

Revised values for the thermodynamic properties of boehmite, AlO(OH), and related species and phases in the system Al-H-O

BRUCE S. HEMINGWAY, RICHARD A. ROBIE

U.S. Geological Survey, Reston, Virginia 22092, U.S.A.

JOHN A. APPS

Lawrence Berkeley Laboratory, Berkeley, California 94720, U.S.A.

ABSTRACT

Heat capacity measurements are reported for a well-characterized boehmite that differ significantly from results reported earlier by Shomate and Cook (1946) for a monohydrate of alumina. It is suggested that the earlier measurements were made on a sample that was a mixture of phases and that use of that heat-capacity and derived thermodynamic data be discontinued. The entropy of boehmite derived in this study is 37.19 ± 0.10 J/(mol·K) at 298.15 K.

A review of recent ^{27}Al solution NMR data and other experiments has shown that the method of preparation of Al-bearing solutions can significantly affect the concentration of monomeric Al species in solution. Because the procedures by which Al solution concentrations are measured in solubility studies determine the quantity of so-called monomeric species present, apparent differences in calculated gibbsite stability most likely arise from differences in experimental procedure rather than from differences in crystallinity, as often suggested. A review of published solubility data for gibbsite suggests that the best values that can be currently estimated from that data for the Gibbs free energies of formation of $\text{Al}(\text{OH})_4^-$ and Al^{3+} are -1305.0 ± 1.3 and -489.8 ± 4.0 kJ/mol, respectively (Hemingway et al., 1978).

Based on our value for the entropy and accepting the recommended Gibbs free energy for $\text{Al}(\text{OH})_4^-$, we have calculated the Gibbs free energy and enthalpy of formation of boehmite to be -918.4 ± 2.1 and -996.4 ± 2.2 kJ/mol, respectively, from solubility data for boehmite. The Gibbs energy for boehmite is unchanged from that given by Hemingway et al. (1978).

INTRODUCTION

Minerals with compositions in the chemical system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ are present in a wide variety of sedimentary and metamorphic rocks and in soils. Metastability of phases in this system has resulted in disparate experimental data and consequent disparate interpretation of the phase relationships of some of the phases in the system. Boehmite, $\text{AlO}(\text{OH})$, is an example of such a phase.

Diaspore, $\text{AlO}(\text{OH})$, is generally accepted to be the stable aluminum hydroxide or oxyhydroxide phase at earth surface temperatures (e.g., Parks, 1972; Perkins et al., 1979; Hemingway, 1982). However, conflicting conclusions have been reached regarding the relative stabilities of other aluminum hydroxides and oxyhydroxides (e.g., Sanjuan and Michard, 1987, have calculated a Gibbs energy for bayerite that would make it slightly more stable than diaspore). Inconsistencies and errors in the thermodynamic data utilized by the several groups may be responsible for some of the disparate interpretations. Parks (1972) and Hemingway et al. (1978) noted and expressed concern that the entropy and heat-capacity data com-

monly attributed to boehmite (Shomate and Cook, 1946) were based on heat-capacity data for a phase described as a monohydrate that produced an X-ray pattern similar to that of bayerite. Kelley and King (1961) were the first to describe the phase as boehmite. Subsequent tabulations of thermochemical data have followed Kelley and King (1961). Recently, Apps et al. (1988) concluded that the entropy (at 298.15 K and 1 bar) of boehmite was too large and Berman et al. (1985) concluded the heat capacities reported for boehmite were too large. We report here heat-capacity measurements for a well-characterized sample of boehmite that validate the concerns expressed by Parks (1972), Hemingway et al. (1978), and Berman et al. (1985) and confirm the prediction of Apps et al. (1988).

Sample

Two samples of boehmite were synthesized by K. Weffers of Alcoa. The first sample was prepared from gibbsite during a 20-h hydrothermal experiment at approximately 473 K. The resulting boehmite was well crystallized, as shown by X-ray diffraction and SEM analysis. Aggregates

TABLE 1. Chemical analysis for synthetic boehmite

Element	Abundance* %
Al	43.4(22) 46.2(23)**
Mg	0.12(12)
Na	0.814(8)
K	<0.06
	ppm
Au	<0.0019
Ba	<5.3
Ca	<0.73
Ce	<0.29
Co	<0.016
Cr	2.96(14)
Cs	<0.017
Dy	<0.040
Fe	71(9)
Ga	44.8(67)
Hf	<0.029
La	<0.14
Mg	119(125)**
Mn	7.43(35)
Mo	5.8(5)
Ni	15.5(11)
Rb	<0.57
Sc	<0.0035
Si	36(25)**
Sm	0.00311(43)
Ta	0.0045(6)
U	0.036(5)
Yb	<0.0092
Zn	19.0(10)

* NAA analyses by Helen V. Michel.

** ICP analyses by Andrew W. Yee.

of crystals average 15 μm in diameter with the individual crystallites 0.2–2 μm in size and displaying well-defined crystal outlines. No evidence of amorphous material was found; however, two additional phases [diaspore, $\text{AlO}(\text{OH})$, and akdalaite, $4\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$] were found in small quantity. This sample was used for all calorimetric studies reported here.

Following identification of diaspore in the first sample, a second sample was synthesized from the same starting material, at the same temperature, but for a shorter period of time. The resulting sample was well-crystallized boehmite in the form of aggregates of very thin platelets of individual crystallites. No evidence of amorphous material or other phases was found. However, the very small crystallites made this sample impractical as a sample for calorimetry because of the low effective packing density and the possibility that the He exchange gas would be adsorbed on the fine crystallites at temperatures less than approximately 15 K.

A chemical analysis of the boehmite sample is listed in Table 1. Combining the results of SEM, X-ray, and chemical analyses, we estimate that the sample contains <1% combined diaspore, $\text{AlO}(\text{OH})$, and akdalaite, $4\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Portions of the first sample were used for both low-temperature and differential scanning calorimetric (DSC) measurements. The sample used for low temperature heat-capacity measurements was 27.3540 g. Superambient heat

TABLE 2. Experimental low-temperature molar heat capacities for boehmite

Temperature K	Heat capacity J/(mol·K)	Temperature K	Heat capacity J/(mol·K)	Temperature K	Heat capacity J/(mol·K)
Series 1		Series 3		Series 4	
305.67	55.51	65.03	3.747	225.65	41.01
309.93	55.93	70.07	4.528	230.38	42.04
314.72	56.67	75.96	5.530	235.18	43.04
319.55	57.45	81.63	6.571	240.03	43.96
324.36	58.14	87.27	7.721	244.90	44.88
329.17	58.89	92.89	8.951	249.79	45.81
333.96	59.36	98.49	10.24	Series 5	
338.74	60.12	103.98	11.53	260.21	47.85
343.55	60.77	109.38	12.83	265.83	49.07
348.38	61.56	114.70	14.15	277.39	50.81
Series 2		119.96	15.47	283.23	51.82
8.38	0.0385	125.14	16.78	289.00	52.80
9.16	0.0292	130.27	18.10	294.72	53.70
10.35	0.0293	135.35	19.40	300.44	54.73
11.70	0.0594	140.38	20.68	306.14	55.71
12.98	0.1004	145.36	21.97	311.82	56.33
14.52	0.1431	150.30	23.24	317.48	57.23
16.29	0.1604	155.21	24.46	Series 6	
18.22	0.1616	160.08	25.72	267.57	49.06
20.30	0.1783	164.92	26.92	269.12	49.27
22.53	0.2093	169.73	28.10	270.68	49.49
25.01	0.2648	174.51	29.30	272.29	49.83
27.79	0.3506	Series 4		273.89	50.11
30.88	0.4806	179.13	30.42	275.48	50.44
34.36	0.6726	184.15	31.65	277.08	50.71
38.27	0.8579	188.85	32.79	Series 7	
42.63	1.257	193.54	34.28	316.98	57.05
47.47	1.652	198.10	35.06	322.56	57.82
52.93	2.194	202.67	36.11	328.18	58.66
58.92	2.907	207.22	37.07	333.86	59.44
Series 3		211.77	38.22	339.52	60.22
55.12	2.456	216.35	39.05	345.19	61.03
60.56	3.134	220.97	40.01		

