

AQUEOUS SOLUBILITY STUDIES OF HIGH-ALUMINA AND CLAY MINERALS

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ABSTRACT

Solubility constants and standard free energies of formation for various high-alumina minerals and clay minerals were calculated from data on concentrations of ions dissolved in aqueous solution from those minerals. That equilibrium was reached by the solutions in contact with clay minerals was shown by the apparent restoration of clay crystal surfaces which had been mechanically disrupted—hence crystallization accompanied dissolution in the same system.

Our best values for standard free energies of formation are:

Dickite	— 904.4 ± 0.7 kcal/F.W.
Kaolinite (in ball clay)	— 904.0 ± 0.2 kcal/F.W.
“Fire clay mineral”	— 900 to 904 (variable)
Halloysite	— 899 ± 1.0 kcal/F.W.
Endellite	— 902.3 ± 0.7 kcal/Al ₂ Si ₂ O ₅ (OH) ₄
Montmorillonite (Cheto)	— 1274.4 ± 0.6 kcal/F.W.
Montmorillonite (Clay Spur)	— 1270 ± 1.2 kcal/F.W.
Gibbsite	— 550.3 ± 0.4 kcal/Al ₂ O ₃ · 3H ₂ O etc.
Boehmite	— 435.2 ± 0.5 kcal/Al ₂ O ₃ · H ₂ O
Diaspore	— 437.2 ± 0.8 kcal/Al ₂ O ₃ · H ₂ O
Pyrophyllite	— 1258.7 ± 0.8 kcal/F.W.
Muscovite	— 1327 (only 1 sample run)

INTRODUCTION

This study is concerned with the dissolution of high-alumina minerals and clay minerals shaken in distilled water at room temperature for periods from 3 to 1000 days. It included three objectives: (1) to determine the products of the aqueous dissolution of high alumina and clay minerals, (2) to determine solubility constants (K_s) of the minerals, and (3) to calculate standard free energies of formation (ΔF_f°) for the various minerals from the analytical data of the aqueous solutions.

LABORATORY PROCEDURE

Prior to dissolution in double-distilled water, mineral samples were disaggregated by three procedures. The preferred method, which was by simple slaking of the clay during agitation in water, is least destructive of the original clay crystals and yields dissolution data

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that are most representative of the clay. Some clay crystals were forcibly separated one from the other by stirring in a blender, by crushing in a steel mortar with slight grinding, wet grinding in a mechanical mortar, and impact crushing in a ball mill. Other clays, such as the flint clays, were reduced by mechanical means to clay-size aggregates of still finer clay crystals. Many of the samples were size fractionated at two microns equivalent settling diameter, but Keokuk-geode kaolinite was separated into fractions of four sizes. Other samples were "bulk," in which no attempt was made to fractionate or "purify" a particular mineral. All samples were washed in double-distilled water after disaggregation.

Clean polyethylene utensils were used during dissolution and presumptive equilibration of the clays in water (equilibration, as used herein, refers to the attempt to establish equilibrium between the solid and aqueous phase). Equilibration times ranged from 3 to over 1,000 days with periodic agitation on a reciprocating shaker at about one or two cycles per second.

After equilibration, a 100-ml aliquot of solution was centrifuged longer than the time necessary to achieve optical clarity and then analyzed. If the total amount of equilibrated solution was about 100 ml, an additional 100 ml of double-distilled water was returned to the dissolution bottle after the removal of each sample aliquot. If about 500 ml of water was equilibrated with the mineral sample, no "fresh" water was added after removal of each aliquot. Each successive aliquot was therefore similar to the preceding one, except that the effective equilibration time was longer.

The hydrogen ion activity was measured with glass-electrode pH meters. The concentration of aluminum was determined fluorimetrically (Goon, 1953). Silicon was determined as monomeric silicic acid, using the method of "reduced silicomolybdate complex" (Shapiro and Brannock, 1952). Sodium and potassium were determined by flame emission. Calcium and magnesium were determined either spectrographically by the porous cup method (Feldman, 1949) or by atomic absorption. A series of standards, which covered the range of expected concentrations, was used for each analytical procedure with every batch of solutions that were analyzed.

