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SURFACE ENTHALPY OF BOEHMITE

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Abstract—The persistence of many seemingly metastable mineral assemblages in sediments and soils is commonly attributed to their sluggish transformation to the stable-phase assemblage. Although undoubtedly kinetics plays a major role, this study shows that thermodynamic factors, particularly surface energy, significantly influence the free energy. Enthalpies of formation of boehmite samples with variable surface area were derived using high-temperature oxide-melt calorimetry. The average surface enthalpy for all faces terminating boehmite particles was calculated at $+0.52 \pm 0.12$ J/m^2. This value represents the surface enthalpy for surfaces exposed to vacuum assuming that H_2O adsorbed on the surface of boehmite is loosely bound. These results show that the enthalpy of formation of boehmite may vary by ≤ 8 kJ/mol as a function of particle size. An overview of published values of surface energies of gibbsite, γ-Al_2O_3, corundum, and the results here indicates that the hydrated phases (boehmite, gibbsite) have lower surface energies than the anhydrous phases (corundum, γ-Al_2O_3). Lower surface energies allow the hydrated phases to maintain high surface area, *i.e.*, small particle size. Similar surface energies of boehmite and gibbsite suggest kinetic control favoring the crystallization of boehmite or gibbsite from aqueous solution. The enthalpy of formation of bulk boehmite from the elements was calculated at -994.0 ± 1.1 kJ/mol. Combining this result with the data in existing thermodynamic databases, we confirm that bulk boehmite is metastable with respect to bulk diaspore at ambient conditions.

Key Words—Boehmite, Enthalpy of Formation, Surface Enthalpy.

INTRODUCTION

Polymorphs of aluminum oxyhydroxide (boehmite, diaspore) and aluminum hydroxide (gibbsite, bayerite, nordstrandite) are common fine-grained constituents of soils, unconsolidated sediments, and sedimentary rocks. Their occurrence in nature is controlled by their thermodynamic properties and the kinetics involved in transformations. The equilibrium state of the system is dictated solely by the free energies of the solid phases and the aqueous phase and can be computed from existing thermodynamic data. However, agreement among published data is rare, rendering the calculation of phase diagrams difficult. The magnitude of Gibbs free energies of reactions among the Al-O-H phases is <15 kJ/mol (Robie and Hemingway, 1995). Therefore, even small discrepancies between published data may significantly alter the topology of the phase diagram. Moreover, the Gibbs free energies of these solids vary as a function of surface area and structural defects. These factors are rarely considered explicitly in either experimental thermodynamic studies or in the calculations of phase diagrams. The small magnitude of the free energy changes can make these factors important. Published data on thermodynamics of the Al-O-H system were critically evaluated by Anovitz *et al.* (1991) who concluded that diaspore is the stable phase at 298.15 K and 1 bar.

This study was prompted by an apparent contradiction between common occurrence of boehmite and gibbsite and the thermodynamic stability of diaspore. It is commonly believed that many mineral assemblages found in sediments and soils owe their occurrence to sluggish rates of transformation to the stable phase assemblage. Indeed, gibbsite and boehmite are the most common minerals of lateritic bauxites (Bardossy and Aleva, 1990). Traces of diaspore have been found in many locations but large quantities of this mineral are reported only from compacted and recrystallized bauxites. In soils, the main aluminum carriers in addition to clays are fine-grained gibbsite and allophane (Buol *et al.*, 1989). Furthermore, fine-grained boehmite is also an important industrial product used because of the relative ease of its synthesis and its ability to retain high surface area. Boehmite serves as a catalyst or precursor of transition metal-Al_2O_3 catalysts and catalyst supports. Anovitz *et al.* (1991) noted that hydromagnesite, anatase, Mg-calcite, and smectites can also persist in metastable equilibrium over geologic time. Although undoubtedly kinetics plays a major role, the present work shows that metastable mineral assemblages of high surface area can be stabilized in a thermodynamic sense, *i.e.*, by reducing the magnitude of Gibbs free energy of reaction between metastable and stable phases. Stabilization can be achieved by decreasing the particle size of the reactants and products, *i.e.*, adding surface energy to the system when reactants and products have different surface energies. The inclusion of the surface energy term can lower the magnitude of free energy, ΔG, of a reaction or, in some cases, even change its sign. Such effects have been previously demonstrated for Al_2O_3 (McHale *et al.*, 1997a), TiO_2 (Gribb and Banfield, 1997), and Al_2SiO_5 (Penn *et al.*, 1999).

