

FREE ENERGIES OF FORMATION AND AQUEOUS SOLUBILITIES OF ALUMINUM HYDROXIDES AND OXIDE HYDROXIDES AT 25°C

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ABSTRACT

Comparison of the standard free energies of formation at 25°C of corundum, diaspore, boehmite, gibbsite, and bayerite estimated from carefully selected aqueous solubility data with those of calorimetric origin permits selection of a set which is more consistent with stabilities observed in field and laboratory than the calorimetric set alone. The selection process involves acceptance of -378.2 and -116.0 kcal per mole for ΔG°_f of $\alpha\text{Al}_2\text{O}_3$ and Al^{3+} (aq) respectively and assignment of -311.0 kcal per mole for the ΔG°_f of $\text{Al}(\text{OH})_4^-$ (aq). Selected values for the solids are:

	kcal/Mole
diaspore	-219.5 ± 0.5
boehmite	-218.7 ± 0.2
gibbsite	-275.3 ± 0.2
bayerite	-274.6 ± 0.1

Solubility-pH curves based on these assignments agree with independent solubility data only if it is assumed that slight supersaturation results during many experiments and leads, upon aging toward equilibrium, to precipitation of gibbsite or bayerite, depending on pH. One set of data which suggests this interpretation is discussed.

INTRODUCTION

There is convincing evidence in phase equilibrium investigations that corundum is unstable with respect to gibbsite in the presence of water at 25° and one bar pressure (Kennedy, 1959). Unfortunately, tabulated free energies of formation (Wagman *et al.*, 1968, and Robie and Waldbaum, 1968) predict the opposite. During an attempt to find free energies of formation with which to calculate solubilities of the aluminum hydroxides, discovery of this discrepancy revealed the need for critical appraisal of available data. It is the purpose of this paper to select the most reliable free energies of formation available for the hydroxides and oxide hydroxides of aluminum.

For the solids, this is done by critically reviewing the sources of tabulated free energies of formation, which are largely calorimetric, and comparing them with independent data derived from solubility measurements. Derivation of free energies from solubility data required review of the free energies of formation of Al^{3+} (aq) and

$\text{Al}(\text{OH})_4^-(\text{aq})$. Following selection of the free energies of formation of the mono-hydroxo complexes it is shown that polymeric hydroxo complexes can be ignored at equilibrium and an attempt is made to check the validity of the entire set of selected free energies by comparing calculated solubility-pH curves with an independent set of solubility data.

TABULATED FREE ENERGIES OF FORMATION OF THE SOLIDS

Most tabulations of thermodynamic data rely heavily on U.S. Bureau of Standards Circular 500, *Selected Values of Chemical Thermodynamic Properties* (Rossini *et al.*, 1952) and *Oxidation Potentials* (Latimer, 1952). The Bureau of Standards is updating Circular 500 and has released interim tables, omitting references. Data for aluminum appear in Technical Note 270-3 (Wagman *et al.*, 1968), one of the interim series. Original references cited for data attributed to Wagman *et al.* in the following paragraphs were provided by Wagman in personal communications to the author (D. D. Wagman, 1969, written communication). The U.S. Geological Survey has also recently published a tabulation of thermodynamic data (Robie and Waldbaum, 1968). The many publications of Pourbaix and his co-workers, collected in the *Atlas of Electro-Chemical Equilibria in Aqueous Solutions* (Pourbaix, 1966) comprise still another exhaustive source of thermodynamic data.

The original sources of free energies of formation in these tabulations have been examined for information useful in permitting selection among differing estimates.

Corundum, $\alpha\text{Al}_2\text{O}_3$

The free energy of formation of corundum reported by Rossini *et al.* (1952) is -376.77 kcal/mole. The value given by Wagman *et al.* (1968) is -378.2 kcal/mole. The latter is based on heat capacities listed by Kelley and King (1961) and heats of combustion of aluminum reported by Roth, Wolf, and Fritz (1940), Snyder and Seltz (1945), Holley and Huber (1951), Schneider and Gattow (1954), Mah (1957), and Kocherov, Gertman, and Geld (1959). The product of combustion was invariably identified by X-ray diffraction. Robie and Waldbaum (1968) report -378.082 ± 0.310 on the basis of heat capacity data attributed to Kelley and King (1961) and Furukawa *et al.* (1956) and the heat of formation reported by Mah (1957).

The difference between 1968 and 1952 estimates reflects new work. It requires revision of free energies of formation of all other sub-

stances for which corundum served as a reference material. This adjustment has been made where necessary in the paragraphs to follow.

Diaspore, α AlOOH

Rossini *et al.* (1952) list data for a monohydrate not identified by name. The free energy of formation of diaspore given by Wagman *et al.*, (1968) is -220 kcal/mole. It is based on an estimate of the enthalpy change associated with dehydration derived from calibrated differential thermal analysis work (Foldvari-Vogl and Kiburszky, 1958) and on low temperature heat capacity data reported for diaspore by King and Weller (1961). Robie and Waldbaum (1968) list only the entropy of diaspore, citing King and Weller (1961) and Kelley and King (1961).

Fyfe and Hollander (1964) report the free energy of formation of diaspore as -219.5 kcal/mole. This estimate is based on the temperature at which diaspore and corundum coexist at equilibrium with liquid water and an estimate of the entropy needed to correct to 25°C . The estimated probable error from all sources is ± 0.44 kcal/mole.

Fyfe and Hollander took extreme pains to insure equilibrium, but DTA methods are dynamic hence unlikely to produce equilibrium reaction products, thus -219.5 ± 0.5 is probably the best estimate of the free energy of formation of diaspore from these sources.

Boehmite, γ AlOOH

The free energy of formation of boehmite given by Wagman *et al.* (1968) is -218.15 kcal/mole. It is based on measurements of the enthalpy change associated with its dehydration reported by Calvet (1962), Foldvari-Vogl and Kiburszky (1958), Michel (1957b), and Eyraud *et al.* (1955) and heat capacity data originally reported by Shomate and Cook (1946). Robie and Waldbaum (1968) report -217.67 ± 3.5 kcal/mole, basing their selection on Rossini *et al.* (1952) and the same heat capacity data. The heat of formation reported by Rossini *et al.*, is a calculated estimate for an AlOOH which is not identified as boehmite.

There are several sources of uncertainty in the data for boehmite. Most important is ambiguity in identification of the solid used in the heat capacity measurements by Shomate and Cook. The purity of boehmites used in dehydration experiments and the characterization of dehydration products are also doubtful.

Shomate and Cook (1946) used a monohydrate of correct chemical composition but reported that "X-ray examination showed . . . the

monohydrate [to have] a structure similar to bayerite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) differing from the latter principally in the intensities of lines." Neither they nor Rossini *et al.* (1952) identified the solid as boehmite. Because the X-ray diffraction patterns for bayerite and boehmite differ in the presence or absence of major lines as well as in relative intensities of lines, identification of the solid as boehmite is not justified on the basis of their data alone. Kelley and King (1961) were the first to use the data of Shomate and Cook referring to the solid as boehmite. Since they apparently had no new data with which to verify this identification (E. G. King, 1970, written communication) the ambiguity remains, in spite of subsequent use of the identification by others. Shomate and Cook themselves state that "the [heat capacity] data may be uncertain by as much as a few percent. They are adequate, however, for ordinary heat balance calculations." Kennedy (1959) refers to low temperature heat capacity measurements made by Kelley and King on a boehmite he supplied but there is no mention of new measurements in publications after 1959.