It is essential that the colloidal clay be separated as completely as possible from the solution before it is analyzed. The filtration method was rejected so as to eliminate the possibility of addition or loss of ions to a filter medium. Centrifuging at 2000 rpm for 8 hours in an International Size 2 centrifuge was usually sufficient to yield an optically clear liquid. To evaluate the effects of suspended colloidal clay on the analytical results, a standard preparation of Beavers Bend illite was divided and processed three ways: (1) as a turbid suspension shaken prior to analysis, (2) standing and settling for 30 minutes which reduced the liquid to heavy opalescence, and (3) centrifuging to optical clarity. Analytical results are shown in Table 1. Greatest difference occurs after only preliminary settling, (actually more than was expected) but all samples were centrifuged to adequate-plus times.

Precision achieved in processing and analysis is illustrated by three runs on San Juanito dickite, of which replicate 100-ml solutions were centrifuged simultaneously in separate tubes and then analyzed, Table 2. The largest deviation in pK_{s2} is 0.41.

The analytical data on the 311 analyses reported herein are expressed as the negative logarithm of the activities, or p values, Table 3.¹ The equilibration time of each solution with a particular mineral is given in days. Solubility constants (K_s) are calculated from the activities of the dissolved ions, and are used to compute the change in free energy of reaction (ΔF_R°) that is necessary in calculating the free energy of formation (ΔF_f°) of the mineral.

¹ Table 3 has been deposited as Document No. 9818 with the American Documentation Institute, Auxiliary Publications Department, Photoduplication Service, Library of Congress, Washington, 25, D. C. Copies may be secured by citing the document number and remitting in advance \$1.25 for photoprints or \$1.25 for 35 mm microfilm.

TABLE 1. EFFECTS OF COLLOIDAL PARTICLES ON CHEMICAL ANALYSIS
PPM GIVEN BELOW (*p*) VALUES

	Beavers Bend (1) (Slurry)	Beavers Bend (2) (Settled)	Beavers Bend (3) (Centrifuged)
<i>p</i> K	2.59 (110.0)	4.12 (3.04)	4.92 (.48)
<i>p</i> Na	4.05 (2.22)	4.41 (.92)	4.41 (.92)
<i>p</i> Ca	3.87 (7.2)	4.93 (.50)	4.75 (.77)
<i>p</i> Mg	2.90 (41.1)	4.22 (1.57)	4.21 (1.62)
<i>p</i> Si	3.56 (7.8)	3.66 (6.2)	3.75 (4.95)
<i>p</i> Al	4.51 (.90)	5.65 (.06)	6.10 (.022)
<i>p</i> H	7.03	6.90	7.10

Minor adjustments or corrections to the K_s were made when the pH of the solution was near the isoelectric point (pH 6.70). As the K_s assumes only one type of aluminum ion to be present, either $\text{Al}(\text{OH})_2^+$ or $\text{Al}(\text{OH})_4^-$, a correction is necessary to discriminate the ions of a particular type from the total ions present. At the isoelectric point there is an equal mixture of both $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_4^-$. Thus, there is twice as much aluminum as should be attributed to each form. Since the logarithm of 2.0 is 0.30, a correction of 0.30 is made for each mole of aluminum in the dissolution equation. All such corrections decrease the value of the solubility constant.

Ionic strengths of the analyzed solutions ranged from 0.000007 in the gibbsite sample to 0.0065 in an acidified solution of Keokuk kaolinite, which contained a small amount of microscopic dolomite. Ionic strengths were most common in the range 10^{-4} to 10^{-5} .

BASIC ASSUMPTIONS AND PRINCIPLES FOR THERMODYNAMIC CALCULATIONS

Calculation of a K_s requires: (1) a measure of the activities of the component ions in solution, (2) the chemical equation for the dissolution reaction, and (3) the attainment of equilibrium, or near-equilibrium, between the solid and solution so that calculated solubility constants have validity. By inserting the value of the K_s in the Nernst equation, $\Delta F_R^\circ = -RT \ln K$, the free energy of the reaction (ΔF_R°) can be calculated.

Lastly, the free energy of formation (ΔF_f°) of substance undergoing dissolution can be calculated by adding algebraically the ΔF_R° and the ΔF_f° of the products undergoing dissolution and any other reactants

TABLE 2. ANALYTICAL RESULTS OF THREE REPLICATE SAN JUANITO DICKITE RUNS (SAN JUANITO (3), RUNS 5-7)

ppm given below (p) values

	San Juanito (3) run 5	San Juanito (3) run 6	San Juanito (3) run 7
pK	5.36 (.17)	5.39 (.16)	5.51 (.12)
pNa	5.81 (.04)	6.28 (.01)	5.54 (.06)
pCa	—	—	—
pMg	5.59 (.06)	5.69 (.05)	5.61 (.06)
pSi	5.02 (.265)	5.01 (.273)	5.02 (.265)
pAl	6.76 (.0047)	6.61 (.0066)	6.88 (.0036)
pH	5.99	5.87	5.77
pKs_2	39.85	39.50	40.26

Solutions were processed for 83 days.