Note: Molar mass = 59.989 g.

capacities reported in this study were determined from measurements on portions that were approximately 25 mg. The 1975 values for the atomic weights (Commission on Atomic Weights, 1976) were used. The molar mass of boehmite is 59.989 g.

Apparatus and procedures

The low-temperature adiabatic calorimeter and data handling procedures are described elsewhere (Robie and Hemingway, 1972; Robie et al., 1976; Hemingway et al., 1984). Low-temperature heat capacities were measured using the intermittent heating method under quasi-adiabatic conditions. The sample was sealed in the calorimeter under a small pressure of pure He gas (approximately 5 kPa).

High-temperature heat capacities were determined by DSC following the procedures outlined by Hemingway et al. (1981). The samples were placed in unsealed Au pans.

LOW-TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS

Experimental heat capacities for boehmite are listed in Table 2 in the chronological order of the measurements. The results are corrected for curvature (e.g., Robie and

Hemingway, 1972), but not for the heat capacity contributions from the diaspore and akdalaite contaminant phases that are discussed below. The observed heat capacities were smoothed using cubic spline smoothing routines and were graphically extrapolated as C_p/T vs. T^2 to 0 K using the experimental and smoothed values for temperatures below 30 K. Smoothed values of the heat capacities and derived thermodynamic functions are listed in Table 3.

The heat capacities of diaspore (Perkins et al., 1979) are smaller than those of the impure boehmite sample at all temperatures below 300 K. Therefore, corrections to the observed heat capacities of the impure boehmite sample for the contribution of diaspore would result in an increase in the calculated heat capacities and entropies. A correction of approximately $+0.02$ J/(mol·K) would be required in the entropy of boehmite at 298.15 K for each 1% of diaspore.

Low-temperature heat capacities have not been reported for akdalaite; however, Mukaibo et al. (1969) have reported heat-capacity measurements for tohdiite at superambient temperatures that may be used to estimate the magnitude of the correction for the akdalaite impurity. (Note that akdalaite and tohdiite are considered to be the same phase, e.g., Fleischer, 1971.) The specific heat of akdalaite is approximately 4% greater than that of corundum at 298.15 K. This difference is expected to increase at lower temperatures. Based on a comparison with boehmite and diaspore, we estimate the average difference in the specific heat of akdalaite between 0 and 298.15 K to be 10%. Using the entropy of corundum from Robie et al. (1979), we estimate the entropy of akdalaite ($4\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) to be 234 J/(mol·K) at 298.15 K. Based on this estimate for the entropy of akdalaite, we estimate that a correction of $+0.04$ J/(mol·K) would be required in the entropy of boehmite at 298.15 K for each 1% of akdalaite impurity.

We estimate the total correction to the entropy calculated for the impure boehmite sample at 298.15 K (Table 3) to be less than 0.06 J/(mol·K). Because the boehmite sample contained a small quantity of very small crystals that would have a slightly higher specific heat than coarser material of the same composition and because we estimate the uncertainty in the calculated boehmite entropy at 298.15 K to be ± 0.1 J/(mol·K), we have not applied a correction for the observed impurity phases (diaspore and akdalaite).

The measurements reported by Shomate and Cook (1946) for a monohydrate of Al and variously attributed to the phase boehmite (e.g., Kelley and King, 1961) may be compared with the heat capacities reported herein. At all temperatures represented by their measurements, the results of Shomate and Cook (1946) are significantly larger than those reported in Table 2. At 100 K the heat capacities differ by approximately 44% and by approximately 21% at 298.15 K. Shomate and Cook (1946) also reported heat capacity data for gibbsite that may be compared with the data for gibbsite reported by Hemingway

TABLE 3. Molar thermodynamic properties of boehmite

Temperature K	Heat capacity C_p^\ddagger	Entropy $S_p^\ddagger - S_p^\circ$	Enthalpy	Gibbs
			function $(H_p^\ddagger - H_p^\circ)/T$	energy function $-(G_p^\ddagger - H_p^\circ)/T$
J/(mol·K)				
5	0.003	0.001	0.001	0.000
10	0.027	0.008	0.006	0.002
15	0.153	0.041	0.033	0.008
20	0.176	0.088	0.065	0.023
25	0.264	0.135	0.094	0.041
30	0.440	0.197	0.136	0.061
35	0.696	0.284	0.198	0.087
40	1.005	0.395	0.277	0.118
45	1.444	0.539	0.382	0.156
50	1.897	0.714	0.511	0.203
60	3.052	1.157	0.833	0.323
70	4.515	1.733	1.251	0.482
80	6.270	2.448	1.766	0.682
90	8.311	3.301	2.377	0.924
100	10.58	4.293	3.082	1.210
110	12.98	5.413	3.872	1.540
120	15.48	6.649	4.735	1.914
130	18.02	7.988	5.659	2.329
140	20.59	9.418	6.634	2.784
150	23.14	10.93	7.649	3.276
160	25.68	12.50	8.697	3.803
170	28.19	14.13	9.770	4.362
180	30.68	15.81	10.86	4.952
190	33.13	17.54	11.97	5.568
200	35.49	19.30	13.09	6.211
210	37.73	21.09	14.21	6.877
220	39.88	22.89	15.33	7.563
230	41.95	24.71	16.44	8.269
240	43.95	26.54	17.54	8.992
250	45.88	28.37	18.64	9.731
260	47.73	30.21	19.72	10.48
270	49.52	32.04	20.79	11.25
280	51.25	33.87	21.85	12.02
290	52.93	35.70	22.89	12.81
300	54.53	37.52	23.92	13.60
310	56.06	39.34	24.93	14.40
320	57.51	41.14	25.93	15.21
330	58.93	42.93	26.91	16.02
340	60.33	44.71	27.87	16.84
273.15	50.07	32.62	21.13	11.49
298.15	54.24	37.19	23.73	13.45

Note: Molar mass = 59.989 g.

et al. (1977), who used a calorimeter that was similar to the one used in this study. The data of Shomate and Cook (1946) were higher at all temperatures, but the maximum difference was approximately 7% at 52.8 K and that difference decreased to 1.5% at 298.15 K. The foregoing comparison suggests that the differences between the heat capacity values reported by Shomate and Cook (1946) and the values reported in this study arise primarily from differences in the sample, not in the equipment or procedures for data processing.