Eyraud *et al.* (1955) reported 4 percent crystalline trihydrate in their boehmite. Eyraud *et al.* also point out that the dehydration product is, at least in some instances, a mixture of polymorphs of Al_2O_3 . Since the other authors reporting dehydration did not report characterization of the dehydration product, some doubt must be admitted about the phase purity and identity of the oxide.

In view of these criticisms, little or no confidence may be placed in the validity of tabulated free energies of formation of boehmite.

Gibbsite, $\alpha\text{Al}(\text{OH})_3$

The free energy of formation of gibbsite given by Wagman *et al.* (1968) is -273.35 kcal/mole. It was selected by consideration of heat capacity data provided by Shomate and Cook (1946), the enthalpy change associated with dehydration to Al_2O_3 reported by Fricke and Severin (1932), Eyraud *et al.* (1955), Michel (1957a), Foldvari-Vogl and Kiburszky (1958), and Schwiete and Ziegler (1958), a heat capacity and the heat of solution in 30 percent NaOH solutions provided by Roth, Wirths, and Berendt (1942) and the heat of formation derived from HF solution calorimetry by Barany and Kelley (1961).

The free energy of formation reported by Robie and Waldbaum (1968) is -273.486 ± 0.310 kcal/mole. It is based on the heat capacity data of Shomate and Cook (1946) and the heat of formation reported by Barany and Kelley (1961).

The free energy of formation reported by Pourbaix (1966) is -277.32 kcal/mole. It is based on the solubility measurements of

Fricke and Jucaitis (1930) and a free energy of formation of $\text{Al}(\text{OH})_4^-$. The free energy of formation of $\text{Al}(\text{OH})_4^-$ was derived from the solubility of boehmite (Fricke and Meyering, 1933) and a free energy of formation of boehmite attributed to Latimer (1952). Latimer's source was Rossini *et al.* (1952), hence his figure is invalid. This, together with the high concentrations of the solvents used by Fricke and Jucaitis (1930) and Fricke and Meyering (1933), which make activity corrections doubtful, unfortunately invalidates Pourbaix's estimate of the free energy of formation of gibbsite.

Bayerite, $\gamma\text{Al}(\text{OH})_3$

The free energy of formation of bayerite is not reported by Wagman *et al.* (1968) nor by Robie and Waldbaum (1968). The value, -276.24 kcal/mole, reported by Pourbaix (1966) is based on solubility data with the same history as that described for gibbsite, hence is doubtful.

FREE ENERGIES OF FORMATION FROM SOLUBILITY DATA

Estimation of ΔG°_f for solids from solubility data requires that the composition of the solution phase be known in detail and that the free energies of formation of the dissolved species be known. Al(III) solutions contain hydroxo-aluminum complexes. There is much controversy about which complexes are stable. Some authors find that their hydrolysis or solubility data are adequately represented by mononuclear complexes of the group $\text{Al}(\text{OH})_n^{3-n}$ with n in the range $0 \leq n < 4$. Some ignore $\text{Al}(\text{OH})_3$ (aq.); some do not. Some find it necessary to assume the existence of polymeric complexes. Miceli and Stuer (1968) point out that the polymers are usually invoked in high ionic strength solutions containing a high concentration of aluminum. Hem and Roberson (1967) and Smith (1969) found evidence of polymeric species in low ionic strength solutions containing no more than 13 ppm aluminum. Several authors decided that the polymers were unstable intermediates in the precipitation of solids and have found that their concentrations depend upon the conditions of mixing and rate of hydrolysis. (Hem and Roberson, 1967; Frink and Sawhney, 1967; Turner, 1968; Smith, 1969; W. Stumm, 1969, oral communication.)

If polymeric species are absent at equilibrium, the composition of the solution can be least ambiguously defined in acid ($\text{pH} < 4$) and basic ($\text{pH} > 8.5$) media where Al^{3+} and $\text{Al}(\text{OH})_4^-$ predominate. We will see later that ignoring polymeric species is at least an acceptable approximation.

To derive free energies of formation of the solids from solubility data we need the free energies of formation of Al^{3+} and $\text{Al}(\text{OH})_4^-$ and reliable solubility products for each solid.

The Free Energy of Formation of Al^{3+} (aq.)

The free energy of formation of Al^{3+} (aq.) reported by Wagman *et al.* (1968) and by Robie and Waldbaum (1968) is -116.0 kcal/mole. Robie and Waldbaum quote an earlier version of the Wagman *et al.* publication and assign an uncertainty of ± 0.300 kcal/mole. Wagman *et al.* based their selection on measurements of the potential of an aluminum electrode by Plumb (1962), the solubilities of alums collected in Seidell and Linke (1958), the solubility of an aluminum hydroxide quoted by Gayer, Thompson, and Zajicek (1958), and an earlier estimate by Latimer and Greensfelder (1928). Latimer and Greensfelder based their estimate on the solubility of a well characterized cesium alum. Unfortunately, there is reason to question much of this information.

Plumb (1962) used 0.2 molar sulfate solutions or phosphate buffered systems in his electrochemical work and did not correct to zero ionic strength or correct for complexing. He reported a free energy of formation of Al^{3+} (aq.) of -114.4 kcal/mole.

Gayer *et al.* (1948) characterized the solid phase used in their work by chemical analysis and X-ray diffraction. It was a trihydrate but was not identified by name. The three major d -spacings they reported correspond most closely to bayerite. Since the free energy of formation of bayerite is unknown or highly suspect in the sources quoted by Wagman *et al.* (1968), the free energy of formation of Al^{3+} based on the data of Gayer *et al.* must also be suspect.

Latimer and Greensfelder (1928) reported -116.9 kcal/mole for the free energy of formation of Al^{3+} (aq.). Latimer (1952) later reported -115.0 , citing recalculation from the earlier work without further explanation.

In view of this confusion, while I have chosen to use -116.00 kcal/mole for the free energy of formation of Al^{3+} in order to retain consistency with the NBS tabulations, an uncertainty of at least one kilocalorie per mole must be admitted.

The Free Energy of Formation of $\text{Al}(\text{OH})_4^-$ (aq.)