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This work addresses the effect of surface area on the thermodynamic stability of boehmite by experimental determination of the surface enthalpy and the enthalpy of formation of bulk boehmite of nominal composition AlOOH. The results are used to discuss the stability of phases in the Al_2O_3-H_2O system under low-temperature conditions. The surface enthalpies of boehmite, gibbsite, γ-Al_2O_3, and corundum are compared to each other and to values for other materials in terms of the probable structure of their hydrated surfaces.

EXPERIMENTAL METHODS

Boehmite samples used in this study were commercial products obtained from ALCAN Chemicals Europe, Uxbridge, England (sample ALCAN) and Condea Chemie, GmbH, Hamburg, Germany (samples PURAL). In addition to boehmite samples, α-Al_2O_3 (Alfa Aesar, Ward Hill, Massachusetts, USA, 99.997% metals basis) was used in the calorimetric experiments.

A Scintag PAD V (CuKα radiation) diffractometer with secondary graphite monochromator was used to check phase purity. Prior to all experiments, the boehmite samples were maintained for 3 d in vacuum at room temperature and thereafter stored in a glovebox with an argon atmosphere with <1 ppm of water. Specific surface area of the samples was determined using the Brunauer-Emmet-Teller (BET) method (Brunauer *et al.*, 1938) with a static Micromeritics Gemini 2360 BET instrument. Measurements were performed in a liquid nitrogen bath with N_2 as the adsorbate gas. A correction for free space was obtained with helium gas. Fifteen data points were collected in the BET range (0.05–0.35 P/P_0) for each measurement. The determination of surface area is based in converting the raw data (volume of the adsorbed gas *versus* reduced pressure) to variables that construct the BET equation, defining a linear trend. The correlation coefficient of the fit for the high surface area samples (PURAL) was >0.9999; the correlation coefficient for the low surface area sample (ALCAN) was >0.96, reflecting the small volume of adsorbed gas. The individual measurements deviated <3% from the mean, except for the low surface area sample (ALCAN) with deviations of ≤90%, suggesting good precision of the method only at moderate and high surface areas. Accuracy of the measurement is more difficult to assess. Kaolinite reference material was used as supplied by the manufacturer before each set of measurements to check proper operation of the instrument. Several laboratories chosen by the manufacturer degassed the reference material by heating at 200°C for 0.5–2 h and analyzed this material in the range 0.05–0.20 P/P_0 with N_2 as the adsorbate gas. The reference material was treated in an identical way as the boehmite samples. The surface area values we obtained for kaolinite were mostly lower than the surface area stated by the manufacturer by 5–10%, with few measurements lower by ~20% or higher by 5%. Repeated measurements on the same kaolinite powder produced a gradual decrease in the measured value. After recognizing this effect, we did not use the same boehmite powder for more than two measurements. Considering these factors, we estimate the accuracy of the technique as ±10% which is in agreement with estimates of Gregg and Sing (1982).

Total water content of the boehmite samples was determined from the weight loss after firing pellets at 1773 K for 12 h. The 'excess' water content (x in $AlOOH \cdot xH_2O$) was calculated by subtraction of the total water content from the stoichiometric water content of AlOOH (15.02 wt.%). Weights were determined on a Mettler semimicrobalance with a precision of ±0.01 mg as stated by the manufacturer. The pellets (~50 mg) were pressed and weighed in argon and fired in corundum crucibles in air. In several cases, the phase composition of the fired material was determined by X-ray diffraction (XRD) and found to be well-crystalline coarse corundum. Because the amount of water sorbed on the surface of coarse corundum is below the detection limit of the microbalance, the fired material was weighed in air. Repeated annealing of empty corundum crucibles (22 experiments) allowed the determination of the accuracy of the method. There is an average ±0.03-mg error associated with this procedure, probably owing to weighing errors and contamination of the crucibles during handling. The errors reported in Table 1 are two standard deviations of the mean.

Aluminum oxide for calorimetry was heated at 1773 K for 12 h in a platinum crucible. There was no weight loss on firing the corundum powder for an additional 12 h at 1773 K.

High-temperature drop solution calorimetry in molten lead borate ($2PbO \cdot B_2O_3$) solvent at 975 K was performed in a twin Calvet-type isoperibol calorimeter (Navrotsky, 1997). The calibration factor was calculated using the heat content of corundum (National Bureau of Standards, SRM 720, NBS Certificate, 1982). To determine enthalpy of formation (ΔH°_f) of boehmite, corundum and boehmite pellets were dropped into molten solvent. The boehmite samples were pressed into pellets and weighed in argon. The heat effect measured by the calorimeter was the sum of the heat content of the pellet, heat of solution of α-Al_2O_3 and, in the case of boehmite, heat of the boehmite to corundum + water transformation. The calorimeter assembly was flushed with 90 cm^3/min argon to remove the evolved water (Navrotsky *et al.*, 1994).