HIGH-TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS

Experimental superambient heat capacities for boehmite are listed in Table 4. The results represent measurements based on several samples, with new samples prepared and used following any partial dehydration of a sample. Although the majority of H_2O was lost in the

TABLE 4. Experimental superambient molar heat capacities for boehmite

Temperature K	Heat capacity J/(mol·K)	Temperature K	Heat capacity J/(mol·K)	Temperature K	Heat capacity J/(mol·K)
Series 1		Series 2		Series 6	
338.9	59.77	408.5	67.07	577.5	78.93
348.9	60.94	418.5	67.97	587.4	79.05
358.8	61.93	428.4	68.91	597.3	79.40
368.8	63.02	438.3	69.83	607.3	79.81
378.7	64.05	448.3	70.57	617.2	80.31
388.6	65.00	458.2	71.61	627.2	80.91
398.6	66.02	468.1	72.37	637.1	81.14
408.5	66.99	478.1	73.18	647.0	81.73
418.5	67.95	488.0	74.00	657.0	82.36
428.4	68.85	497.0	74.85	666.9	83.21
438.3	69.81	Series 3		Series 7	
448.3	70.48	607.3	79.86	537.7	77.40
458.2	71.50	616.2	81.35	547.6	77.77
468.1	72.24	Series 4		557.6	78.20
478.1	73.03	468.1	72.11	567.5	78.63
488.0	73.90	478.1	72.75	577.5	78.97
497.0	74.66	Series 5		587.4	79.32
Series 2		597.3	79.53	597.3	79.61
338.9	59.82	607.3	79.88	607.3	80.30
348.9	60.97	616.2	81.79	617.2	80.55
358.8	62.03	Series 6		627.2	81.11
368.8	63.08	537.7	77.39	637.1	81.44
378.7	64.09	547.6	77.76	647.0	81.69
388.6	65.07	557.6	78.24	657.0	82.56
398.6	66.07	567.5	78.53	666.9	83.54

Note: Molar mass = 59.989 g.

temperature interval of 680–710 K, some loss occurred as low as 450–600 K and resulted in the calculated heat capacities for that interval having a U-shaped curvature. Weight loss calculated after such experiments was generally of the order of a few hundredths of a percent of the sample weight and probably represented loss of adsorbed H₂O from some of the very small crystals. Each scan presented in Table 4 represents one continuous set of measurements or the average of several continuous sets of measurements.

Smoothed values of the heat capacities and thermodynamic functions are listed in Table 5. Smoothed values of the low-temperature heat capacities between 298.15 and 350 K were combined with the high-temperature heat capacities and the combined data set was fit by least squares to a 4-term polynomial with the constraint that the equation exactly fit the smoothed heat capacity at 298.15 K. The resultant Equation 1,

$$C_p = 205.721 - 0.034921T - 2635.27T^{-0.5} + 1.02666 \times 10^6 T^{-1} \quad (1)$$

fits the data with an average deviation of $\pm 0.3\%$ and is valid from 298 to 600 K.

The measurements presented here may be compared with the data of Shomate and Cook (1946) who measured the heat content of their sample from 321 to 520 K. Shomate and Cook (1946) terminated their measurements at approximately 520 K because H₂O evolved irreversibly from the sample and condensed in the sample capsule.

Between 300 and approximately 420 K, the heat capacities derived from the data of Shomate and Cook (1946) are larger than those reported here. Above approximately 420 K, they are smaller.

As noted earlier, the most reasonable explanation for the difference between the data presented by Shomate and Cook (1946) for a monohydrate of Al and the results presented here is that the monohydrate studied by Shomate and Cook (1946) was not pure boehmite. Bayerite was identified by X-ray analysis to be a constituent of the sample studied by Shomate and Cook (1946). Mukaibo et al. (1969) give 473 K as the temperature of dehydration of bayerite, consistent with the observation of Shomate and Cook (1946) that significant H₂O loss occurred at temperatures at or below 520 K. In addition, the density of the sample used by Shomate and Cook (1946) was determined and found to be 2.83 g/cm³, considerably lower than the theoretical value of 3.07 g/cm³ for boehmite; however, the value of 2.45 g/cm³ reported in the same study for gibbsite is identical with the theoretical value for gibbsite, suggesting that analytical error was not a factor.

The procedure reported by Shomate and Cook (1946) for the preparation of their monohydrate alumina sample was followed as closely as possible. Dehydration of gibbsite yielded a fine-grained, poorly crystallized mixture of boehmite and akdalaite. The presence of akdalaite in our synthesis may indicate a possible cause of the nonstoichiometry (low H₂O content) of the sample prepared by Shomate and Cook (1946). Also, the addition of H₂O to our sample with subsequent heating at 80 °C (following the procedure of Shomate and Cook, 1946) yielded strong X-ray peaks for bayerite and significant loss of boehmite X-ray peak intensities. Thus, several lines of evidence suggest that the monohydrate sample studied by Shomate and Cook (1946) was a mixture of phases.

FREE ENERGY OF BOEHMITE

The entropy derived in this study cannot be combined with the enthalpy of formation of boehmite to estimate directly the Gibbs energy of formation, as the enthalpy of formation of boehmite has not been established independently. Estimates of the Gibbs free energy of boehmite may be developed from phase equilibria and solubility data.

Ervin and Osborn (1951) developed a phase diagram for the system Al₂O₃-H₂O based upon a study of unreversed synthesis experiments. Fields of stability are shown for gibbsite, boehmite, diasporite, and corundum based on the products of crystallization of Al₂O₃ gel and γ -alumina. Equilibrium was considered to be proved if both starting materials (i.e., structurally different materials) yielded the same product. Boehmite commonly formed and then slowly recrystallized to form diasporite or corundum in the *P-T* regions designated as the stability regions for those phases. Therefore, the synthesis experiments provide only a limit as to the minimum or maximum free energy that a phase may have. Realistically, the ex-

TABLE 5. Molar thermodynamic properties for boehmite

Temperature K	Heat capacity C_p^0	Entropy S_p^0	Enthalpy function $(H_p^0 - H_{298}^0)/T$	Gibbs energy function $-(G_p^0 - H_{298}^0)/T$	Formation from elements	
					Enthalpy kJ/mol	Gibbs free energy
298.15	54.24 ± 0.10	37.190 ± 0.100	0.000	37.190	-996.389 ± 2.100	-918.400 ± 2.200
300	54.51	37.526	0.335	37.191	-996.415	-917.916
350	61.02	46.433	8.553	37.880	-996.846	-904.720
400	66.41	54.944	15.459	39.485	-997.269	-891.595
450	70.85	63.030	21.375	41.656	-997.367	-878.351
500	74.51	70.691	26.511	44.180	-997.365	-865.153
550	77.54	77.939	31.017	46.922	-997.058	-851.917
600	80.04 ± 0.32	84.797 ± 0.320	35.001	49.796	-996.990 ± 2.300	-838.740 ± 2.400
$H_{298}^0 - H_0^0$ 7.075 \pm 0.020 kJ				Molar volume		1.9535 \pm 0.001 J/bar
Transitions in phase				Transitions in reference state elements		
				Al		M.P. 933.45 K
Equations						
$C_p^0 = 205.721 - 0.034921T - 2635.27T^{-0.5} + 1028660T^{-2}$						
(Valid range: 298.15 to 600 K; Average absolute percent deviation: 0.50)						
Note: Molar mass = 59.989 g.						

perimentally determined phase boundaries may represent only those regions in which the kinetics of recrystallization are rapid enough to be observed during the duration of the experiments performed by Ervin and Osborn (1951), and boehmite may not be stable under any of the P - T conditions studied by Ervin and Osborn (1951).