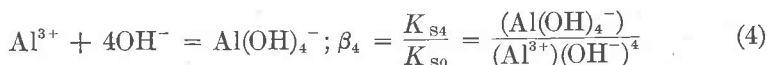
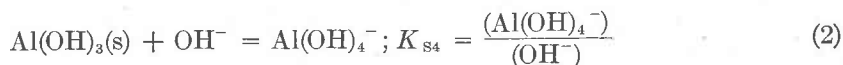
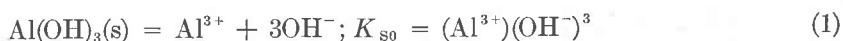
The free energy of formation of $\text{Al}(\text{OH})_4^-$ reported by Wagman *et al.* (1968) is -310.2 kcal/mole. It is based on experiments involving the hydrolysis of Al^{3+} (aq.) and re-solution of the solid formed as

reported by Oka (1938), Lacroix (1949), and Goto (1960), and on the solubility data of Gayer, Thompson, and Zajicek (1958).

The free energy of formation of AlO_2^- reported by Pourbaix (1966) is -200.71 kcal/mole, corresponding to -314.09 kcal/mole for $\text{Al}(\text{OH})_4^-$. This estimate is based on the solubility of boehmite (Fricke and Meyering, 1933) and the free energy of formation of boehmite invalidated above.

Latimer (1952) reports the free energy of formation of AlO_2^- and H_2AlO_3^- separately, giving -204.7 kcal/mole and -255.2 kcal/mole respectively. These correspond to -318.08 and -311.89 kcal/mole for $\text{Al}(\text{OH})_4^-$. These estimates, too, are based on solubilities of hydroxides which are not well characterized.

The equilibrium constants K_{s0} , K_{s4} , $*K_{s4}$, and β_4 are defined as follows (Sillen and Martell, 1964):



Quantities in parentheses are thermodynamic activities.

A free energy of formation of $\text{Al}(\text{OH})_4^-$ based on the free energy of formation of Al^{3+} can be derived from β_4 . β_4 may be determined directly through hydrolysis experiments involving undersaturated solutions. Such data are reported in Sillén and Martell (1964) but none are derived from direct experiment. Sullivan and Singley (1968) report enough data in a set of hydrolysis experiments to permit estimation of β_4 but they did not correct to zero ionic strength and there is nearly an order of magnitude difference in equilibrium constants determined at two dissolved aluminum concentrations. Dezelic, Bilinski, and Wolf (1971) report hydrolysis constants at low ionic strength (<0.01 molar) but did not correct to zero ionic strength.

Use of K_{s0} and K_{s4} to derive β_4 requires that the identical solid be present during determination of the two constants. If the solid is produced by hydrolysis of Al^{3+} and subsequently dissolved in more basic solutions to yield $\text{Al}(\text{OH})_4^-$ or vice versa, this condition is perhaps met. If K_{s0} is determined by hydrolysis of Al^{3+} solutions to yield a solid and K_{s4} by separate hydrolysis of $\text{Al}(\text{OH})_4^-$ solutions, also yielding a solid, the solids produced are not likely to be the same.

Different hydroxides precipitate from acidic than from basic solutions (Schoen and Roberson, 1969; Hem and Roberson, 1967; Hsu, 1966; and Barnhisel and Rich, 1965). Among investigations yielding K_{S0} and K_{S4} and not used by Wagman *et al.*, those by Hem and Roberson (1967), Kittrick (1966) and Szabo, Csanyi and Kawai (1955) appear to involve a single solid.

Free energies of formation of $Al(OH)_4^-$ derived from these sources and Wagman's are summarized in Table 1. Unfortunately, Hem and Roberson determined K_{S0} through hydrolysis experiments yielding crystalline gibbsite after equilibration times exceeding eleven days while the experiments yielding K_{S4} involved equilibration times of one day or less. Inasmuch as they themselves showed that even after the longest aging times their gibbsite was microcrystalline, with a particle size small enough to increase the solubility, we have no guarantee that the solids involved in deriving K_{S4} and K_{S0} had the same free energy of formation. The investigations of Szabo, Csanyi, and Kawai; Oka; Lacroix; and Goto involve hydrolysis experiments based on titrating or mixing Al^{3+} solutions with NaOH or KOH solutions with equilibration times of a few hours. It is doubtful that equilibrium was attained in these experiments since the technique may result in local high concentrations of OH^- , hence local premature precipitation of solids which equilibrate extremely slowly (Biedermann and Schindler, 1967). Gayer, Thompson, and Zajicek determined K_{S0} and K_{S4} through study of the pH dependence of the solubility of a pre-synthesized solid hydroxide. They do not describe precautions taken to insure equilibrium but state that their method was similar to earlier work (Garrett and Heiks, 1941 and Garrett, Vellenga, and Fontana, 1939) in which equilibrium was approached from under and oversaturation and with equilibration times of 20 days or more. The more recent

TABLE 1

Estimates of the Free Energy
of Formation of $Al(OH)_4^-$

<u>Source</u>	$\Delta G_f^\circ (Al(OH)_4^-)$ Kcal/mole
Hem and Roberson (1967)	-312.67
Kittrick (1966)	-311.03
Gayer, Thompson and Zajicek (1948)	-310.61
Szabo, Csanyi, and Kawai (1955)	-312.06
LaCroix (1949)	-314.46
Oka (1938)	-312.46

solubility investigations of Kittrick and Hem and Roberson demonstrate that equilibration requires months to years.

With these arguments in mind, it is not difficult to understand the wide variation in the free energies summarized in Table 1. The investigation least subject to criticism is Kittrick's, hence the free energy of formation of $\text{Al}(\text{OH})_4^-$ is probably closest to -311.02 (based on ΔG_f° for Al^{3+} of -116 kcal/mole). Kittrick estimates a probable error of ± 0.07 kcal/mole. It is certainly not justified to claim significance beyond -311.0 ± 0.1 . Because ΔG_f° for $\text{Al}(\text{OH})_4^-$ is based on ΔG_f° for Al^{3+} to which we have assigned a probable uncertainty of ± 1 kcal/mole, ΔG_f° for $\text{Al}(\text{OH})_4^-$ is also uncertain to at least 1 kcal/mole in spite of the much smaller experimental probable error.

Selected Solubility Products and Derived Free Energies of Formation

Sillen and Martell (1964) record a long list of estimates of K_{s0} and K_{s4} . Choosing, from these and a few more recent papers, investigations in which the solid phase is well characterized, the solution ionic strength very low or corrected to zero, corrections for hydrolysis are small, and in which specific effort was taken to insure equilibrium, leaves few sources of data suitable for estimation of free energies of formation of aluminum oxide hydrates. Kittrick (1966), Hem and Roberson (1967), and Frink and Peech (1962) report K_{s0} , and Russell *et al.* (1955) report K_{s4} . The equilibrium constants and free energies of formation derived from them and the free energies of formation of Al^{3+} and $\text{Al}(\text{OH})_4^-$ are listed in Table 2. The solubility product chosen by Feitknecht and Schindler (1963) for amorphous $\text{Al}(\text{OH})_3$ is included for comparison.

The very painstaking work of Reesman and Keller (1968) and Reesman, Pickett, and Keller (1969) has not been used because their solids were not pure, single phase materials. Their work will be used to judge selected free energies of formation, however.