The slope and intercept of the line defined by our experimental data (enthalpy of drop solution *versus* surface area) have a physical meaning and these data are the primary result of this work. There is no simple formula for error estimation on these quantities. We

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Table 1. Surface area, enthalpy of drop solution (ΔH_{dsol}), excess water content, and derived enthalpy of formation of the samples from elements (ΔH°_f) at standard temperature and pressure.

Sample	Surface area (m^2/g)	ΔH_{dsol} (kJ/mol)	Excess water (mol)	ΔH°_f (kJ/mol)
corundum	<1	108.5 ± 0.7 (20)	—	—
boehmite:				
ALCAN	1.5[1] ± 1.4[2] (3)[3]	105.9 ± 0.7 (18)	0.069 ± 0.003 (13)	−993.2 ± 1.1
PURAL 400	26.7 ± 0.6 (3)	103.9 ± 0.5 (15)	0.025 ± 0.003 (12)	−994.2 ± 0.9
PURAL NF	127 ± 2 (4)	105.0 ± 0.3 (18)	0.104 ± 0.003 (14)	−989.8 ± 0.8
PURAL SB1	274 ± 4 (3)	104.1 ± 0.4 (22)	0.154 ± 0.002 (13)	−985.5 ± 0.9

[1] Average.
[2] Two standard deviations of the mean.
[3] Number of measurements.

used the bootstrap method (Efron and Tibshirani, 1993) based on a random sampling of the data sets with replacement. The algorithm repeatedly selected a bootstrap sample from the measured enthalpies of drop solution and water content of the boehmite samples. To account for the inaccuracy of the BET measurements, the surface area data of the bootstrap samples were generated as a uniform deviate around the measured mean, with a spread of 10% for the high surface area samples (PURAL) and 90% for the low surface area sample (ALCAN).

RESULTS

Table 1 presents data on composition, surface area, and enthalpy of drop solution of the boehmite (ΔH_1) and corundum (ΔH_3) samples. The enthalpy of formation of the boehmite samples from the elements (ΔH_7, Table 2) was calculated from the thermochemical cycle given in Table 2. The relationship of enthalpy of formation of boehmite samples from oxides (ΔH_6 in Table 2) and their surface area (in m^2/mol) is shown in Figure 1. The surface enthalpy of boehmite is equal to the slope of the best-fit line through the data and is equal to $+0.52 \pm 0.12$ J/m^2. This value represents an average surface enthalpy for all faces terminating the boehmite particles. Our data show that the enthalpy of formation of boehmite may vary by ≤8 kJ/mol as a function of particle size for the range of particle sizes used in these experiments. The enthalpy change for reaction (ΔH_{rxn}) between boehmite and other Al-O-H phases therefore also varies significantly as a function of the particle size of the solids. Variations of ΔH_{rxn} between boehmite and corundum are plotted in Figure 2. The enthalpy of formation of bulk boehmite of nominal composition AlOOH is equal to the intercept of the fitted line with the vertical axis (hypothetical surface area of 0 m^2/mol) and is calculated at -994.0 ± 1.1 kJ/mol.

DISCUSSION

Excess water in boehmite

The boehmite samples contain H_2O and OH^- in several forms, all of which must be considered in the

Table 2. Thermochemical cycle for calculation of the enthalpy of formation of boehmite from oxides (ΔH_6) and elements (ΔH_7).

	Reaction number and reaction	Enthalpy
(1)	$AlOOH(cr, 298\ K) + xH_2O(1, 298\ K) = \frac{1}{2}Al_2O_3(sol, 975\ K) + (\frac{1}{2} + x)H_2O(g, 975\ K)$[1]	$\Delta H_1 = \Delta H_{dsol}$ of boehmite[2]
(2)	$H_2O(1,298\ K) = H_2O(g, 975\ K)$	$\Delta H_2 = H^\circ_{973(gas)} - H^\circ_{298(liquid)} = 69.0$ kJ/mol[3]
(3)	$Al_2O_3(cr, 298\ K) = Al_2O_3(sol, 975\ K)$	$\Delta H_3 = \Delta H_{dsol}$ of corundum[2]
(4)	$2Al(cr, 298\ K) + 1.5O_2(g, 298\ K) = Al_2O_3(cr; 298\ K)$	$\Delta H_4 = \Delta H^\circ_f$ of corundum $= -1675.7 \pm 1.3$ kJ/mol[4]
(5)	$H_2(g, 298\ K) + \frac{1}{2}O_2(g, 298\ K) = H_2O(1, 298\ K)$	$\Delta H_5 = \Delta H^\circ_f$ of water $= -285.8 \pm 0.1$ kJ/mol[4]
(6)	$\frac{1}{2}Al_2O_3(cr, 298\ K) + \frac{1}{2}H_2O(1,298\ K) = AlOOH(cr, 298\ K)$	$\Delta H_6 = -\Delta H_1 + (\frac{1}{2} + x)\Delta H_2 + \frac{1}{2}\Delta H_3$
(7)	$Al(cr, 298\ K) + O_2(g, 298\ K) + \frac{1}{2}H_2(g, 298\ K) = AlOOH(cr, 298\ K)$	$\Delta H_7 = -\Delta H_1 + (\frac{1}{2} + x)\Delta H_2 + \frac{1}{2}\Delta H_3 + \frac{1}{2}\Delta H_4 + \frac{1}{2}\Delta H_5$