We may use the experimental reaction boundaries given by Ervin and Osborn (1951) to calculate minimum and maximum free energy values for boehmite. Transformation of gibbsite to boehmite is estimated to occur at approximately 400 K and 3 bars. Thus the minimum free energy of boehmite at 400 K is estimated to be -883.0 kJ/mol at 400 K and -909.8 kJ/mol at 298.15 K (using ancillary data from Robie et al., 1979). Transformation of boehmite to corundum is estimated to occur at approximately 658 K and 136 bars. From these results and ancillary data from Robie et al. (1979), the maximum free energy for boehmite is estimated to be -922.1 kJ/mol at 298.15 K. Similarly, the maximum free energy for diaspore is estimated to be -922.7 kJ/mol from the reaction boundary for the reaction 2 diaspore = corundum + H₂O given by Ervin and Osborn (1951). Within the foregoing calculation and in subsequent calculations involving gibbsite and corundum, the thermodynamic properties listed in Robie et al. (1979) are assumed to be good estimates of the true values for these phases and, therefore, are used as fixed values. Results and evaluations presented by Haas et al. (1981), Hemingway et al. (1978), Hemingway (1982), and Apps et al. (1988) provide support for this assumption.

Boehmite was considered by Kittrick (1969) to be more stable than gibbsite, based on a comparison of thermochemical data (see also Parks, 1972; and Hemingway et al., 1978). However, Kittrick (1969) selected free energy of formation values for gibbsite and boehmite that were

based on different values for the free energy of formation of Al³⁺. Correcting the data for gibbsite to the same Al reference value internally consistent with the boehmite data set reverses the relative stability of the two phases at 298.15 K (assuming the activity of H₂O is unity), but the difference is less than the experimental uncertainty. The contrary conclusion of Chesworth (1972), that gibbsite and H₂O at unit activity are stable with respect to boehmite at near-surface conditions, must also be considered suspect because it is based on the highly uncertain estimate for the Gibbs energy of boehmite given by Rosini et al. (1952).

Parks (1972) and later Hemingway et al. (1978) selected the solubility data of Russell et al. (1955) for boehmite as the best data set from which to determine the free energy of formation of boehmite. The result of the calculation is -918.4 \pm 2.1 kJ/mol for the Gibbs free energy of formation of boehmite at 298.15 K, and it suggests that boehmite + H₂O is more stable than gibbsite. In this case, the assumptions made are (1) that the solubility product at 298.15 K can be calculated from the extrapolation of solubility data at higher temperatures, (2) that the solution species involved in the higher temperature solubility experiments is the same species as that commonly referenced at lower temperatures, and (3) that the free energy of formation is accepted for that species.

The estimate of the Gibbs free energy of formation of boehmite given by Hemingway et al. (1978) is consistent with two recent studies. Hovey et al. (1988) calculated a revised value for the Gibbs free energy of formation of Al(OH)₃ from solubility data for boehmite and a value for the Gibbs free energy of formation of boehmite obtained from Apps et al. (1988, then in preparation). The result, $\Delta_f G_{298}^0 = -1305.6$ kJ/mol, is in agreement with the value derived by Hemingway et al. (1978) but was

derived somewhat circularly. Apps et al. (1988) derived a value for the Gibbs free energy of formation of boehmite from the thermodynamic properties of gibbsite (Hemingway and Robie, 1977a) and from solubility data for gibbsite and boehmite. Apps et al. (1988) reported values of $\Delta_f G_{298}^0$ of -917.5 and -1304.8 kJ/mol, respectively, for boehmite and $\text{Al}(\text{OH})_4^-$. From these results, we may only conclude that a Gibbs free energy of formation for boehmite of -918 kJ/mol is consistent with the solubility data for gibbsite and boehmite and with a value of -1305 kJ/mol for the Gibbs free energy of formation of $\text{Al}(\text{OH})_4^-$. However, since the value for the Gibbs free energy of boehmite determined by Apps et al. (1988) is referenced to solubility data interpreted to represent gibbsite solubility, the results and interpretations are subject to the same questions posed for the studies of Hemingway et al. (1978) and Hemingway (1982) that are discussed in the next section.

DISCUSSION

Recent work by May et al. (1979), Couturier et al. (1984), and Sanjuan and Michard (1987) have questioned the free energy of formation of $\text{Al}(\text{OH})_4^-$ derived by Hemingway et al. (1978) and Hemingway (1982). Specifically at issue is the question of the phase or phases that control the solubility of Al in solutions with $\text{pH} > 6$ at 298.15 K and at higher temperatures. Of more general concern is the question of the relative stabilities of the aluminum hydroxide and oxyhydroxide phases and the mechanisms by which precipitation of these phases are controlled. In the discussion that follows, we provide a detailed review of research that establishes the relative stability of the $\text{Al}(\text{OH})_3$ polymorphs (bayerite, nordstrandite, and gibbsite). We select a set of solubility data to represent conditions of metastable equilibrium between gibbsite and Al solution species and calculate the Gibbs free energies of formation of Al^{3+} and $\text{Al}(\text{OH})_4^-$. Finally, we provide an explanation for the apparent variation of gibbsite solubility that has variously been attributed to grain size, acid pretreatment, or sample crystallinity.

Historical perspective

Hemingway and Robie (1977a) identified an error in the calorimetric procedure upon which the enthalpy and free energy of formation of gibbsite were based and reported a revised set of thermodynamic values for gibbsite. In subsequent work, Hemingway and Robie (1977b) and Hemingway et al. (1978) reported revised values for the free energy of formation of Al^{3+} and $\text{Al}(\text{OH})_4^-$ based on solubility studies for gibbsite by Kittrick (1966) and Singh (1974) and reported the revised value for the free energy of gibbsite. Implicit in the work of Hemingway et al. (1978) is the assumption that gibbsite controlled the Al solubility observed by Kittrick (1966). The validity of this assumption was first questioned in the study of May et al. (1979).

May et al. (1979) determined solubilities for a natural and a synthetic gibbsite at several pH values between pH

4 and 9 using several organic pH buffers. May et al. (1979) obtained two subparallel curves, one for each sample, that displayed offsets toward lower solubility at approximately $\text{pH} = 7$. May et al. (1979) concluded that, in basic solutions, the solubility of Al was controlled by a phase more stable than gibbsite (when synthetic gibbsite was used as the starting material). May et al. (1979) tentatively identified the phase as boehmite, although no evidence for a phase other than gibbsite was found. May et al. (1979) utilized the solubilities determined from measurements obtained from the natural gibbsite sample in solutions with $\text{pH} > 7$ to calculate a revised value for the free energy of formation of $\text{Al}(\text{OH})_4^-$ and, subsequently, to calculate the free energy of boehmite as -920.9 kJ/mol. May et al. (1979) concluded that the difference in solubilities observed between the natural and synthetic gibbsites in acid solutions was a consequence of a difference in crystallinity of the two samples; however, they also argued that, in basic solutions, the similar difference in observed solubilities resulted from control of solubility by two phases. The apparent inconsistencies in interpretation of the solubility data led Hemingway (1982) to question the interpretations.