SELECTION OF THE FREE ENERGY OF FORMATION OF THE SOLIDS

Gibbsite

One estimate of ΔG_f° for gibbsite derived from solubility data is very close to the calorimetric value quoted earlier, near -273 kcal/mole. Two estimates from solubility data, one from K_{s0} and one from K_{s4} are close to -275 kcal/mole. Both pairs include experiments of quite different histories and the close agreement within one pair if considered alone would be persuasive evidence of the validity of the estimate. However, gibbsite must be more stable than corundum in

TABLE 2. Solubility Products and Associated Free Energies of Formation at 25°C

Solid	Solid Particle Size	Solubility Product	ΔG_f° , Kcal/Mole	Source
Gibbsite ^a	2-6 micron	$\log K_{So} = -33.5$	-274.4 ₇	Frink and Peech (1962)
Gibbsite ^b	0.05 micron	$\log K_{So} = -34.06 \pm .09$	-275.13 \pm .06	Kittrick (1966)
Gibbsite ^b	50 micron	$\log K_{So} = -33.98 \pm .01$	-275.34 \pm .01	Kittrick (1966)
Gibbsite ^c	0.04 micron	$\log K_{So} = -32.65 \pm 0.3$	-273.34 \pm 0.4	Hem & Roberson (1967)
Gibbsite ^d	not reported	$\log^*K_{S4} = -15.27$	-275.1 \pm 0.1	Russell et al. (1955)
Bayerite ^d	not reported	$\log^*K_{S4} = -14.82$	-274.6 \pm 0.1	Russell et al. (1955)
Bayerite ^e	not reported	$\log^*K_{S4} = -13.96 \pm 0.2$	-273.4 \pm 0.3	Hem & Roberson (1967)
Boehmite ^d	not reported	$\log^*K_{S4} = -15.27$	-218.7 ₄ \pm 0.1	Russell et al. (1955)
am. Al(OH) ₃	not reported	$\log K_{So} = -31.2$	-271.3 ₄	Feitknecht & Schindler (1963)

^a Solid precipitated from Al(OH)₃ solution with CO₂ at 95°, washed in 4N HCl and H₂O, dried at 110°C. Identified by petrographic methods. Equilibration from both sub- and supersaturation for 30 days or more. K_{So} corrected to zero ionic strength.

^b Commercial gibbsites identified by X-ray diffraction and DTA. For 0.05 micron material equilibrated from both sub- and supersaturation for at least 267 days. 50 micron material equilibrated from supersaturation only.

^c Solid is a product of hydrolysis from dilute perchlorate solutions at 25°, identified by X-ray diffraction and crystal morphology. Equilibration time eleven to 135 days. K_{So} corrected to zero ionic strength.

^d *K_{S4} was determined as a function of temperature and NaOH concentration then corrected to zero ionic strength. Bayerite was produced by CO₂ acidification of an aluminate solution and identified by X-ray diffraction. The probable errors assigned to free energies reflect only the minimum probable error in $\Delta G_f^\circ(\text{Al(OH)}_3)$ hence are minimums.

^e Product of hydrolysis in dilute basic perchlorate solutions at 25°C. Identified by X-ray diffraction. Equilibration time one day or less. *K_{S4} corrected to zero ionic strength.

liquid water at one bar pressure (Kennedy, 1959), hence the free energy of formation of gibbsite must be more negative than -274 kcal/mole if that of corundum is -378.2 kcal/mole.

Kittrick (1966) observed that his free energy of formation for gibbsite was more negative than earlier estimates and considered differences in particle size and crystallinity among the solids involved in explanation. Observing a barely significant particle size effect in his solubility work, he attributed the discrepancy to differences in crystallinity between his gibbsite and those used in earlier investigations which yielded less negative values of ΔG_f° . The difference in ΔG_f° between material of two different particle sizes is related to particle size through the surface free energy as follows (Schindler *et al.*, 1965):

$$\Delta G = \frac{2}{3} \frac{M\alpha\bar{\gamma}}{\rho} \left(\frac{1}{d_2} - \frac{1}{d_1} \right)$$

$$\Delta G = \frac{2}{3} \frac{M\alpha\bar{\gamma}}{\rho d_2} \quad \text{if } d_2 \ll d_1$$

where

M = formula weight of solid

ρ = density of solid

$\bar{\gamma}$ = mean surface free energy

d = characteristic particle dimension, $d_1 > d_2$

α = a shape factor, the ratio of particle surface area to particle volume multiplied by d .

For gibbsite crystals in the form of thin hexagonal plates as observed by Hem and Roberson (1967), α is about 14. Ideally, at equilibrium, there should be only one particle size present. In most real systems there is a particle size distribution and the minimum size present at apparent equilibrium determines the solubility, hence the apparent free energy of formation.

The surface free energies of oxides in equilibrium with their saturated aqueous solutions range from ~ 120 erg/cm² for a hydrated silica gel (Adamson, 1960) to 890 ± 240 erg/cm² for CuO (Schindler *et al.*, 1965). A mean surface free energy of 100 erg/cm² is consistent with the small apparent particle size effect observed by Kittrick. However, his particle size estimates were made before equilibration and the possibility of grain growth during the experiment must be admitted. If grain growth did occur, his results would be consistent with a larger $\bar{\gamma}$. Hem and Roberson (1967) describe a single 0.04 micron hexagonal plate observed in an electron micrograph of gibbsite from an equilibrium system. This is neither a maximum nor a minimum particle size, judging from the published micrograph. The two kilocalorie difference between their ΔG_f° for gibbsite and Kittrick's can be attributed to a particle size effect if $\bar{\gamma}$ is about 1100 erg/cm². If the minimum particle size present were 0.01 micron, $\bar{\gamma}$ would have to be about 270 erg/cm².

The assumptions needed to attribute the difference between the maximum and minimum ΔG_f° listed in Table 2 for gibbsite to a particle size effect are not unreasonable. Admitting the probability that differences in particle size and crystallinity are responsible for the differences in free energies of formation observed dictates selection of the most negative estimate as closest to the true value for well crystallized, large particles. On this basis, -275.3_4 kcal/mole, with a probable error of perhaps ± 0.2 kcal/mole is the free energy of formation of gibbsite. This assignment requires the assumption that the gibbsite used by Barany and Kelley (1961) be poorly crystalline or very fine grained ($\sim .05$ micron) and that the gibbsite used by Russell *et al.* (1955) be well crystallized and relatively coarse grained (> 0.5 micron).

None of the gibbsite used by Barany and Kelley is available today (E. G. King, written communication, 1970), so a direct check of particle size is impossible. It was prepared by G. C. Kennedy but no records of the preparation are available (G. C. Kennedy, written communication, 1970). The gibbsite was synthetic, probably prepared by

hydrothermal alteration of synthetic bayerite, hence, probably very fine grained (G. C. Kennedy, written communication, 1970).

The work of Russell *et al.* (1955) involved concentrated NaOH solutions, high temperatures, and equilibration times up to two months, thus the probability that grain growth would occur is higher than in Kittrick's investigations. Unfortunately no particle size measurements were reported.