[1] cr = crystalline; l = liquid; g = gas; sol = solution in lead borate; x = excess water content (Table 1).
[2] This study; values in Table 1; dsol = drop solution.
[3] Calculated from Robie *et al.* (1978).
[4] Robie and Hemingway (1995).

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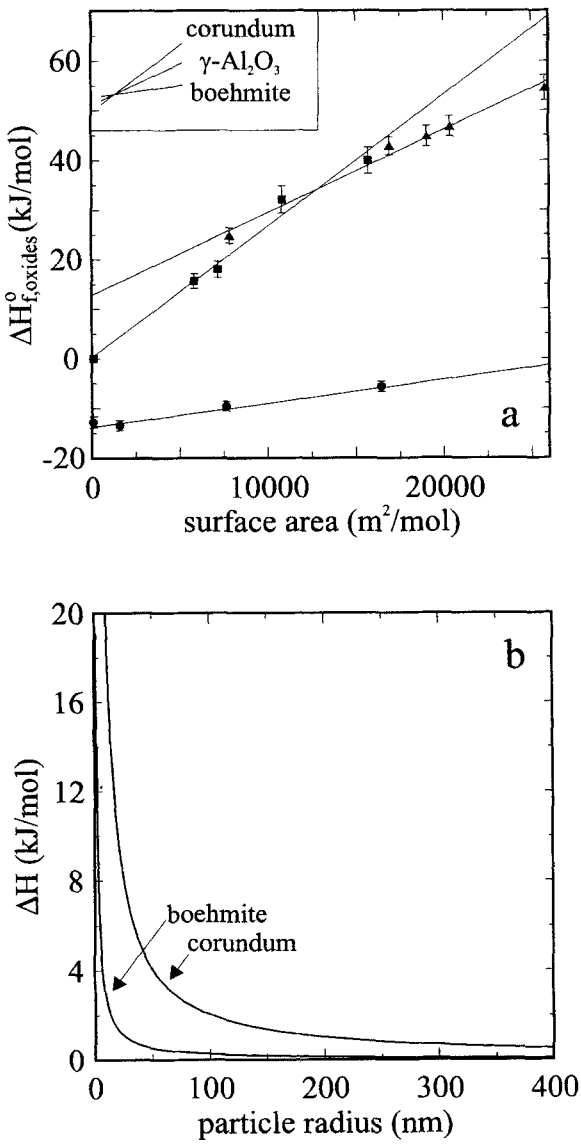


Figure 1. (a) Enthalpy of formation from oxides ($\Delta H^{\circ}_{f,oxides}$) (coarse α-Al_2O_3 or coarse $\frac{1}{2}\alpha$-Al_2O_3 + $\frac{1}{2}H_2O$) as a function of surface area for boehmite (circles), γ-Al_2O_3 (triangles), and corundum (squares). Surface enthalpy is equal to the slopes of the lines, shown for easier comparison in the inset. Data for anhydrous oxides from McHale *et al.* (1997a). (b) Surface enthalpy as a function of particle size of corundum and boehmite, assuming spherical shape of particles.

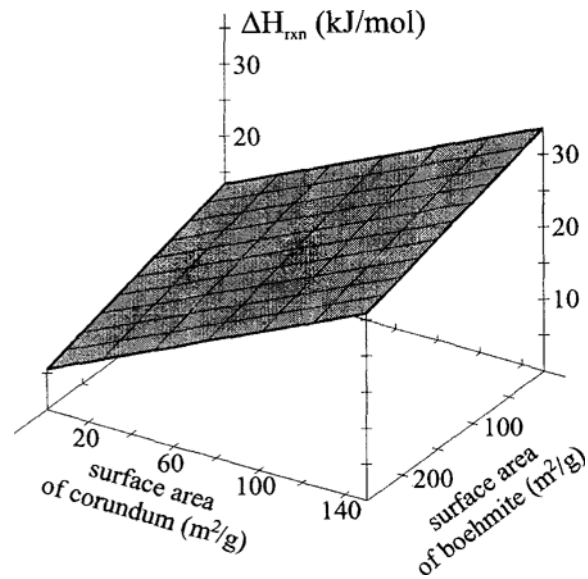


Figure 2. Enthalpy change for the reaction (ΔH_{rxn}) boehmite → corundum + water as a function of surface area of boehmite and corundum. Surface enthalpy of corundum from McHale *et al.* (1997a).