Hemingway (1982) combined the results of May et al. (1979) with other solubility studies from the literature to provide an alternative explanation for the features observed in the solubility data of May et al. (1979). As Al hydrolysis progresses, the nature and characteristics of the aqueous Al species change. The observed offset in solubility curves corresponds with the change from the dominance of species traditionally considered to be of the form $\text{Al}(\text{OH})_3^{3-}$ to the form $\text{Al}(\text{OH})_4^-$ (e.g., Baes and Mesmer, 1981). Hemingway concluded that a change in the mechanism of precipitation accompanied the change in species structure. Hemingway (1982) reasoned that this change in precipitation mechanism allowed bayerite to precipitate only in solutions with a pH greater than approximately 6. Hemingway (1982) concluded that in the experiments performed by May et al. (1979) supersaturation with respect to phases other than gibbsite occurred and that the subparallel solubility curves resulted from control of solution concentration of Al by precipitation of $\text{Al}(\text{OH})_3$ phases, nordstrandite and gibbsite in the acid region, and bayerite and nordstrandite in the basic region. Hemingway (1982) further concluded that bayerite was the least stable of the three $\text{Al}(\text{OH})_3$ phases and that gibbsite was the most stable.

Sanjuan and Michard (1987) measured the solubility of gibbsite at 323 K using procedures similar to those of May et al. (1979), obtained a similar offset in the observed solubility curve, and concluded that both the interpretations of May et al. (1979) and Hemingway (1982) were incorrect. Their interpretation was based on evidence that bayerite is either found in alkaline solutions or replaces gibbsite in alkaline solutions (Verdes and Gout, 1987; Schoen and Roberson, 1970) and that $\text{Al}(\text{OH})_4^-$ has a stability constant similar to that reported by May et al. (1979) (Couturier et al., 1984). Although both Sanjuan

and Michard (1987) and Hemingway (1982) questioned the phase or phases controlling Al solubility in the alkaline region, they reached different conclusions with respect to the relative stability of bayerite and gibbsite, and with respect to the free energy assigned to $\text{Al}(\text{OH})_4^-$. The latter difference, in particular, must be resolved before the free energy of boehmite can be calculated.

Bis-Tris, an organic pH buffer used by May et al. (1979) in their solubility studies of gibbsite, has a strong tendency to form a complex with the aluminate ion (Wesolowski et al., 1990). The increase in total dissolved Al resulting from this process is thought by Wesolowski et al. (1990) to be the cause of the offset observed in the solubility curves published by May et al. (1979). Tris, the organic pH buffer used by May et al. (1979) at high pH, does not show a strong tendency to complex aluminate ion (Wesolowski et al., 1990). Thus, the results of May et al. (1979) may not represent equilibrium between gibbsite and only hydrolyzed Al solution species in the pH range buffered by Bis-Tris, and the presence of a phase more stable than gibbsite may not be needed to explain the solubility curve for gibbsite published by May et al. (1979) and by Sanjuan and Michard (1987). The enhanced solubility of Al is consistent with the arguments of Hemingway (1982) and with the observation of bayerite in such solutions by Verdes and Gout (1987).

Solubilities lower than those found by May et al. (1979), Singh (1974), and Kittrick (1966) were reported by Bloom and Weaver (1982) and Peryea and Kittrick (1988) for several gibbsite samples that had previously been studied by others (Kittrick, 1966; Frink and Peech, 1962). Bloom and Weaver (1982) attributed the lower solubility they observed in acid solutions to the removal of fine crystals of gibbsite or reactive surfaces by acid pretreatment of each sample, and they ascribed the downward shift of solubility seen in the results of May et al. (1979) to more rapid Ostwald ripening of gibbsite in basic solutions.

Bloom and Weaver (1982) have compared their solubility results with one of several sets of results reported by Frink and Peech (1962) also for acid pretreated materials. Bloom and Weaver (1982) did, in fact, find a lower solubility than the set they chose, but other data provided by Frink and Peech (1962) are equivalent to the solubility reported by Bloom and Weaver (1982). Hemingway (1982) compared the data of Frink and Peech (1962) to the model he proposed (his Fig. 5). AlCl_3 solutions to which Frink and Peech (1962) added HCl and gibbsite, and that were aged one month, showed solubilities equivalent to those reported by Bloom and Weaver (1982). AlCl_3 solutions to which no HCl or gibbsite were added hydrolyzed and showed solubilities after 3 months that were equivalent to those found by May et al. (1979) for their natural gibbsite. A similar solution to which gibbsite was added showed solubilities for $\text{pH} < 4$ that were equivalent to the solubilities for the solution equilibrated without gibbsite, whereas those with solution $\text{pH} > 4$ showed solubilities equivalent to those given by May et al. (1979) for synthetic gibbsite. Finally, solutions that

contained no added AlCl_3 , but contained gibbsite and were acidified with HCl, showed the lowest solubilities. The results reported by Bloom and Weaver (1982) are equivalent to the results reported by Frink and Peech (1962) where the same experimental parameters were maintained.

Bloom and Weaver (1982) observed a significant difference in the solubility of two sized fractions of Fisher ACS $\text{Al}(\text{OH})_3$. The sample FC with the smaller size fraction showed the greater solubility. The sample FF with the larger size fraction was pretreated with dilute acid whereas sample FC was not. The solubility difference observed by Bloom and Weaver (1982) was ascribed to the acid pretreatment processes. However, the solution in which sample FC was suspended was 0.01 M KNO_3 and resulted in a somewhat different chemistry for the studies of FC and FF. The effect of this difference is discussed below.

Bloom and Weaver (1982) have shown that acid pretreated gibbsite samples FF, C-730, and C-33 yield identical solubility products. Samples C-730 and C-33 were studied previously by Kittrick (1966, solubility study) and Hemingway et al. (1978, solution calorimetry). Hemingway et al. (1978) also measured the enthalpy of solution of Fisher $\text{Al}(\text{OH})_3$, similar to samples FC and FF. Bloom and Weaver (1982) and Hemingway et al. (1978) concluded from their studies that all of the gibbsite samples had equivalent free energies.

Peryea and Kittrick (1988) have used a similar procedure to that used by Bloom and Weaver (1982) to study the solubility of corundum, gibbsite, boehmite, and diaspore. Peryea and Kittrick (1988) found Al concentrations in apparent equilibrium with gibbsite sample C-730 lower than that reported by Kittrick (1966), and in agreement with the results reported by Bloom and Weaver (1982). Peryea and Kittrick (1988) calculated the free energy of formation of the four Al-bearing phases based on the solubilities they measured using the value of the free energy of Al^{3+} given by Hemingway et al. (1978). The results of these calculations were free energy values that were considerably more negative than those listed in several recent tabulations. However, there is an error in the procedure followed by Peryea and Kittrick (1988) in the calculation of the free energies of the phases (Hemingway et al., 1989). The free energy of formation of Al^{3+} reported by Hemingway and Robie (1977b, incorrectly cited previously as Hemingway et al., 1978) is based on the assumption that gibbsite solubility was accurately determined by Kittrick (1966). If the revised solubility for gibbsite is accepted, then the free energy of formation of Al^{3+} must be recalculated because the Gibbs free energy of formation of gibbsite has been determined by calorimetric methods and represents the reference value for Al in the calculation. The revised free energy of formation of Al^{3+} would be -487.5 kJ/mol and the corrected Gibbs free energies of formation of corundum, boehmite, and diaspore would be -1583.7 , -919.1 , and -923.4 kJ/mol, respectively (Hemingway et al., 1989). These results

are approximately -1.5 kJ/mol more negative than results reported in recent tabulations (e.g., Robie et al., 1979).

