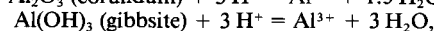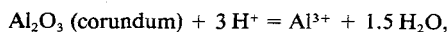# RELATIVE SOLUBILITY OF CORUNDUM, GIBBSITE, BOEHMITE, AND DIASPORE AT STANDARD STATE CONDITIONS[1]

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Abstract—The solubilities of HCl-treated samples of corundum, gibbsite, boehmite, and diaspore in aqueous solutions at 298 K and one atmosphere pressure were determined from undersaturated and supersaturated initial conditions. Solution characteristics at apparent equilibrium were measured and used to calculate equilibrium constants (K_r) for mineral dissolution reactions:

$$Al_2O_3 \text{ (corundum)} + 3\,H^+ = Al^{3+} + 1.5\,H_2O,$$
$$Al(OH)_3 \text{ (gibbsite)} + 3\,H^+ = Al^{3+} + 3\,H_2O,$$
and
$$AlOOH \text{ (boehmite or diaspore)} + 3\,H^+ = Al^{3+} + 2\,H_2O.$$

Assuming solid phase and water activities of unity, $\log K_r = 3pH - pAl^{3+}$ for all three equations. The calculated $\log K_r$ values were: 9.01 ± 0.05 (corundum), 7.76 ± 0.14 (gibbsite), 7.49 ± 0.09 (boehmite), and 6.75 ± 0.24 (diaspore), indicating that the relative thermodynamic stabilities under the experimental conditions were: corundum < gibbsite < boehmite < diaspore. The gibbsite value agreed well with that determined independently by another research group using acid-treated subsamples of the same source mineral (7.70 ± 0.02). The calculated Gibbs free energies of formation (kJ/mole) were: -1587.4 ± 2.1 (corundum), -1156.7 ± 1.6 (gibbsite), -921.0 ± 1.5 (boehmite), and -925.1 ± 2.0 (diaspore). The ΔG_f° values of the acid-treated minerals were 1.8 to 12.4 kJ/mole more negative than values recently compiled for untreated mineral samples. This result is attributed to the removal of reactive surface coatings that isolated the bulk mineral phases from the solution phase.

Key Words—Acid solubility, Aluminum, Boehmite, Corundum, Diaspore, Gibbsite.

INTRODUCTION

The presence of gibbsite [$Al(OH)_3$], boehmite (AlOOH), diaspore (AlOOH), and corundum (Al_2O_3) in lateritic soils and near-surface bauxites suggests the absence of thermodynamic equilibrium. Hemingway (1982) suggested that diaspore is the stable phase under surface weathering conditions and that gibbsite and boehmite are metastable phases whose presences are in large part due to slow rates of transformation. Direct precipitation of diaspore from Al solutions has rarely been observed (Chesworth, 1978), although Wefers and Bell (1972) indicated that the presence of goethite (FeOOH) induced the precipitation of its isomorph diaspore at temperatures <298 K. Keller (1978) reported evidence for the recrystallization of diaspore in a clay deposit under surface weathering conditions.

Gibbsite and its $Al(OH)_3$ polymorphs readily precipitate under a wide variety of experimental conditions (Hemingway, 1982). Certain inorganic and organic ligands appear to be necessary to promote the precipitation of boehmite over other Al hydroxides and to ensure its stability after precipitation (Violante and

Huang, 1984). Hemingway (1982) concluded that in natural waters the rapid polymerization of dissolved hydroxyaluminum ions favors the metastable precipitation of $Al(OH)_3$ at the expense of AlOOH phases. Gibbsite should therefore be more likely to form than boehmite and diaspore in lateritic soils and bauxites. Once formed, gibbsite, boehmite, and diaspore show little propensity to alter to other minerals within the timescale of most laboratory experiments. The chemical activity of water appears to be a major factor driving the progressive dehydration of the minerals at 298 K (Troland and Tardy, 1987); however, water activity is rarely controlled at less than unity in laboratory experiments. The slow kinetics of transformation have prompted numerous attempts to establish the relative stabilities of the minerals on the basis of thermochemical data; however, the large errors associated with the Gibbs free energies of formation (ΔG_f°) of the minerals do not permit unambiguous determination of the directions of the gibbsite-boehmite, gibbsite-diaspore, and boehmite-diaspore reactions (Hsu, 1977).