thermochemical cycle, with the largest portion represented by structural OH groups. The enthalpy of removal of this OH from boehmite at 298.15 K is equal to the enthalpy of transformation of boehmite to corundum + water at the same temperature. In addition to the structural OH groups, each sample contained excess water (Table 1) which occurs in different locations. The surfaces of boehmite, as all ionic oxides, are covered by chemisorbed and physisorbed H_2O and OH^- molecules. Bellotto *et al.* (1998) suggested that all excess water in boehmite is sorbed on the surface of the particles. Baker and Pearson (1974) presented XRD and nuclear magnetic resonance evidence supporting this. On the other hand, Tsukada *et al.* (1999) reported that excess water also occurs within the structure of boehmite. They assumed that the weak bonding between the $Al(O,OH)_6$ sheets, facilitated by hydrogen bonds, allows intercalation by H_2O molecules. Tettenhorst and Hofmann (1980) determined that the intercalated H_2O, if present, is either randomly or regularly arranged between the $Al(O,OH)_6$ sheets. Using transmission electron microscopy, Anovitz *et al.* (1999) found a minor amount of thin plate-like inclusions in their boehmite sample, synthesized from gibbsite. The inclusions were tentatively identified as gibbsite that could account for excess water in the sample. We found no evidence of gibbsite in our samples although the XRD characterization used in this study may not be sufficiently sensitive to detect a small amount (<3%) of an impurity. Desorption enthalpy and enthalpy of removal of intercalated H_2O should be included in the thermochemical cycle (Table 2) via an additional equation [see Table 2 for Equations (1)–(7)]:

$$AlOOH{\cdot}xH_2O\ (crystal,298\ K) = AlOOH\ (crystal,298\ K) + xH_2O\ (liquid,298\ K). \quad (8)$$

Because we know neither these enthalpies nor the position of excess water in the samples, we set enthalpy of water removal, ΔH_8, to 0 kJ/mol, implying

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Table 3. Compilation of published measured and calculated surface internal energies (ΔE), enthalpies (ΔH), and free energies (ΔG) of the Al-O-H phases.

Phase	Surface thermodynamic function (J/m²)	Reference	Method
corundum	ΔE = 2.57–3.27	Tasker, 1984	static lattice calculation
	ΔE = 2.03–2.50	Mackrodt *et al.*, 1987	MD simulation
	ΔE = 4.89–5.56	Causa *et al.*, 1989	*ab initio* calculation
	ΔE = 2.04–8.39	Blonski and Garofalini, 1993	MD simulation
	ΔH = 2.64	McHale *et al.*, 1997a	high-temperature calorimetry
γ-Al_2O_3	ΔE = 0.79–2.54	Blonski and Garofalini, 1993	MD simulation
	ΔH = 1.66	McHale *et al.*, 1997a	high-temperature calorimetry
gibbsite	ΔG = 0.15 ± 0.02	Smith and Hem, 1972	solubility in aqueous solution
	ΔG = 0.66	Apps *et al.*, 1988	solubility in aqueous solution
	ΔE = 0.22–0.75	Fleming *et al.*, 2000	*ab initio* calculation
boehmite	ΔH = 0.52 ± 0.12	this work	high-temperature calorimetry

that the excess water behaves energetically as bulk liquid water. This is probably a reasonable approximation but it potentially introduces a small systematic error. The surface enthalpy determined in this study decreases by 0.05 J/m² per increment of 10 kJ/mol in ΔH_8. The enthalpy of water removal, ΔH_8, is assumed equal to or smaller than the enthalpy of bulk dehydroxylation (~30 kJ per mol of H_2O). Taking a non-zero value for ΔH_8 does not lead to a significant change of the surface-enthalpy value of +0.52 ± 0.12 J/m². After applying the correction for the adsorbed water by choosing a value for ΔH_8, the calculated value represents the surface enthalpy of a surface exposed to vacuum. The error relating to the neglect of desorption enthalpies was shown to be significant in the case of anhydrous Al oxides (corundum, γ-Al_2O_3) (McHale *et al.*, 1997a, 1997b). The difference between desorption enthalpies of corundum and boehmite is related to bond strength between surface species and hydroxyl groups or water. At the surface of corundum, the most strongly bound is the first monolayer of hydroxyl groups, whereas the surface of boehmite is hydroxylated by the structural OH groups. The lack of a strongly bound first monolayer of OH in boehmite (or hydroxide surfaces, in general) accounts for smaller adsorption enthalpies. For boehmite, weak bonding between the structural sheets causes preferable exposure of the (010) face. The bonds broken between the sheets are expected to be weaker than the hydroxylated dangling bonds at the corundum surface, further amplifying the difference between the adsorption enthalpies.