The free energy of formation of Al^{3+} is subject to adjustment, as discussed above, if acid pretreatment is shown to result in the best solubility data for gibbsite in acid solutions. Assuming the other solubility results given by Peryea and Kittrick (1988) to also be the best solubility values for corundum, diaspore, and boehmite in acid solutions, then the free energy of formation of Al^{3+} can be calculated from these data and the free energies of formation of -1582.2 kJ/mol (CODATA, Cox, 1978), -922.9 kJ/mol and -918.4 kJ/mol (Hemingway et al., 1978), respectively, for corundum, diaspore, and boehmite. These calculations yield -486.8 , -487.0 , and -486.8 kJ/mol, respectively, for the free energy of formation of Al^{3+} . The values are less negative than the value obtained from the calculations based upon gibbsite solubility, but the results agree within experimental error. If the solubility for gibbsite given by Bloom and Weaver (1982) is used in place of the data from Peryea and Kittrick (1988), one obtains -487.3 kJ/mol for the free energy of formation of Al^{3+} . Whether or not the free energy for Al^{3+} should be modified, these results demonstrate that the free energies for the phases corundum, diaspore, boehmite, and gibbsite, as given above, are consistent. This, of course, assumes that each phase has equilibrated with the same Al solution species.

RELATIVE STABILITY OF THE $\text{Al}(\text{OH})_3$ POLYMORPHS

Before the Gibbs free energy of formation of boehmite can be calculated, the Gibbs free energy of formation of Al^{3+} or $\text{Al}(\text{OH})_4^-$, or both, must be established. To do this, the relative stability of the $\text{Al}(\text{OH})_3$ polymorphs must be established.

If the evidence cited by Sanjuan and Michard (1987) is substantiated (discussion in an earlier section), then the conclusions they reached would directly follow and establish the free energy of formation of $\text{Al}(\text{OH})_4^-$. It is appropriate, therefore, to evaluate the supporting studies. The results of Couturier et al. (1984) and Schoen and Roberson (1970) are critical and are discussed below. The result of Verdes and Gout (1987) supports either viewpoint and thus is not definitive.

Couturier et al. (1984) have reported that they measured the stability constants of hydroxocomplexes of Al^{3+} and $\text{Al}(\text{OH})_4^-$ with oxalic acid. The authors chose this procedure because they believed that only dissolved species would be involved in their study, thus eliminating the problem of identifying the controlling $\text{Al}(\text{OH})_3$ phase that is necessary in the application of solubility studies (e.g., May et al., 1979; Hemingway, 1982). Using thermodynamic properties for Al^{3+} (Hemingway and Robie, 1977b), Couturier et al. (1984) calculated the free energy of formation of $\text{Al}(\text{OH})_4^-$ as -1311.3 kJ/mol, a value substantially more negative than the value of -1305 kJ/

mol, calculated by Hemingway et al. (1978) and Hemingway (1982).

Couturier et al. (1984) assumed that the strong complexes that occur between Al solution species and oxalic acid would prevent precipitation of $\text{Al}(\text{OH})_3$ phases. Couturier et al. (1984) also assumed that no mixed hydroxyl-oxalate complexes were formed. These assumptions appear to be valid in acidic solutions ($\text{pH} < 5$), but may be invalid in more basic solutions (Sjöberg and Öhman, 1985; Bilinski et al., 1986). Sjöberg and Öhman (1985) studied the equilibria between Al solution species, hydroxide, and oxalic acid from pH 0.2 to approximately 7. The upper pH limit in their study (coincidentally the pH region in which May et al., 1979, observed an offset to lower solubility) was set by the onset of precipitation as determined by turbidity measurements. Violante and Violante (1980) studied the effect of pH and chelating organic anions on the synthesis of aluminum hydroxides and oxyhydroxides. Oxalic acid was found to not inhibit bayerite precipitation in alkaline solutions at low concentrations, but as the concentration (with respect to Al) was increased, bayerite precipitation was inhibited and nordstrandite or gibbsite precipitated. The studies of Sjöberg and Öhman (1985) and Violante and Violante (1980) show that precipitation of $\text{Al}(\text{OH})_3$ phases does occur in the presence of oxalic acid in slightly basic solutions. Thus, the assumption made by Couturier et al. (1984) is invalid for basic solutions and precipitation can be expected. Where precipitation does occur, the precipitation mechanism will control the Al solution concentration and the equilibria with respect to oxalic acid will adjust accordingly. Therefore, the free energy of formation of $\text{Al}(\text{OH})_4^-$ calculated by Couturier et al. (1984) must be questioned.

The second critical study cited by Sanjuan and Michard (1987) was that of Schoen and Roberson (1970) who reported that they had observed a gradual disappearance of gibbsite in solutions precipitating bayerite. Schoen and Roberson (1970) concluded that bayerite was more stable than gibbsite in basic solutions. However, examination of the data presented by Schoen and Roberson (1970) suggests that nordstrandite was misidentified as gibbsite. Schoen and Roberson (1970) identified early formed solids on the basis of one or two X-ray diffraction peaks (or calculated d -values) they considered definitive. Observed d -values were commonly from 4.7 to 4.9, and approximately 4.4 and 2.2 Å. The d -values of 4.4 and 2.2 were assigned to bayerite and the 4.7–4.9 Å d -values were assigned to gibbsite. Although bayerite exhibits a d -value of 4.71 Å, the early formed bayerite was considered to have crystallized with poorly developed basal planes. Although nordstrandite was not considered by Schoen and Roberson (1970), it appears to be likely because Violante and Violante (1980) assigned d -values of 4.72 Å to bayerite, 4.79 Å to nordstrandite, and 4.85 Å to gibbsite formed and examined under similar conditions.

The discussion given above strongly questions the interpretations and results of Couturier et al. (1984) and

Sanjuan and Michard (1987) with respect to the relative stabilities of the $\text{Al}(\text{OH})_3$ polymorphs and their calculated value for the free energy of formation of $\text{Al}(\text{OH})_4^-$. However, the interpretations given above support, but do not prove, the interpretations of Hemingway (1982), Hovey et al. (1988), and Apps et al. (1988).

Verdes and Gout (1988) provide evidence for the relative stability of bayerite and gibbsite that is consistent with the results of this study. On the basis of solubility measurements, Verdes and Gout (1988) conclude that gibbsite is more stable than bayerite and obtain a value for the Gibbs energy of formation of $\text{Al}(\text{OH})_4^-$ similar to that proposed by Hemingway et al. (1978) and Hemingway (1982). Further, using the free energy of $\text{Al}(\text{OH})_4^-$, Verdes and Gout (1988) have calculated -916 and -921 kJ/mol for the Gibbs free energy of formation of boehmite and diaspore, respectively, from a combination of solubility measurements and from crystallization from amorphous oxides.