The present study was undertaken to determine by solubility methods the relative thermodynamic stabilities of corundum, gibbsite, boehmite, and diaspore at 298 K, one atmosphere pressure, and water activity of unity. Calculated values of the equilibrium constants for the respective dissolution reactions were used to quantify the stability relations. This procedure avoided the cumulative errors introduced in calculating ΔG_f°
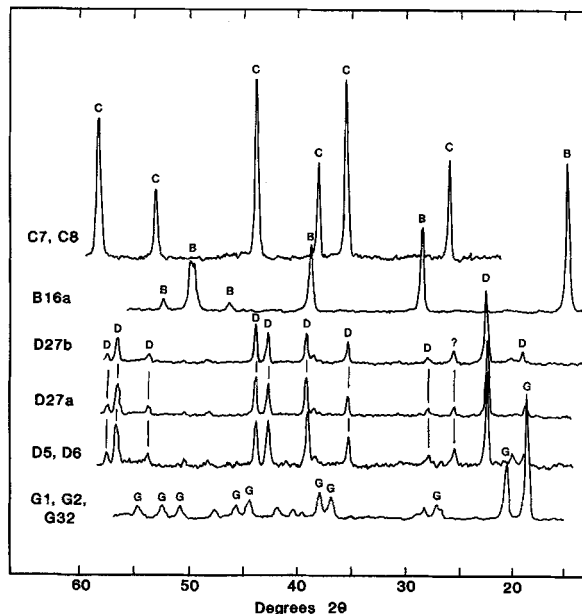
Figure 1. X-ray powder diffraction patterns of corundum (C), boehmite (B), diaspore (D), and gibbsite (G). Ni-filtered CuKα radiation.

values for the minerals and subsequent free energy changes of the mineral transformation reactions. The mineral samples were treated with HCl prior to the solubility experiments to remove surface materials that may differ in chemical composition and reactivity from the bulk mineral phase (Bloom and Weaver, 1982).

MATERIALS AND METHODS

Materials

Corundum samples C7 and C8 were replicate samples of tabular Alumina T-61 obtained from the Aluminum Company of America. X-ray powder diffraction (XRD) showed only corundum (Figure 1). Scanning electron microscopy (SEM) indicated that the samples consisted of particles <5.7 μm. Gibbsite samples G1, G2, and G32 were replicate samples of commercial Alcoa hydrated alumina C-730 obtained from the Aluminum Company of America. This mineral sample was described in detail by Kittrick (1966) and by Bloom and Weaver (1982). XRD showed only gibbsite (Figure 1). SEM indicated particle sizes <1.0 μm. Boehmite sample 16a was synthesized using the procedure for generating Sample 31 of Tettenhorst and Hofmann (1980). XRD showed only boehmite (Figure 1). The 020 XRD reflection was at 14.68°2θ, CuKα radiation. SEM indicated particle sizes <0.9 μm. Diaspore samples D5 and D6 were replicate samples from a single specimen obtained from Ward's Natural Science Establishment, Rochester, New York. The mineral originated in Missouri. XRD showed only diaspore (Figure 1). SEM indicated particle sizes <2.5 μm. Diaspore samples D27a and D27b were collected by W. D. Keller

from the deposits indicated in Figures 3 and 4 of Keller (1978) in the Schaefferkoetter clay pit, Owensville, Missouri. XRD showed only diaspore (Figure 1). SEM indicated particle sizes <2.5 μm.