The work of Reesman and Keller (1968) and Reesman, Pickett, and Keller (1969) lends credence to the selected ΔG°_f for gibbsite. They originally reported a ΔG°_f based ultimately on acceptance of the ΔG°_f for boehmite listed by Rossini *et al.* (1952). Using their data and the selected ΔG°_f for $\text{Al}(\text{OH})_4^-$ (Table 5), to avoid the discredited data for boehmite, yields -275.9 kcal/mole for ΔG°_f of gibbsite, in good agreement with the value selected here.

Bayerite

Of the two estimates of the free energy of formation of bayerite in Table 2, the more negative is probably to be preferred, again because the solid phase resulting in the less negative estimate was probably microcrystalline, having been produced by low temperature hydrolysis. On this basis, the free energy of formation of bayerite is -274.6 ± 0.1 kcal/mole.

Diaspore

No solubility data for diaspore, reliable by the criteria applied, are available. The selected free energy of formation remains -219.5 ± 0.5 kcal/mole.

Revision of the free energy of formation of diaspore reported by Reesman and Keller (1968) to reflect the selected free energy of formation of $\text{Al}(\text{OH})_4^-$ (Table 4) yields -218.2 kcal/mole for the ΔG°_f of diaspore. In view of this result the uncertainty in the free energy of formation of diaspore may be as much as one kilocalorie per mole.

Boehmite

Having rejected calorimetric estimates of the free energy of formation of boehmite, only the one estimate based on solubility data remains. The free energy of formation of boehmite, on this basis, should be -218.7 ± 0.1 kcal/mole. However, boehmite is considered metastable with respect to the other oxide hydrates (Kennedy, 1959), so that its free energy of formation should be less negative than -218.6 kcal/mole. For this reason, the probable error associated with the free energy of formation of boehmite is probably at least ± 0.2 .

Reversing the calculations of Reesman, Pickett, and Keller (1969) and using the selected free energy of formation of $\text{Al}(\text{OH})_4^-$ (Table 4) yields an estimate of ΔG°_f for boehmite, -217.3 kcal/mole. In view of this result, the uncertainty in the free energy of formation of boehmite may be as much as one kilocalorie per mole.

Summary

Selected free energies of formation of the solids are collected in Table 3. Except for corundum, the probable uncertainties indicated are minimums, reflecting only experimental reproducibility, and not the much larger probable uncertainty introduced through use of ΔG°_f of Al^{3+} . The free energies of formation of Al^{3+} and $\text{Al}(\text{OH})_4^-$ upon which the data in Table 3 are based are collected with the free energies of formation of the monohydroxo complexes in Table 4.

SOLUBILITY-pH CURVES AND THE ACCURACY OF SELECTED FREE ENERGIES OF FORMATION

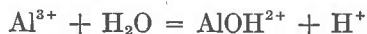
Some solubility data have not been used in selection of free energies of formation of the solids. These data are largely in the pH range in which hydroxoaluminum complexes are important. Comparison with solubility data calculated from selected free energies of formation of the solids requires selection of free energies of formation of both mononuclear and polymeric hydroxoaluminum complexes and demonstration that polymeric species are not significant at equilibrium.

The Free Energies of Formation of Hydroxoaluminum Complexes

All estimates of the free energy of formation of the hydroxo complexes are derived from stability constants. In selecting the data for this purpose, experiments involving solids were rejected unless the data available in a single paper permitted derivation of stability constants independent of the properties of the solid. If K_{S_2} alone was reported, for example, it was not used. If K_{S_2} and K_{S_0} were reported the data were accepted and used to derive β_2 , thus permitting calculation of a ΔG°_f for $\text{Al}(\text{OH})_2^+$ independent of the identity of the solid phase.

Mononuclear Complexes

Estimates of $\log {}^*K_1$, corresponding to the reaction,



range from -4.49 to -5.9 (Sillen and Martell, 1964; Holmes *et al.*, 1968; Sullivan and Singley, 1968; and Nazarenko and Nevskaya,

TABLE 3

Selected Free Energies of Formation
of Aluminum Oxide, Hydroxides, & Oxide Hydroxides

Species	ΔG_f° (25°C) kcal/mole ^a
α Al ₂ O ₃ , corundum	-378.2 ± 0.3
α AlOOH , diaspore	-219.5 ± 0.5
γ AlOOH , boehmite	-218.7 ± 0.2
α Al(OH) ₃ , gibbsite	-275.3 ± 0.2
γ Al(OH) ₃ , bayerite	-274.6 ± 0.1

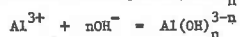
^a The uncertainty in ΔG_f° for bayerite and gibbsite may be larger than one kilocalorie owing to the uncertainty in the ΔG_f° of Al³⁺. The uncertainty in ΔG_f° for boehmite and diaspore may be larger than one kilocalorie since the one available independent estimate of ΔG_f° in each case is about one kilocalorie less negative than the selected value (see Text).

TABLE 4

Selected Formation Constants
and Corresponding Gibbs Free Energies of Formation
of Mononuclear Hydroxoaluminum (III) Complexes at 25°C

Complex	$\log \beta_n^a$	Free Energy of Formation ΔG_{298}° kcal/mole
Al ³⁺	-	-116 ± 1
AlOH ²⁺	+8.99 ± .04	-165.84
Al(OH) ⁺	+19.3 ± 0.1	-217.5
Al(OH) ₃ (aq)	+26.8 ± 0.1	-265.3
Al(OH) ₄ ⁻	+32.7 ± 0.1	-311.0 ± 0.1

^a The reaction corresponding to β_n is



1969). Among the estimates at 25°C and zero ionic strength, the most reliable, by these criteria: attainment of equilibrium, absence of complexing anions, awareness of the possibility of polymer formation, etc., are those by Frink and Peech (1963), Raupach (1963), and Schofield and Taylor (1954). The average of $\log {}^*K_1$ among these estimates is -5.01 and the range is only ± 0.04 .

The formation constant of the dihydroxo complex, β_2 , corresponds to the reaction,



Several investigators report data from which β_2 can be derived. The values of $\log \beta_2$ obtained from work with estimated ionic strengths below 0.01 molar are 19.36 ± 0.1 (Gayer, Thompson, and Zajicek, 1958), 17.72 ± 0.3 (Sullivan and Singley, 1968), and 19.19 (Dezelic, Bilinski, and Wolf, 1971). Work by Nazarenko and Nevskaya (1969) was done at 0.1 molar ionic strength. All of these investigations involved solids and relatively short equilibration times. Agreement between the work of Gayer *et al.* involving approach to equilibrium from subsaturation and that of Dezelic *et al.* which involved approach to equilibrium from supersaturation is perhaps sufficient grounds for assuming equilibrium was actually attained and for selecting the average of the two results, 19.3 ± 0.1 as the preferred value of $\log \beta_2$.

Sillen and Martell (1964) report one estimate of β_3 and two others can be calculated from the data of Dezelic *et al.* (1971) and Nazarenko and Nevskaya (1969). Again omitting the data Nazarenko and Nevskaya obtained at 0.1 m ionic strength, the average value of $\log \beta_3$ in dilute solutions is $+ 26.8 \pm 0.1$.