Surface enthalpies of other Al-O-H phases

We are not aware of any other determination of surface enthalpy or energy of boehmite. However, surface thermodynamic properties of some Al-O-H phases have been determined (Table 3). McHale *et al.* (1997a) measured the surface enthalpy of α-Al_2O_3 and γ-Al_2O_3 by the techniques employed here (Figure 1a). The surface area is expressed in units of m²/mol instead of m²/g to allow comparison between surface enthalpies of phases with different composition (Al_2O_3, AlOOH). Figure 1b shows the magnitude of enthalpy increase due to increasing surface area as a function of particle size, assuming spherical shapes of the particles. The surface enthalpies of the three phases studied by high-temperature calorimetry are compared in the inset of Figure 1a. Note that the surface enthalpy decreases in order of corundum > γ-Al_2O_3 > boehmite. Apps *et al.* (1989) estimated the surface free energy of gibbsite (Table 3) from the solubility experiments of Packter (1979). Packter (1979) synthesized samples by aging amorphous Al-rich precipitates for 8–1000 h and these samples were described as pure gibbsite with a variable surface area. In contrast with the results of Packter (1979), our syntheses, as well as experiments of others (McHardy and Thomson, 1971; Chesworth, 1972) showed that fine-grained gibbsite is usually associated with fine-grained boehmite. In addition, Packter (1979) measured the length of the hexagonal gibbsite platelets and Apps *et al.* (1989) used these data to calculate the surface area. Such calculations carry an implicit assumption, which may not be correct, that each particle has the shape of a hexagonal prism and acts as one coherently diffracting domain. Furthermore, Smith and Hem (1972) derived the surface energy of gibbsite (Table 3) assuming that polynuclear aluminum species in solution are structurally similar to crystalline gibbsite. Bloom and Weaver (1982), Peryea and Kittrick (1988), and Wesolowski and Palmer (1994) noted that the solubility of Al oxides, oxyhydroxides, and hydroxides decreases after acid treatment. Wesolowski and Palmer (1994) found a difference of 0.4 log units in solubility of gibbsite between the studies listed above and earlier work (May *et al.*, 1979) in which no acid pre-treatment was used. This difference, which amounts to ~2.5 kJ/mol, is explained by removal of fine particles during acid pretreatment and is consistent with the surface-energy estimate for gibbsite (Apps *et al.*, 1989).

In addition to experimental data, theoretical computational methods were applied also to relaxed surfaces of aluminum oxides and gibbsite (Table 3). Blon-

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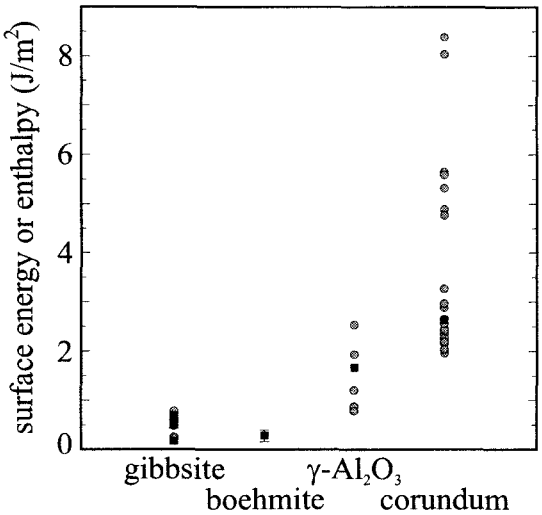


Figure 3. Results of experimental measurements (solid squares) and computations (gray circles) of surface energies or enthalpies of gibbsite, boehmite, γ-Al_2O_3, and corundum. Numerical values, techniques, and reference given in Table 3.