Sample equilibration, chemical analyses and speciation

All mineral samples were reacted with 0.1 M HCl (1:1 solid:acid) for 14 days to minimize the influence of reactive surface material (Bloom and Weaver, 1982). The treated samples were washed three times with 0.01 M HCl (samples C7, C8, G1, and G2) or twice with water (G32, B16a, D5, D6, D27a, and D27b). Five to ten grams of each sample was placed in 50-ml polypropylene centrifuge tubes and subjected to a series of consecutive equilibration reactions. Distilled water (8–10 ml) or 0.01 M HCl (8–10 ml) was added per tube for equilibration from undersaturated initial conditions. Ten milliliters of 0.001 M AlCl$_3$, adjusted to pH 4.4 or 4.5 with NaOH or KOH, were added per tube for equilibration from supersaturated initial conditions. The tubes were covered with paraffin film containing several small perforations for gas exchange and placed in a temperature-controlled cabinet. The temperature and relative humidity were maintained at 298 K and 100%, respectively. The samples were equilibrated for 15 to 49 days and were manually resuspended on an irregular basis. Supernatant solutions were obtained after equilibration using the immiscible displacement procedure of Kittrick (1980). The isolated solutions were determined to be free of suspended solids by Tyndall beam inspection.
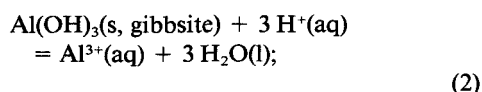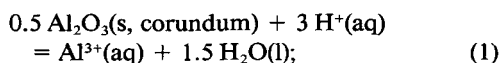
The supernatant pH was measured using a combination microelectrode after removing aliquots for chemical analysis. Total dissolved Al was determined by atomic absorption (AA) spectrophotometry using KCl to suppress ionization of Al in the nitrous oxide-acetylene flame. Sanjuan and Michard (1987) indicated that AA analysis may overestimate total Al in filtered acidic solution because of small solid particles that pass through the filtering medium. We believed that our supernatant isolation method should have eliminated this interference. If it did not, the effect would be over-estimation of Al^{3+} concentration and activity in the solutions. The Al mineral phases would therefore be less soluble than determined in the present analysis, a result that would more strongly support the conclusions reached below. Total dissolved Na and K were determined by flame emission spectrophotometry. The fraction of total dissolved Al occurring as Al^{3+} was calculated using a chemical equilibrium computer model patterned after the GEOCHEM algorithm (Sposito, 1981). The aqueous species Al^{3+}, AlOH^{2+}, Al(OH)$_2^+$ and Al(OH)$_4^-$ were considered in the model. Polynuclear Al-OH species were not included because they appear to be insignificant under the experimental conditions (Sanjuan and Michard, 1987). The

$Al(OH)_3^0$ ion-pair was not included because it should have been insignificant at 298 K (May *et al.,* 1979).
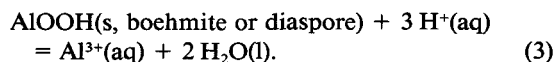
Because the concentration of Na and K ion-pairs should have been small relative to the free metal ions (Lindsay, 1979), dissolved Na and K were assumed to have been completely dissociated and were included in the calculation of ionic strength. Equilibrium constants for the pertinent ion-association reactions were obtained from Lindsay (1979) and are listed in Table 1. Single-ion activity coefficients were calculated by the Davies equation (Sposito, 1981). A set of coupled, nonlinear algebraic equations was derived for the considered free ionic and ion-pair species. These were solved numerically by successive iterations until constant ionic strength was indicated. The relative molar distribution of dissolved Al species predicted by the present model ranged from 89 to 99.9% Al^{3+}, 0 to 7.5% $AlOH^{2+}$, 0 to 3.6% $Al(OH)_2^+$, and <0.001% $Al(OH)_4^-$.

Stability calculations

The mineral solubility reactions under consideration were:

$$0.5\ Al_2O_3(s,\ corundum) + 3\ H^+(aq)$$
$$= Al^{3+}(aq) + 1.5\ H_2O(l); \quad (1)$$

$$Al(OH)_3(s,\ gibbsite) + 3\ H^+(aq)$$
$$= Al^{3+}(aq) + 3\ H_2O(l); \quad (2)$$

and

$$AlOOH(s,\ boehmite\ or\ diaspore) + 3\ H^+(aq)$$
$$= Al^{3+}(aq) + 2\ H_2O(l). \quad (3)$$

Assuming activities of unity for the solid phases and water, the log transformations of the respective equilibrium equations were identical,

$$\log K_r = 3\ pH - pAl^{3+}, \quad (4)$$

where K_r denotes the constant of reaction and the suffix p indicates the $-\log$ transformation.