Formation constants and corresponding free energies of formation of the mononuclear complexes are summarized in Table 4. The ranges indicated for $\log \beta_n$ in Table 4 are ranges only, not probable errors. No attempt has been made to estimate probable error in the free energies of formation.

Polymeric Complexes:

A wide variety of hydroxoaluminum complexes containing more than one aluminum atom have been proposed. Aveston (1965) reviewed the subject in 1965. In most investigations yielding equilibrium constants, the authors have pointed out that their results could probably be explained equally well by some complex other than the one they chose, or by a series of complexes. We have seen that polymeric complexes may not be present at equilibrium. They are probably present in

TABLE 5

Cumulative Formation Constants For
Polymeric Hydroxoaluminum (III) Complexes

Complex $Al_m(OH)_q^{3m-q}$	Temp. °C	Medium	$\log \beta_{qm}^*$ (Note 1)	Investigator	Source
$Al_2(OH)_2^{4+}$	25	0.12Ba(NO ₃) ₂	-8.06	Faucherre (1948)	Sillen & Martell (1964)
"	25	0.60mBa(NO ₃) ₂	-8.24	Faucherre (1948)	"
"	25	+ 0	-7.55	Kentamma (1955)	"
"	25	+ 0	-6.27	Kubota (1956)	"
"	25	1mNaClO ₄	-7.07 + 0.06	Aveston (1965)	Aveston (1965)
$Al_6(OH)_{15}^{3+}$	40	2mNaClO ₄	-47.00	Brosset (1954)	Sillen & Martell (1964)
$Al_7(OH)_{17}^{4+}$	50	3mNaClO ₄	-48.8	Biedermann (1962)	"
$Al_{13}(OH)_{34}^{5+}$	50	3mNaClO ₄	-97.6	Biedermann (1962)	"
$Al_{13}(OH)_{32}^{7+}$	25	1mNaClO ₄	-104.5 ± 0.06	Aveston (1965)	Aveston (1965)

Note 1: $\beta_{qm}^* : mAl^{3+} + qH_2O \rightleftharpoons Al_m(OH)_q^{3m-q} + qH^+$

supersaturated solutions, however, and provisional stability constants have been derived. These are collected in Table 5.

For illustrative purposes only I have selected:

$$\log \beta_{2,2}^* = -7.1$$

$$\log \beta_{17,7}^* = -48.8$$

$$\log \beta_{32,13}^* = -104.5$$

Evidence for polymeric anionic complexes has been reported (Plumb and Swaine, 1964), but not corroborated in more recent work (Yoshio *et al.*, 1970). No data are readily available from which to estimate stabilities.

SOLUBILITY-pH CURVES

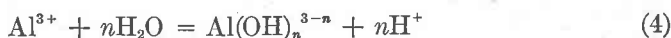
At any pH, the solubility of an aluminum oxide or hydroxide, S , is defined by the equation

$$S = \sum_n [Al(OH)_n^{3-n}] + \sum_m \sum_q m [Al_m(OH)_q^{3m-q}] \quad (1)$$

Bracketed quantities are concentrations. The activities of the various complexes may be derived from the activity of Al^{3+} , the appropriate cumulative complex stability constants, S , and K_{80} . Thus, for mono-nuclear complexes, and a generalized solid phase,



$$*K_{Sn} = \frac{\{Al(OH)_n\}^{3-n}}{\{H^+\}^{(3-n)}}; \quad *K_{S0} = \frac{\{Al^{3+}\}}{\{H^+\}^3} \quad (3)$$



$$*\beta_n = \frac{\{Al(OH)_n\}^{3-n} \{H^+\}^n}{\{Al^{3+}\}} \quad (5)$$

$$*K_{Sn} = *\beta_n *K_{S0} \quad (6)$$

Quantities in braces are activities.

For polymeric complexes;

$$*K_{Sqm} = \frac{\{Al_m(OH)_q\}^{3m-q}}{\{H^+\}^{(3m-q)}}; \quad *K_{S0} = \frac{\{Al^{3+}\}}{\{H^+\}^3} \quad (7)$$

$$*\beta_{qm} = \frac{\{Al_m(OH)_q\}^{3m-q} \{H^+\}^q}{\{Al^{3+}\}^m} \quad (8)$$

$$*K_{Sqm} = *\beta_{qm} *K_{S0}^m \quad (9)$$

Combination of equations (1), (6), and (9) yields a relationship among S , $*K_{S0}$ and the $*\beta$'s if activities and concentrations are assumed to be identical:

$$S = \sum_n *\beta_n *K_{S0} [H^+]^{(3-n)} + \sum_m \sum_q m *\beta_{qm} *K_{S0}^m [H^+]^{(3m-q)} \quad (10)$$

The influence of polymeric complexes on the shape of solubility curves can be seen if $*K_{S0}$ is brought outside the sums, insofar as possible,

$$S = *K_{S0} \left[\sum_n *\beta_n [H^+]^{(3-n)} + \sum_m \sum_q m *\beta_{qm} *K_{S0}^{(m-1)} [H^+]^{(3m-q)} \right] \quad (11)$$

The solubilities of many oxides and hydroxides are high in solutions of extreme pH and minimum at some intermediate pH. The $[H^+]$ corresponding to the minimum may be found by differentiating equation (11) to obtain (12).

$$\frac{dS}{d[H^+]} = *K_{S0} \left[\sum_n (3-n) *\beta_n [H^+]^{(2-n)} + \sum_m \sum_q m(3m-q) *\beta_{qm} *K_{S0}^{(m-1)} [H^+]^{(3m-q-1)} \right] \quad (12)$$

At the solubility minimum the derivative is equal to zero and equation (12) may be solved for $[H^+]_{\min}$ or pHMS, the pH corresponding to minimum solubility.

Equations (11) and (12) provide tests for the presence or absence of polymeric species in concentrations sufficient to affect solubility. The relative contributions of individual polymeric complexes to S

depends on $*K_{s0}$, see equation (11), hence the shape of the log S -pH curve depends on $*K_{s0}$ or upon the solubility itself. The relative contributions of individual monomeric complexes do not depend on $*K_{s0}$, hence the shape of the log S -pH curve is independent of $*K_{s0}$ or solubility if polymers are absent. This second observation means that all solubility curves should coincide if normalized with respect to concentration.

Should polymers be the predominant dissolved species at any pH, the slope of the log S -pH curve, $3m - q$, will exceed 3.0. This is illustrated in Figure 1. The pHMS should be the same for all solids if polymers are absent since, in equation 12, K_{s0} is absent from terms corresponding to monomeric species. The pHMS should be different for each solid if polymers are present.

Raupach (1963) has published solubilities of several aluminum oxides over a wide pH range. All of these data are plotted in Figure 2 after normalization at pH 4.5 to 5 for all solids. Ignoring the calculated curve in the figure, and within the scatter inherent in each set, most of these data can be said to fall on a single curve for $6 < \text{pH} < 8$, to include no portions with slope greater than 3, and to have a single, common minimum. Within the accuracy of the experimental data, polymeric complexes may be considered absent.

