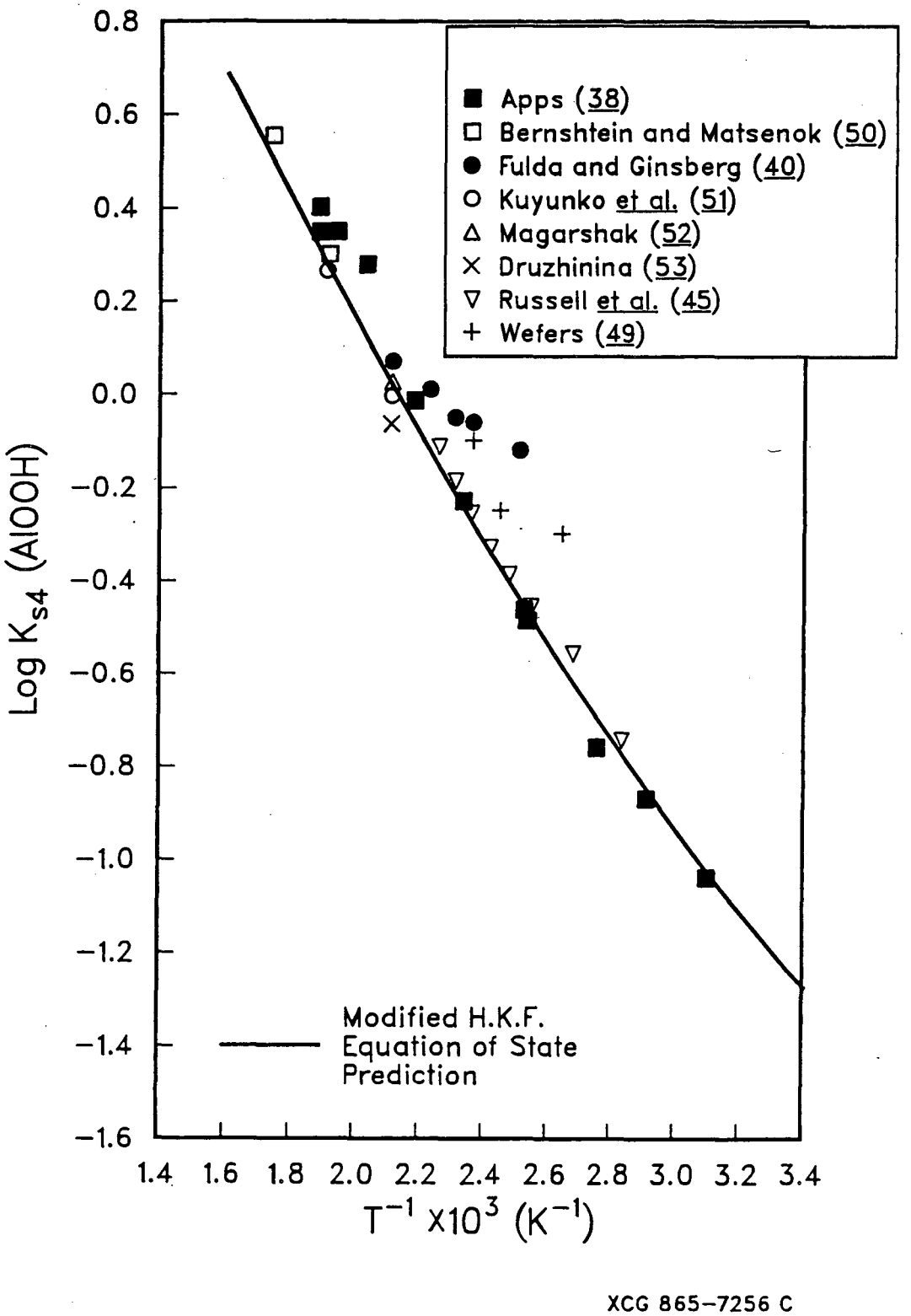

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Figure 2. Plot of log K_{s4}(AlOOH) versus the reciprocal of absolute temperature in which solubility measurements attributed to boehmite are compared. The experimental precision of the solubility measurements produces a maximum 2σ uncertainty of $\leq \pm$ 0.1 in log K_{S4} and $\leq \pm$ 4K in temperature.