At 298 K and one atmosphere, the standard-state free energy change of reaction is related to the equilibrium constant by

$$\Delta G_r^\circ = 5.708\ \log K_r, \quad (5)$$

where ΔG_r° has units of kJ/mole. The ΔG_r° for Reactions (1), (2), and (3) is related to the ΔG_f° of the reactants and products by

$$\Delta G_r^\circ = \Delta G_f^\circ[Al^{3+}(aq)] + a\Delta G_f^\circ[H_2O(l)]$$
$$- b\Delta G_f^\circ(solid) - 3\Delta G_f^\circ[H^+(aq)], \quad (6)$$

where a and b are the stoichiometric coefficients for H_2O and the solid phase in the pertinent reactions. Rearranging,

$$\{\Delta G_f^\circ(solid) = \{\Delta G_f^\circ[Al^{3+}(aq)] + a\Delta G_f^\circ[H_2O(l)]$$
$$- 3\Delta G_f^\circ[H^+(aq)] - \Delta G_r^\circ\}/b. \quad (7)$$

Table 1. Ion-association constants used in supernatant chemical speciation model.

Reaction	log K_r
$Al^{3+} + H_2O = AlOH^+ + H^+$	−5.02
$Al^{3+} + 2\ H_2O = AlOH_2^+ + 2\ H^+$	−9.30
$Al^{3+} + 4\ H_2O = AlOH_4^- + 4\ H^+$	−23.33

The standard deviation (SD) for the uncertainty of ΔG_f° (solid) was estimated as

$$SD[\Delta G_f^\circ(solid)] = [SD_r^2 + \Sigma_j(v_j SD_j)^2]^{1/2}, \quad (8)$$

where SD_r is the standard deviation associated with the mean ΔG_r° value calculated from the current study, v_j is the stoichiometric coefficient, and SD_j is the uncertainty in the ΔG_f° value for the jth term on the right-hand side of Eq. (7).

The value of log K_r for each solubility determination was calculated using the measured pH and the computer model-generated chemical activity for $Al^{3+}(aq)$. The ΔG_f° values and uncertainties (kJ/mole) used to solve Eqs. (7) and (8) for Reactions (1), (2), and (3) were: $Al^{3+}(aq)$, -489.4 ± 1.4; $H_2O(l)$, -237.18 ± 0.08; and $H^+(aq)$, 0.00 ± 0.00 (Hemingway *et al.,* 1978).

RESULTS AND DISCUSSION

Tables 2 and 3 present the experimental results and calculated thermodynamic parameters. The mean log K_r values for the four minerals were: 9.01 ± 0.05 (corundum), 7.74 ± 0.14 (gibbsite), 7.49 ± 0.09 (boehmite), and 6.75 ± 0.24 (diaspore). The mean values for gibbsite and boehmite are significantly different according to the t-distribution test at $\alpha > 0.01$ (Dixon and Massey, 1969). The greater error associated with the diaspore value is attributed in part to the use of multiple samples of natural sources of the mineral. The log K_r values after 15 days of reaction did not differ significantly from those after 49 days (Figure 2). Furthermore, the mean log K_r values were generated from both undersaturated and supersaturated initial conditions. These observations suggest that the reaction systems were at unstable equilibrium as defined by Hemingway (1982), in which changes in the system are too slow to be detected within the time frame of the experiment. The log K_r values indicate that the relative thermodynamic stabilities of the minerals (in order of increasing stability at 298 K, one atmosphere pressure, and water activity of unity) are corundum < gibbsite < boehmite < diaspore. This conclusion must be qualified by a number of considerations concerning the stabilities of pure hydrous Al oxide minerals.

Hemingway (1982) concluded that gibbsite is less soluble than its polymorphs nordstrandite and bayerite and that gibbsite solubility is related to particle size. Sanjuan and Michard (1987) indicated that the scientific literature fails to confirm the relative stabilities

Table 2. Consecutive solubility determinations for corundum and gibbsite samples.