The relative stability of the three common $\text{Al}(\text{OH})_3$ polymorphs also may be inferred from results presented by Violante and Violante (1980) who studied the influence of chelating organic anions on the synthesis of aluminum hydroxides and oxyhydroxides. The authors found that, in alkaline solutions, increasing the ratio of the complexing organic anion to dissolved Al produced a change in the phase that precipitated, from bayerite to nordstrandite to gibbsite. This information is consistent with the inference that bayerite is the least stable polymorph and gibbsite is the most stable.

SOLUBILITY OF GIBBSITE

Various studies have concluded that a range of free energies will be shown by gibbsite samples as a consequence of differences in crystallinity (e.g., Helgeson et al., 1978; May et al., 1979; Bloom and Weaver, 1982; Sanjuan and Michard, 1987). In acid solutions, there are three fairly consistent data sets that may be represented as three subparallel curves of Al concentration vs. pH in the acid region (see Fig. 5 of Hemingway, 1982). Frink and Peech (1962) used the same gibbsite sample, but report solubilities that fall along the three curves (one of which is defined by some of their data). Because the same gibbsite sample was used in these experiments, the crystallinity of the gibbsite cannot be the cause of the observed solubility differences. Also, it is unlikely that equivalent degrees of crystal imperfection could be obtained in different gibbsite samples (note agreement of Kittrick, 1966; Singh, 1974; May et al., 1979). Therefore, it would appear that variations in sample crystallinity are not the major cause of observed differences in gibbsite solubility.

It does not appear that the acid pretreatment utilized by Bloom and Weaver (1982) and Peryea and Kittrick (1988) is the cause of the lower solubility observed by these authors. Kittrick (1966), Singh (1974), and May et al. (1979, synthetic gibbsite) used different gibbsite samples but obtained nearly identical solubility values for Al in acid solutions. The solubility reported by Bloom and

Weaver (1982) for the treated sample studied by Kittrick (1966) is lower, but it is in agreement with results reported by Frink and Peech (1962) where the same general experimental approach was used. Of greatest importance is the fact that Frink and Peech (1962), using the same gibbsite sample but different experimental parameters, found different solubilities, some of which agreed with those of Kittrick (1966), Singh (1974), and May et al. (1979). Also, May et al. (1979) pretreated their gibbsite samples by repeated suspension (seven times) in deionized H_2O followed by centrifugation. Thus the sample used by May et al. (1979) is as likely to have had fine-grained gibbsite particles removed and active surface defects modified as that sample studied by Bloom and Weaver (1982).

Several studies have shown that Cl^- has an inhibiting effect on the formation of crystalline $\text{Al}(\text{OH})_3$ (e.g., Thomas and Whitehead, 1931; Hsu and Bates, 1964; Hsu, 1967; Turner and Ross, 1970; Ross and Turner, 1971). In the latter two studies, the concentrations of mononuclear and polynuclear Al ions were determined by the eight-quinolinolate extraction method (Turner, 1969) and the amount of Al in the solid phase was calculated as the difference between the initial total of the dissolved Al and the sum of the mononuclear and polynuclear species. Of critical importance was the observation that after approximately 12 d, the concentration of mononuclear species remained essentially constant for periods of 100 d or more and the solid phase showed no evidence of an $\text{Al}(\text{OH})_3$ phase. The solid phase consisted of a basic aluminum hydroxychloride that was X-ray amorphous except at higher chloride ion concentrations and times of approximately 300 d. The period in which the concentration of mononuclear species remained constant increased with increase in the concentration of Cl^- . Following this period, gibbsite appeared in the crystalline phase, the concentration of polynuclear species decreased to 0, and the concentration of mononuclear species increased (e.g., Fig. 2B, Turner and Ross, 1970). The differences in the solubilities of gibbsite reported by Bloom and Weaver (1982) and Peryea and Kittrick (1988), as compared to those of Kittrick (1966), Singh (1974), and May et al. (1979) are consistent with the results of these studies and suggest an alternative explanation to that of acid pretreatment. The extended period in which the concentration of the mononuclear species remains nearly constant and in which any aluminum hydroxychloride is X-ray amorphous could easily be mistakenly interpreted as showing equilibrium between gibbsite suspended in such solutions and the mononuclear species.

The most probable cause of the observed differences in Al solubility lies in differences in the experimental procedures used in the various studies. Recent advances in solution nuclear magnetic resonance (NMR), in particular the use of the Fourier-transform procedure beginning in the 1970s, has allowed extensive documentation of the behavior of Al in solutions, and that information is applicable to this study. A major contributor in this area is

Akitt who, with his coworkers (Akitt et al., 1972a, 1972b, 1981; Akitt and Farthing, 1981a, 1981b, 1981c, 1981d, 1981e; Akitt and Elders, 1985), has provided much of the information that will be drawn upon in the following discussion.

It has been known for many years that Al-bearing solutions behave differently when the solutions have somewhat different chemistries (e.g., Hsu, 1967; Ross and Turner, 1971; Hemingway, 1982 and references therein; Tsai and Hsu, 1984, 1985). Until recently, the nature of some of these differences has been obscure. Akitt and Farthing (1981b) used solution NMR and gel-permeation chromatography to study the Al species present in two solutions prepared with different procedures. Both solutions were prepared to have a ratio (*m*) of OH/Al of 2.5. Both solutions were prepared at approximately 100 °C. The first solution was prepared by hydrolysis of AlCl₃ by the rapid addition of Na₂CO₃. In the second, aluminum metal was dissolved in an AlCl₃ solution. The first solution showed one peak in the NMR spectrum which was assigned to the species [AlO₄Al₁₂(OH)₂₄(OH₂)₁₂]⁷⁺ which will be described by the usual symbol Al₇⁺. The second solution spectrum was more complex and interpretation by Akitt and Farthing (1981b) suggested at least four Al species, two of which were assigned to Al₇⁺ and [Al(OH₂)₆]³⁺ (designated as Al³⁺). Akitt and Farthing (1981b) indicated that other hydrolysis methods yielded solutions showing spectra that differed from those described above, but exhibited the same general features, that is, varying ratios of the same Al species. Necessarily, these alternative hydrolysis methods involve changes in the bulk chemistry of the solution [e.g., the use of Al(NO₃)₃ in place of AlCl₃] as well as in the preparation procedures, but the work of Akitt and Farthing shows that the different procedures lead to differences in speciation of Al. Akitt et al. (1972b, p. 605) have shown that the concentration of monomer Al species is dependent on the procedure followed in the preparation of solutions with 0 < *m* < 2.6.