ski and Garofalini (1993) compared the surface energy of two Al-O-H solids. They concluded that γ-Al_2O_3 has a lower surface energy than corundum. The results of McHale *et al.* (1997a) (surface enthalpies from experiments) and Blonski and Garofalini (1993) (surface internal energies) are comparable. For solids, surface energy (ΔE) and surface enthalpy (ΔH) terms can be equated at standard pressure because the $P\Delta V$ term (P = pressure, ΔV = change in volume) is negligible. It is difficult to evaluate the reliability of the results of theoretical computations because of the paucity of detail on the computational procedure and lack of error estimation. Blonski and Garofalini (1993) used a Born-Mayer-Huggins potential modified from previous studies of aluminosilicate glasses to obtain reasonable values of pressure in their simulation. They also adjusted the lattice parameter of γ-Al_2O_3. Mackrodt *et al.* (1987) used a potential function previously shown to satisfactorily predict bulk properties of α-Al_2O_3. Owing to an expensive *ab initio* computational procedure, Causa *et al.* (1989) used only a thin slab of α-Al_2O_3 structure to simulate the surface properties. They noted that convergence of the results with respect to slab thickness was achieved for the basal (0001) face but not for the prismatic ($10\bar{1}0$) face. The agreement of the computational results, despite the great variability of approaches, suggests that the values listed in Table 3 are reasonable.

The results of experimental studies and theoretical calculations are shown in Figure 3. Because of the difficulties in assessing the individual data sets (Table 3), the figure is an uncritical collection of data for different thermodynamic functions (ΔE, ΔH, ΔG) obtained by fundamentally different techniques. Nevertheless, the data show that the hydrated phases (gibbsite, boehmite) have lower surface energies that the anhydrous oxides (corundum, γ-Al_2O_3). In a first approximation, surface energy of an ionic solid will be proportional to the charges of the ions within the structure (Tosi, 1964). Thus, replacing the oxygen anions with hydroxyls will lower the surface energy, in agreement with experiment.

The interaction of metal oxide surfaces with water gives additional information about their relative surface energies. A molecular dynamics simulation (Haas *et al.*, 1998) has shown that a dry α-Al_2O_3 surface exposed to H_2O molecules will adopt an $Al(OH)_3$-like terminal configuration, indicating that the dry surface is metastable with respect to the hydrated surface, in agreement with the experimental results (Table 3). Similarly, Dyer *et al.* (1993) used infrared and Raman spectroscopy and XRD to show that the hydrated surface of γ-Al_2O_3 attains a bayerite-like configuration whereas bulk γ-Al_2O_3 remains unreacted. Lindan *et al.* (1996) showed that H_2O molecules dissociate on the surface of TiO_2 and SnO_2. However, dissociation of H_2O on MgO surfaces requires the presence of defects on the surface (Langel and Parrinello, 1995). More experimental and theoretical work is needed to understand how surfaces interact with water and the relative stability of surfaces.

A striking result of this study is that boehmite and gibbsite exhibit surface energies/enthalpies that are relatively small (<1.0 J/m^2) and similar to one another despite the profound differences in surface structures. Gibbsite consists of hexameric rings of protonated, edge-sharing AlO_6 octahedra. These six-membered rings are similar to those in other aluminum hydroxide phases, such as bayerite, and to the aluminous basal surfaces of dioctahedral aluminosilicate clays, such as kaolinite. These minerals have planar habit in soils, with the basal plane exposed. The basal gibbsite surfaces expose μ_2-OH groups, where the μ_i sites refer to ligands that bridge "i" cations. Boehmite, in contrast, has a surface chemistry that is more complicated than that of gibbsite. The bulk structure of boehmite consists of layers of staggered edge- and corner-sharing AlO_6 octahedra and, on an area basis, there are equal numbers of μ_2-OH bridges and μ_4-oxo groups on the basal planes of boehmite. The edges of boehmite crystallites expose μ_3-oxo groups and coordinated H_2O molecules or coordinated hydroxyl groups. The edges of planar crystallites of boehmite and gibbsite, of course, expose terminal H_2O molecules and terminal hydroxyl groups. The similarity of surface energy/enthalpy of gibbsite and boehmite indicates that the hydroxyl bridges and coordinated H_2O molecules have a disproportionately large effect on the surface energies. The μ_4-oxo groups on the surface of boehmite have apparently little influence on the energetics, despite their relative high surface concentration on the basal

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planes. The exposed hydroxyl groups and H_2O molecules dramatically lower the surface free energies of aluminum hydroxides relative to oxides.

We speculate that other soil aluminum oxyhydroxide phases, diaspore, bayerite, and nordstrandite also exhibit low surface free energies, similar to those for gibbsite and boehmite. The assignment of the important functional groups of diaspore is difficult because the surfaces are not planar. The structure, however, exposes only oxygen atoms and hydroxyl groups that have a lower number of coordinated aluminum atoms than boehmite. Hence, we estimate that the surface energy for diaspore is also 0.2–0.8 J/m^2.