Sample	Reaction time (days)	pH	Total dissolved[1] Na or K ($\times 10^{-3}$ M)	Al ($\times 10^{-4}$ M)	pAl^{3+}	log K$_r$	ΔG_f^o (kJ/mole)
Corundum							
C7	24	4.01	1.177	34.283	3.10	8.93	−1588.39
	49[2]	4.14	1.335	12.045	3.36	9.06	−1586.91
	15[2]	4.16	1.611	8.895	3.46	9.02	−1587.37
C8	24	4.04	1.816	31.503	3.13	8.99	−1587.71
	49[2]	4.12	1.320	14.825	3.30	9.06	−1586.91
	15[2]	4.14	1.611	10.748	3.40	9.02	−1587.37
Mean						9.01	−1587.44
Standard deviation						0.05	2.06
Gibbsite							
G1	24	3.55	0.409	44.290	3.05	7.60	−1157.56
	15	3.63	0.077	54.482	3.02	7.87	−1156.02
	49[2]	3.75	0.174	17.419	3.25	8.00	−1156.19
G2	24	3.54	0.230	38.360	3.07	7.55	−1155.28
	15	3.60	0.059	43.734	3.05	7.75	−1156.70
	49[2]	3.69	0.141	18.531	3.23	7.84	−1156.19
G32	27	3.82	0.000	4.336	3.62	7.84	−1156.19
	17[2]	3.75	2.379	7.950	3.49	7.76	−1156.65
	18[2]	3.75	2.404	7.894	3.49	7.76	−1156.65
	46[2]	3.68	2.588	8.450	3.47	7.57	−1157.79
Mean						7.76	−1156.69
Standard deviation						0.14	1.64

[1] Na: samples C7, C8, G1, G2; K: sample G32.
[2] Indicates equilibration from supersaturated initial conditions.

Table 3. Consecutive solubility determinations for boehmite and diaspore samples.

Sample	Reaction time (days)	pH	Total dissolved[1] Na or K ($\times 10^{-3}$ M)	Al ($\times 10^{-4}$ M)	pAl^{3+}	log K$_r$	ΔG_f^o (kJ/mole)
Boehmite							
B16a	27	3.64	0.000	6.671	3.48	7.44	−921.29
	17[2]	3.64	2.558	15.789	3.29	7.63	−920.21
	18[2]	3.63	2.916	9.673	3.44	7.45	−921.24
	46[2]	3.60	2.445	11.119	3.38	7.42	−921.41
	42[2]	3.63	3.095	12.231	3.37	7.52	−920.83
Mean						7.49	−921.00
Standard deviation						0.09	1.49
Diaspore							
D5	24	3.39	0.537	25.944	3.14	7.03	−923.63
	49[2]	3.41	1.381	17.419	3.24	6.99	−923.86
	15[2]	3.46	1.715	13.342	3.32	7.06	−923.46
D6	24	3.29	2.302	12.601	3.34	6.52	−926.54
	49[2]	3.34	1.519	14.084	3.30	6.72	−925.40
	15[2]	3.45	1.739	11.489	3.36	6.99	−923.85
D27a	27	3.98	0.000	0.130	5.00	6.94	−924.15
	17[2]	3.30	2.404	7.672	3.50	6.40	−927.23
	18[2]	3.39	2.660	7.672	3.50	6.67	−925.69
	46[2]	3.45	3.606	8.673	3.48	6.87	−924.55
D27b	27	3.77	0.000	0.130	4.99	6.32	−927.68
	17[2]	3.35	2.379	6.449	3.56	6.50	−926.66
	18[2]	3.42	2.660	7.672	3.50	6.76	−925.17
	46[2]	3.48	3.519	8.895	3.47	6.97	−923.98
Mean						6.75	−925.13
Standard deviation						0.24	2.00

[1] NA: samples D5, D6; K: samples B16a, D27a, D27b.
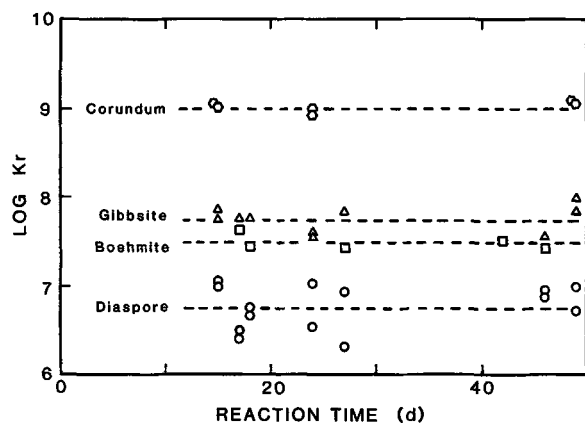[2] Indicates equilibration from supersaturated initial conditions.