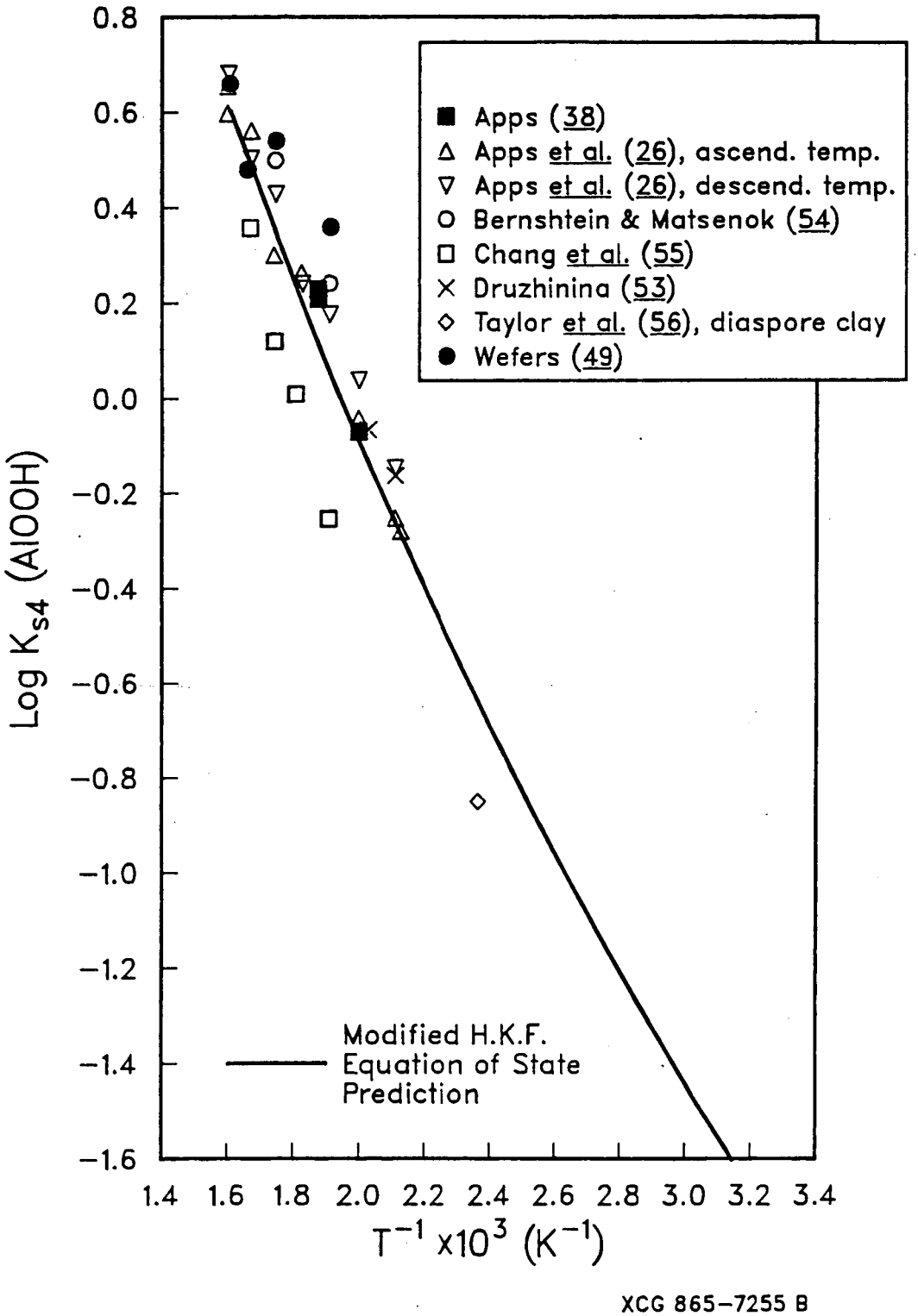

Figure 3. Plot of log K_{s4}(AlOOH) versus the reciprocal of absolute temperature, in which solubility measurements attributed to diaspore are compared. The experimental precision of the solubility measurements produces a maximum 2σ uncertainty of $\leq \pm$ 0.2 in log K_{S4} and $\leq \pm$ 4K in temperature.