Aluminum hydroxide minerals probably crystallize by accretion of metastable dissolved polyoxocations (Fu *et al.*, 1991; Bradley *et al.*, 1993; Bradley and Hanna, 1994) and not from *de novo* nucleation from dissolved monomers in solution. Using spectroscopy, metastable dimers, trimers, and multimeric polyoxocations have been identified in solution. The most familiar polyoxocation is the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$(aq) complex with the ϵ-Keggin structure. Another polyoxocation of aluminum was crystallized from solution that is relatively flat and clay-like, with the stoichiometry: $Al_{13}(OH)_{24}(H_2O)_{24}^{15+}$(aq) (Seichter *et al.*, 1998). The metastability of both clusters is a manifestation of the low surface energies of hydrous aluminum hydroxide structures. These clusters have 13 aluminum cations, and condense into larger molecules at a slow rate. We hypothesize that the type of aluminum hydroxide mineral present in a given soil or sediment is kinetically controlled by the structure of the precursor cluster. This speculation is supported by the small and nearly equal surface energies of the aluminum hydroxide phases.

Enthalpy of formation of boehmite

Apps *et al.* (1989) estimated the enthalpy (ΔH°_f) (−995.3 kJ/mol) and entropy of formation of boehmite at standard temperature and pressure by iterative regression of experimental data obtained from diaspore, boehmite, and gibbsite. Hemingway *et al.* (1991) estimated ΔH°_f of boehmite (−996.4 ± 2.2 kJ/mol) from their measurement of third-law entropy (S^o) and an estimate of ΔG°_f from the solubility measurements of Russell *et al.* (1955). The first experimental determination of ΔH°_f of boehmite was performed by McHale *et al.* (1997b) by high-temperature oxide-melt calorimetry. Their measurements, without any excess water correction applied, yielded −995.4 ± 1.6 kJ/mol. Our estimate (−994.0 ± 1.1 kJ/mol) is less negative than ΔH°_f adopted by Anovitz *et al.* (1991) (−996.4 ± 0.9 kJ/mol, determined from their ΔG°_f and S°) in calculation of the phase diagram of the Al-O-H system. Our estimate makes boehmite even more unstable in enthalpy with respect to diaspore (by 2.4 kJ/mol) and does not modify the topology of the proposed phase diagram of Anovitz *et al.* (1991). Hence, bulk boehmite is metastable with respect to bulk diaspore at ambient conditions.

Surface energy in natural assemblages

The present results emphasize the complexity of assigning thermodynamic stability or instability to low-temperature phase assemblages. One mineral, occurring both in the detrital and authigenic fraction of a sediment, may be simultaneously stable and metastable, depending on particle size. Obviously, this work does not claim that a decrease in particle size will always convert metastable phases into stable phases. Instead, a decrease in particle size may further reduce the driving force for the transformation to a stable phase assemblages. In some cases, however, the change in sign of ΔG of a reaction may occur as a result of variable particle size of reactants and products (*e.g.*, McHale *et al.*, 1997b; Penn *et al.*, 1999). Low surface energy does not preclude Ostwald ripening or coalescence of ultrafine particles, and the persistence of such particles cannot be explained solely by thermodynamic analysis. Such particles are metastable with respect to coarsening, followed by phase transformation. These processes are kinetically controlled.

The available thermodynamic data show that ΔG of the diaspore = boehmite transformation is 2–6 kJ/mol, depending on the reference. Surface energy of diaspore that is larger than the surface energy of boehmite by a few tenths of J/m^2 is sufficient to convert fine-grained boehmite to a stable phase with respect to fine-grained diaspore. The results also suggest that relatively low surface energies (enthalpies) allow hydrated phases to attain high surface areas (small particle size). The destabilization of fine-grained anhydrous phases with respect to hydrated phases (gibbsite and boehmite *versus* corundum) is demonstrated by observations from other similar systems, especially Fe-O-H (ferrihydrite, lepidocrocite, goethite *versus* hematite). Ferric oxide and oxyhydroxide samples are presently being studied to determine surface enthalpies and to compare surface properties to Al-O-H solids.

The influence of surface energy on the relative stability of phases is anticipated also in other common natural systems with substances having surface areas of >100 m^2/g. Mineral assemblages most sensitive to differences between surface energies of reactants and products are those where ΔG values of the reactions are small (<15 kJ/mol) in magnitude, including Fe-O-H and Mn-O-H systems, clays, and zeolites. We expect that the difference in surface energies of polymorphs or phases with similar composition exposed to aqueous media is smaller than the difference between the same surfaces exposed in vacuum. The influence of defects on the ΔG of the solids and variations of chemical

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potential of water further complicates thermodynamic analysis.

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