Figure 2. Influence of reaction time on log K_r values. Log K_r values at reaction time = 0 days were $+10.3$ (supersaturated systems) and $-\infty$ (undersaturated systems).

Table 4. Gibbs free energies of formation (kJ/mole) at 298 K and one atmosphere pressure.

Mineral	This study	Tardy and Nahon (1985)	Hemingway and Sposito (1988)
Corundum	-1587.4	-1580.41	-1582.2
Gibbsite	-1156.7	-1154.14	-1154.9
Boehmite	-921.0	-916.15	-915.9
Diaspore	-925.1	-912.70	-920.9

of the $Al(OH)_3$ minerals. Troland and Tardy (1987) concluded that the solubility of natural iron oxides, oxyhydroxides, and hydroxides is strongly influenced by particle size. Bloom and Weaver (1982) found that particle size does not appreciably influence the solubility of natural or synthetic gibbsites; however, the presence of reactive surface material or internal structural defects enhances the apparent solubility. These authors demonstrated that acid pretreatment reduces the solubility of commercially prepared gibbsite. They reported a log K_r value of 7.70 $\pm$ 0.02 for the acid-treated gibbsite sample C-730, in agreement with our value of 7.76 $\pm$ 0.14 for the acid-treated gibbsite sample C-730 in the current experiment.

Bloom and Weaver (1982) indicated that solution equilibrium for acid-treated gibbsite at a 1:20 (w/v) solid : solution ratio was achieved after 3 days from undersaturated initial conditions and after 19 days from supersaturated initial conditions. Kittrick (1980) found that apparent solution equilibrium with gibbsite was achieved in 4–6 days using a 1:0.6 to 1:0.8 (w/v) solid : solution ratio. This procedure generated a log K_r value of 7.98 $\pm$ 0.06 for untreated gibbsite C-730, which was identical to the log K_r value of 7.97 $\pm$ 0.05 for untreated gibbsite C-730 based on long-term solubility experiments (Kittrick, 1966). We used 1:1 to 1:1.6 (w/v) solid : solution ratios and reaction times of 15 to 49 days in the current experiment. Presumably, these reaction conditions permitted the attainment of unstable equilibrium in the corundum, gibbsite, boehmite, and diaspore systems. This assumption is supported by the correspondence of log K_r values found in the systems equilibrated from both undersaturated and supersaturated initial conditions, as well as agreement of the log K_r value for the acid-treated gibbsite sample with that of Bloom and Weaver (1982).

Table 4 compares the mean ΔG_f° values calculated using the data of the current experiment with the values cited in two recent compilations of thermochemical

data (Tardy and Nahon, 1985; Hemingway and Sposito, 1987). The experimental values are more negative by 1.8 to 12.4 kJ/mole than the corresponding compiled values. This observation suggests that corundum, boehmite, and diaspore behave like gibbsite, in that acid treatment reduces their apparent solubilities.

In summary, the relative thermodynamic stabilities of the four Al oxide minerals at 298 K, one atmosphere pressure, and water activity of unity are: corundum < gibbsite < boehmite < diaspore. Acid treatment of the minerals appears to reduce their apparent solubility. The prevalence of gibbsite relative to boehmite and diaspore in highly weathered soils and many bauxite deposits suggests that these geochemical environments are not at equilibrium or that other factors determined the relative stabilities of the minerals, such as water activity, temperature, particle size, and bulk chemical composition (Troland and Tardy, 1987). Furthermore, as indirectly illustrated by the current study and by Bloom and Weaver (1982), the solubilities of hydrous Al oxide minerals may be controlled by surface coatings which mask the influence of the bulk mineral phase. The physical and chemical properties of the reactive surface materials are poorly characterized and will be the focus of future research.

ACKNOWLEDGMENT

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