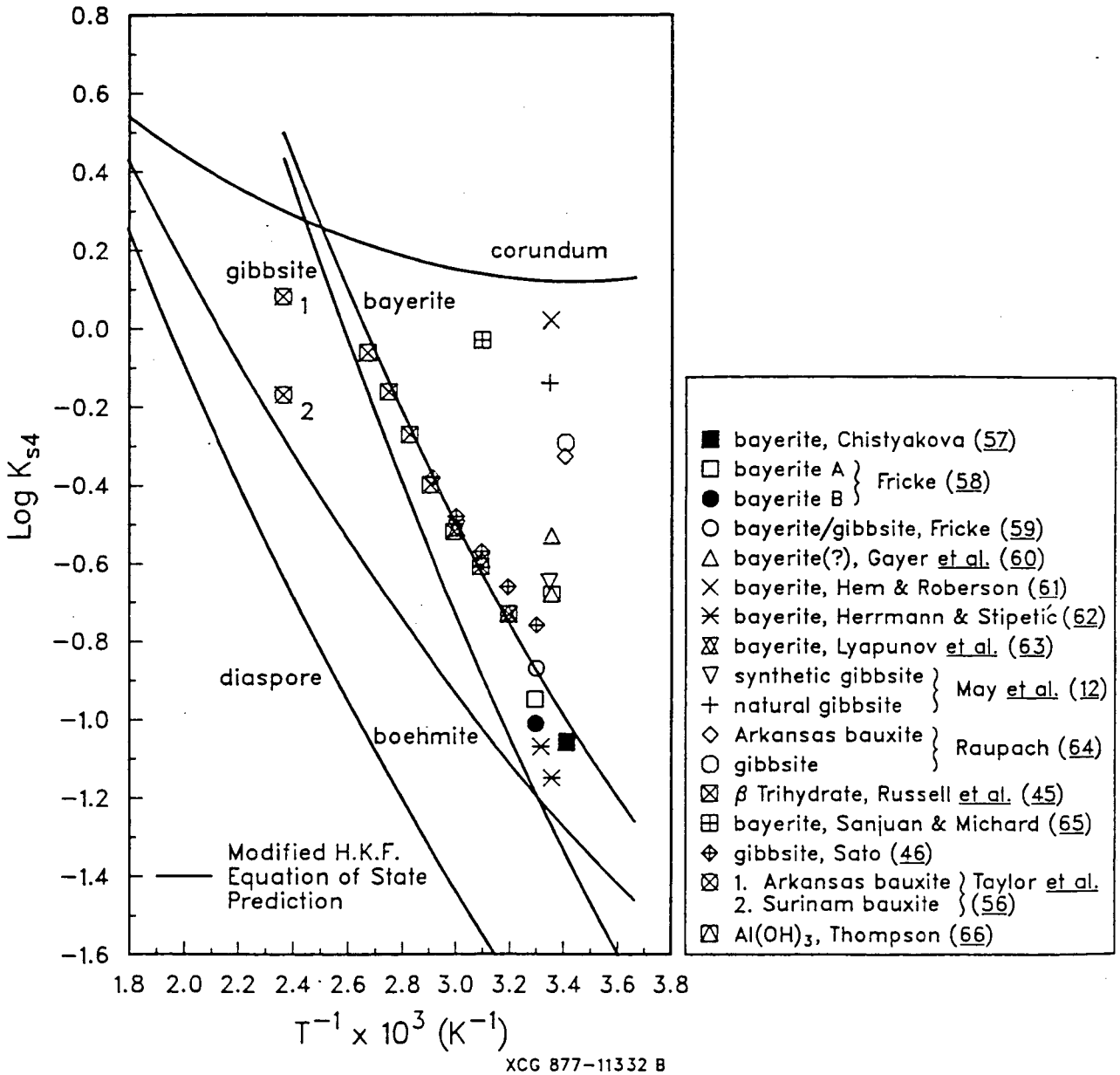

Figure 4. Plots of log K_{s4} versus the reciprocal of absolute temperature, comparing the corresponding dissolution constants for bayerite, gibbsite, boehmite, diaspore and corundum. The experimental precision of the plotted solubility measurements produces a maximum 2σ uncertainty of $\leq \pm 0.2$ in log K_{S4} and $\leq \pm 4K$ in temperature.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720