Accuracy of Calculated Solubility-pH Curves

A solubility-pH curve calculated with the free energies in Tables 3 and 4, assuming the same ionic strength used by Raupach (1963), is

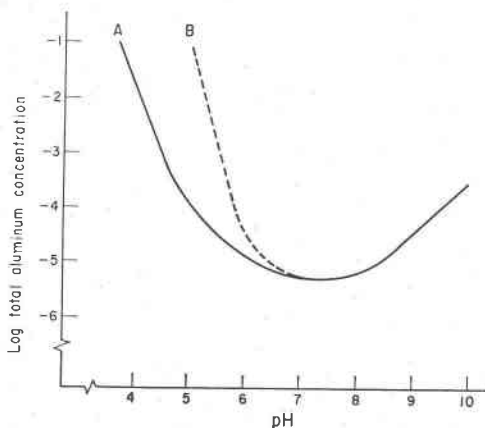


FIG. 1. Change in slope of solubility-pH curves caused by the polymeric complex $\text{Al}_7(\text{OH})_{17}^{4+}$. (A. polymer absent; B. polymer present. Curves drawn for a microcrystalline $\text{Al}(\text{OH})_3$ with $\Delta G^\circ_f = -274.3$ kcal/mole).

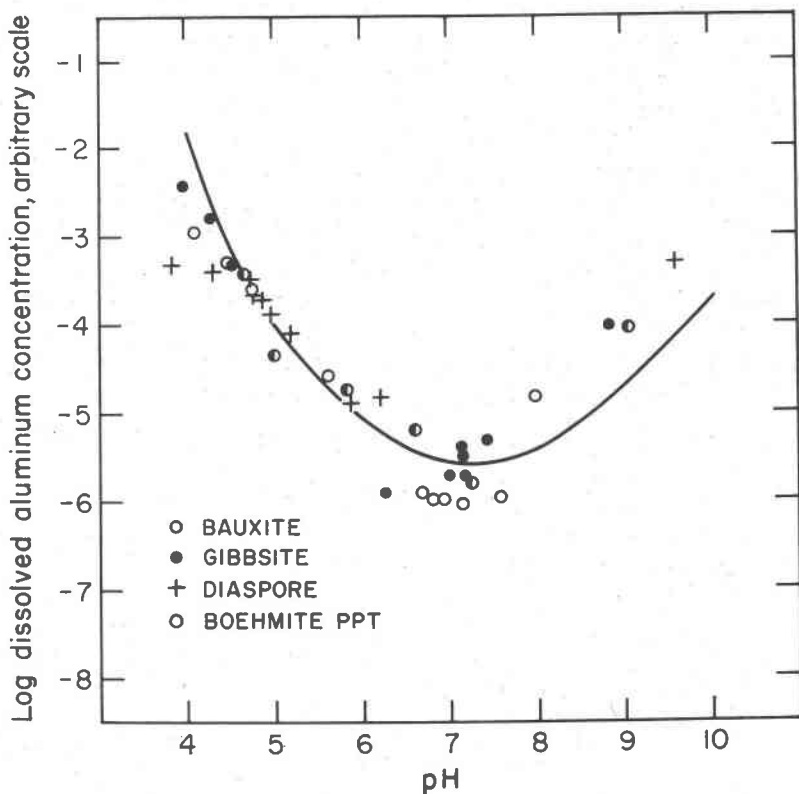


FIG. 2. Experimental and calculated variation of the solubilities of aluminum hydroxides and oxide hydroxides with pH. (Experimental data at 20° in 0.01 m K_2SO_4 from Raupach, 1963. The solid curve was calculated from the selected 25° free energy data corrected to 0.03 ionic strength.)

compared with his data for all minerals in Figure 2. The data and calculated curve are normalized at pH 4.5. In the vicinity of minimum solubility, the total concentration of dissolved aluminum is a few parts per million. Accidental contamination of the analyzed solution by colloidal solids must result in a high analysis; the increment will be particularly damaging near the minimum solubility. If all observed data were high with respect to the calculated curve this might explain the discrepancy. If observed data were low with respect to the calculated curve, the ΔG° chosen for $Al(OH)_3(aq)$ would be suspect. As it is the data support neither possibility but perhaps indicate a large probable error in the free energy of formation of $Al(OH)_3(aq)$.

The experimental solubility is high with respect to the calculated

curve on the basic branch in all cases. There are two possible explanations of the discrepancy between calculated and observed solubilities when $\text{Al}(\text{OH})_4^-$ predominates in solution. The free energy of formation of $\text{Al}(\text{OH})_4^-$ upon which the calculation is based, -311.0 kcal/mole, may be wrong; perhaps the true value is nearer the more negative end of the wide range of estimates available. If the free energy is changed in this direction, however, the discrepancies between estimates of the free energy of formation of gibbsite based on K_{S0} and those based on K_{S4} and between estimates based on solubility data in general and those of calorimetric origin are increased.

Study of the experimental details reported by Raupach (1963) reveals an alternate explanation of the discrepancy between calculated and observed solubility. Of the four samples he studied, gibbsite and diaspore alone are pure with respect to other phases. For gibbsite, he recorded the changes in pH and dissolved aluminum concentration which occurred as the system evolved toward equilibrium. The data are plotted separately in Figure 3. Some points selected as representative of equilibrium represent solutions which at one time in their history contained a higher concentration of dissolved aluminum than was found at apparent equilibrium. Aluminum must have precipitated from these solutions. We have already seen that the solids precipitated by hydrolysis are different in acidic than in basic media. If this difference persists in spite of possible nucleation by the originally intended solid and if the precipitated material reaches a meta-equilibrium state more rapidly than the original solid, the composition of the solution may be determined by the precipitated material rather than by the intended solid.

On the assumption that something of this sort happens, we should expect to find that a system in which the concentration of dissolved aluminum increases throughout the experiment will end up at an aluminum concentration characteristic of the most soluble solid present among relatively stable solids, or at a lower concentration if insufficient time has been allowed. In a system which evolves toward equilibrium in such a way that the concentration of dissolved aluminum decreases at any stage the solubility observed at apparent equilibrium will probably be that characteristic of a microcrystalline gibbsite if the solution is acidic or of bayerite if the solution is basic. These arguments assume that true equilibrium among solids is not attained, but that precipitated solids do reach a meta-equilibrium state with respect to the solution phase in a matter of a few days or perhaps weeks. Can we expect a precipitated hydrous oxide to reach a meta-stable equilibrium with respect to a solution phase? Hem and