Of importance to this study is the observation that for equivalent ratios of OH/Al, solutions to which hydrochloric acid was either added or was an initial component had a lower concentration of monomer Al species than those prepared with solutions of AlCl₃ or Al(NO₃)₃ (Akitt et al., 1972b). Peryea and Kittrick (1988), Bloom and Weaver (1982), and Frink and Peech (1962) used HCl as part of the preparation of their experimental solutions. May et al. (1979) and Couturier et al. (1984) utilized nitrate solutions. Singh (1974) used AlCl₃ solutions. Kittrick (1966) adjusted the pH of his samples with HCl; however, Kittrick did not pretreat his sample to remove fine Al(OH)₃ material, and evidence (see Bloom and Weaver, 1982; Kittrick, 1966) suggests that the fine material reacted rapidly to cause the solutions Kittrick studied to quickly become oversaturated with respect to gibbsite. Based on the results from ²⁷Al solution NMR and the procedures used to extract Al, one would anticipate that Peryea and Kittrick (1988), Bloom and Weaver

(1982), and Frink and Peech (1962, HCl added) would observe lower concentrations of Al in monomeric species than would Frink and Peech (1962, HCl not added), Kittrick (1966), Singh (1974), or May et al. (1979) simply as a consequence of the experimental approach followed in the studies.

Akitt et al. (1972a) studied sulfato-aluminum complexes using ²⁷Al solution NMR spectroscopy. The authors observed no change in the solution species upon addition of small amounts of sulfuric acid, but observed the destruction of the complex when hydrochloric acid was added. Although sulfate is a strong complexing agent and may result in basic aluminum sulfate precipitation (e.g., Johansson, 1960, 1962; Johansson et al., 1960), the presence of chloride results in reduction of the sulfato-aluminum complex. These results support earlier studies, described above (also see Barnhisel and Rich, 1965), that suggest that chloride appears to alter Al hydrolysis and to inhibit precipitation of aluminum hydroxides.

The precipitation mechanism for AlOOH and Al(OH)₃ phases has not been determined as it has for the basic aluminum sulfates. The addition of sulfate ion to acidic Al solutions may result in the precipitation of two basic aluminum sulfate phases (Johansson, 1960, 1962). The structure of the Al within these phases is considered by Johansson and coworkers to reflect the structure of the Al polymers in the solutions from which the phases were precipitated. The Al polymers are the dimer and Al₇⁺. Bertsch et al. (1986a, 1986b) have shown that rapid neutralization of Al-bearing solutions to high *m* values results in a lower production of Al₇⁺ and a greater production of pseudoboehmite. However, it is not clear whether Al₇⁺ is involved in the formation of the gelatinous pseudoboehmite or whether competing reactions decrease the Al solution constituents required for the production of Al₇⁺. Tsai and Hsu (1984 and references therein) have shown that the Al₇⁺ ion is lost through aging of Al solutions with the development of a more stable polymer (also see Akitt and Farthing, 1981d; Bertsch et al., 1986a, 1986b). The structure of this polymer is unknown; however, Tsai and Hsu (1984) have shown that development of the polymer results in a change in the morphology and structure of basic aluminum sulfate that precipitates from the solution and may result in gibbsite precipitation. Tsai and Hsu (1984, 1985) suggest that these polymers may resemble fragments of crystalline Al(OH)₃, as was suggested earlier by, for example, Smith and Hem (1972). Tsai and Hsu (1985) found that the negative logarithm of the solubility product (pK_{sp}) of the initial solutions containing the metastable (by the definition of Tsai and Hsu, 1984 and 1985) Al₇⁺ was 32.32. This value is consistent with that given by Hem and Roberson (1967) and Smith and Hem (1972) for the solubility of what they called microcrystalline gibbsite. Tsai and Hsu (1985) found that the aged solutions that lost the Al₇⁺ species, but retained the more stable polymer, had a pK_{sp} of approximately 33.4 to 33.5. This value is consistent with the pK_{sp} calculated from the data of Frink and Peech

(1962, 1963) and of May et al. (1979) for solubility of the natural gibbsite sample and is consistent with the pK_{sp} Hemingway (1982) postulated for nordstrandite.

Using ^{27}Al solution NMR, the structure of Al in the more stable polymer proposed by several authors (e.g., Tsai and Hsu, 1985) cannot be determined, nor can it be proved that a polymer rather than a crystalline material is present. However, work reported by Bottero et al. (1980) has shown that $\text{Al}(\text{OH})_4^-$ and Al_7^{3+} can be present in solutions prepared at 20 °C with m as low as 0.5. Consequently, additional studies are necessary to determine the species actually involved in the precipitation of AlOOH and $\text{Al}(\text{OH})_3$ phases.

CONCLUSIONS

The results discussed above provide only a glimpse of the complexity of the system under study. Chloride ion clearly interacts with Al and changes the mechanism of hydrolysis in a manner that is different from that of the nitrate ion. ^{27}Al solution NMR has not yet focused on these processes and may not be able to resolve the structural differences. However, the technique has established beyond doubt that the method of preparation of Al solutions may result in differences in the type and amount of species present and, together with the preponderance of other experimental data, supports the choice of the data sets of Kittrick (1966), Singh (1974), and May et al. (1979) to determine the Gibbs free energies of Al^{3+} (-489.8 ± 4.0 kJ/mol) and $\text{Al}(\text{OH})_4^-$ (-1305.0 ± 1.3 kJ/mol). Based upon the measurements reported here, this analysis and the analyses of Hemingway et al. (1978), Hemingway (1982), Hovey et al. (1988), and Apps et al. (1988), the recommended values for the entropy, Gibbs free energy, and enthalpy of formation of boehmite are 37.19 ± 0.1 J/(mol·K), -918.4 ± 2.1 kJ/mol, and -996.4 ± 2.2 kJ/mol, respectively. The recommended Gibbs free energy of formation of boehmite is intermediate between the value of -917.5 kJ/mol calculated by Apps et al. (1988) from solubility studies in basic solutions and the corrected value from Peryea and Kittrick (1988) of -919.1 kJ/mol based upon solubility studies in acidic solutions.

The recommended results are consistent with the analyses of Hovey et al. (1988) and Apps et al. (1988); however, these analyses are not totally independent. Hovey et al. (1988), using the Gibbs free energy of boehmite and set of solubility data recommended by Apps et al. (1988, then in preparation), calculated a value for the Gibbs free energy of formation of $\text{Al}(\text{OH})_4^-$ of -1305.6 ± 0.2 kJ/mol. Apps et al. (1988) used the same solubility data to establish the Gibbs free energy of formation of boehmite (-917.5 kJ/mol) and then calculated a consistent value for the Gibbs free energy of formation of $\text{Al}(\text{OH})_4^-$ (-1304.8 kJ/mol). Consequently, differences in the interpretation of models employed and model fit to experimental data result in small variations in the specific values reported for either the Gibbs free energy of boehmite or $\text{Al}(\text{OH})_4^-$.

Both differences in sample crystallinity and acid pre-

treatment were examined as possible causes for observed differences in gibbsite solubility. Neither of these factors were shown to be significant. Gibbsite would appear to crystallize with an ordered and well-defined crystal structure for which a single value of the Gibbs free energy is appropriate. However, as with any mineral, grinding of gibbsite may result in distortion of the crystal surface and may result in a surface energy contribution in some types of measurements. Differences observed for the solubility of gibbsite and commonly ascribed to differences in gibbsite crystallinity or acid pretreatment of gibbsite samples more probably are caused by differences in the procedures used in the experiments which results in a final state for the Al that is different from that assumed by the investigator.

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