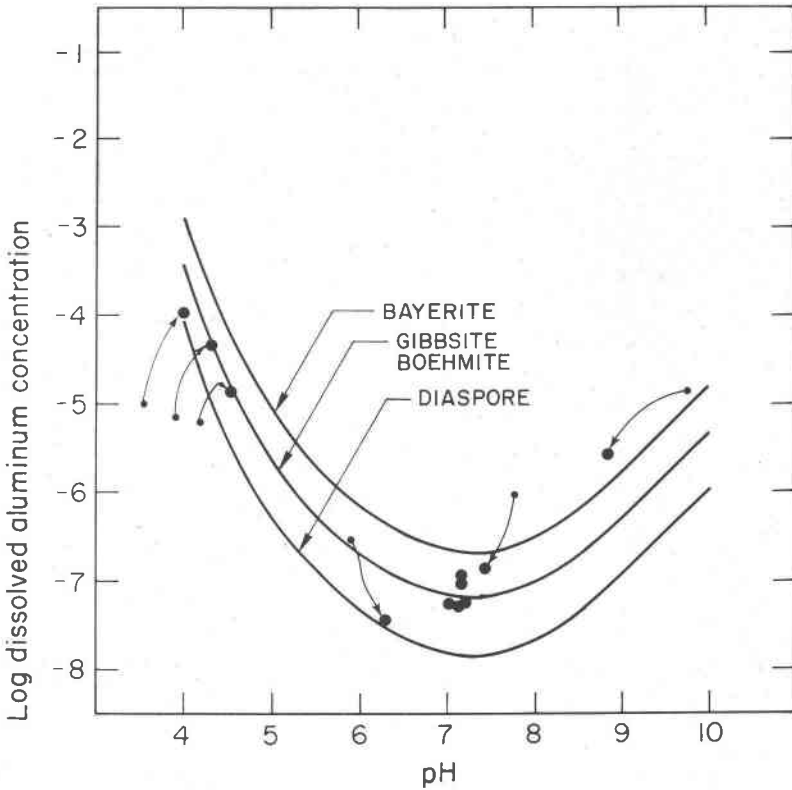


FIG. 3. Detailed comparison of experimental and calculated solubilities of gibbsite (data after Raupach, 1963). Fine lines trace the evolution of solution composition toward the final state. Heavy lines are solubility curves calculated from the selected 25° free energy data and are corrected to an ionic strength of 0.03. Raupach's data were obtained at 20°C in 0.01 m K_2SO_4 .

Roberson (1967) report the data on apparent solubilities of young precipitates plotted in Figure 4. The fact that the solubility of their one day old bayerite changes linearly with pH in the basic range lends confidence to the supposition that accidental contamination by solid hydrolysis products may lead to behavior expected of true equilibrium systems.

Look again at Figure 3. In the range of $pH < 7$, most apparent equilibrium points have evolved upward only. In this range, calculated and observed data agree well for gibbsite. The concentration of dissolved aluminum decreases with time on the basic branch of the solubility curve equilibrating closer to the calculated curve for bay-

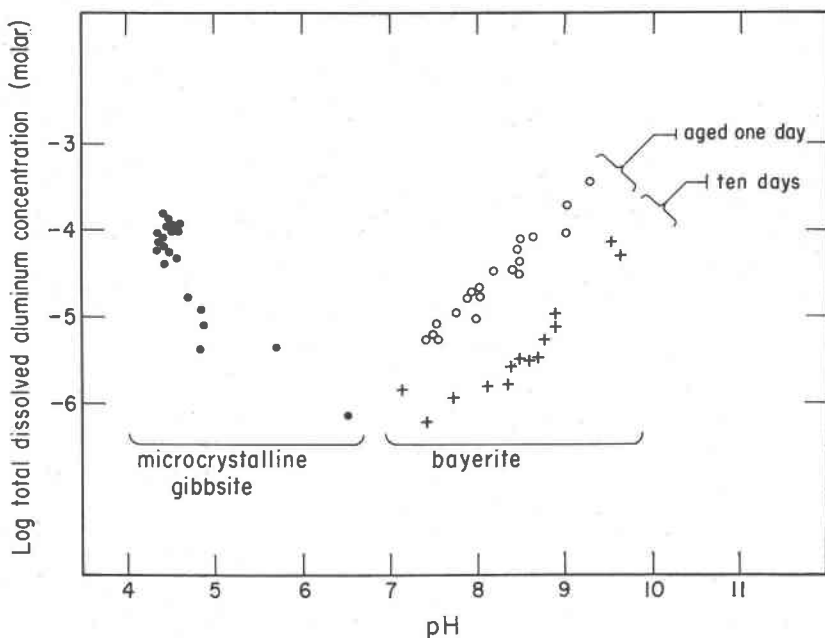


FIG. 4. Experimental pH dependence of the solubility of precipitated gibbsite and bayerite (from Hem and Roberson, 1967).

erite. Unfortunately, the data are inconclusive. They will permit the interpretation proposed but agreement is not sufficiently consistent to be convincing. Direct observation of the bayerite proposed would obviously help a great deal, but has not been reported.

CONCLUSIONS

Recommended free energies of formation of the solids are given in Table 3 and of the hydroxo-complexes in Table 4.

Judging from Kennedy's (1959) review of phase equilibrium data and evidence in natural occurrences, gibbsite is more stable than bayerite, boehmite has only a metastable existence, and corundum is unstable with respect to hydrates in the presence of water at 25°C and one bar pressure. The recommended free energies of formation, with the exception of that for boehmite, are consistent with these requirements. The free energies of formation show that diaspore is the most stable hydrate under these conditions. The metastability of boehmite with respect to all other hydrates is not confirmed by the free energy selected and for this reason it must still be considered

doubtful. It has not been possible to reconcile the selected free energies in detail with the one independent set of solubility data involving carefully characterized solids, Raupach's, without unverified reinterpretation. The interpretative model proposed does not call for startling assumptions, however.

The entire selection process underscores the pessimistic view that, as usual, more work is needed. It also offers repeated reminders of the absolute necessity of careful characterization of the solid phases after equilibration by techniques capable of detecting trace phase impurities and measuring particle size. In any system in which metastable or microcrystalline solids are possible, they must be expected until proven absent. We can probably predict no more than a lower limit of solubility. Use of solubility in phase identification appears unwise unless a variety of evidence is provided in proof that the solid is well crystallized in large particles and is at equilibrium with the solution.

ACKNOWLEDGMENTS

Many of my students have endured repeated discussions of this topic. They deserve thanks for their patience and ideas. Tefvik Utine, John Baca, and Robert Railey helped with calculations and computer programming. I am indebted to J. D. Hem of the U.S. Geological Survey; Professors K. B. Krauskopf, W. C. Luth, and F. W. Dickson of Stanford; R. M. Garrels of the Scripps Institute of Oceanography; H. C. Helgeson of the University of California at Berkeley; and The American Mineralogist referees for thought provoking criticism. The project originated in the work of Dr. G. K. Korpi and Dr. T. Paces under the sponsorship of the U.S. Atomic Energy Commission, was aided immeasurably by the work of Dr. Ross W. Smith of the University of Nevada and was completed under the sponsorship of the National Science Foundation, Division of Earth Sciences, Grant GA 1451.

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Manuscript received, December 16, 1969; accepted for publication, March 31, 1972.