(generally water) needed in writing the dissolution equation used in determining the Ks .

The raw data for the calculations were the concentrations of ions determined by analysis, and expressed in parts per million (ppm) in the clay-water solutions, Table 3. From these concentrations, the activities of individual ions and the logarithms of these were then computed on an IBM 1620 Computer, using the Debye-Huckel method.

A balanced chemical equation written for the dissolution reaction expresses, and implies, knowledge of the products of dissolution. Although the equations may not express completely, or explicitly, all the actual solution products, assurance that these equations are adequate to allow for meaningful Ks is shown by the general uniformity of the calculated Ks . For example, an equation used to express the dissolution of ideal kaolinite is:



This equation and others describing the reactions for the aqueous dissolution of minerals, imply that:

1. The ions K^+ , Na^+ , Ca^{2+} , represent those elements in solution, a condition which is consistent with other studies of inorganic salts of these cations in dilute solutions.

2. Silicon in solution, which was determined by the molybdate reaction, is considered to be monomeric silicic acid (H_4SiO_4). Although this procedure may not determine all forms of soluble silicon in solution, it is applicable to the problem at hand because the procedure has been standardized with solutions of known silicon concentration.

3. The species of aluminum ion in solution is controlled by the pH of the solution. At pH values above 6.70, a singly charged anionic species, $Al(OH)_4^-$, is assumed to be present. From a pH of 6.70 to below 3.0 the dominant ion is assumed to be $Al(OH)_2^+$ (Reesman, 1966).

4. Balance of charge is maintained in the dissolution equation by hydrogen or hydroxyl ions.

5. Although the amount of water available to enter the dissolution reactions is not limited, only the amount of water necessary to hydrate or hydroxylate the silicic acid and the aluminum ion, and to produce the electrical balancing of the solution (H^+ or $(OH)^-$), is designated in the balanced dissolution equations.

Solubility constants. Solubility constants for various dissolution reactions of minerals are, in effect, special equilibrium constants in which the product of the activities of ions produced by dissolution are raised to the power of their molar concentration divided by the activities of the reacting substances raised to the power of their molar concentrations. The K_s is simplified because the activities of the solid undergoing dissolution and the relatively pure water are considered to be unity. Thus, the denominator of the K_s is reduced to unity, *i.e.*:

$$K_{s_2} = \frac{[Al(OH)_2^+]^2[H_4SiO_4]^2[(OH)^-]^6}{[kaolinite][H_2O]^5}$$

$$K_{s_2} = \frac{[Al(OH)_2^+]^2[H_4SiO_4]^2[(OH)^-]^6}{[1][1]^5}$$

The brackets in the above equation symbolize the activities of the particular substance enclosed. Notations for solubility constants (K_{s_2}) are taken from Sillén (1964); these represent the approved notation of the International Union of Pure and Applied Chemistry, where K_{s_2} corresponds to a constant (K) of solubility (s) with two hydroxyl ligands. Inasmuch as aluminum is thought to be the major variable as far as ligand

TABLE 4. STANDARD FREE ENERGIES OF FORMATION USED IN THIS STUDY

Formula		ΔF_f° kcal	Source
Al(OH) ₃	(amorphous)	-271.9	Latimer (1952)
AlO(OH)	(boehmite)	-217.5	Rossini, <i>et al.</i> (1952)
Al(OH) ₂ ⁺		-216.1	Reesman, 1966
Al(OH) ₄ ⁻		-311.3	Reesman, 1966
Ca ²⁺		-132.18	Rossini, <i>et al.</i> (1952)
H ⁺		0.0	Latimer (1952)
H ₂ O	(water)	-56.7	Rossini, <i>et al.</i> (1952)
H ₄ SiO ₄		-312.65	see text
K ⁺		-67.46	Rossini, <i>et al.</i> (1952)
Mg ²⁺		-108.99	Rossini, <i>et al.</i> (1952)
Na ⁺		-62.59	Rossini, <i>et al.</i> (1952)
OH ⁻		-37.6	Rossini, <i>et al.</i> (1952)
SiO ₂	(quartz)	-204.71	Weise, <i>et al.</i> (1962)

changes are concerned the subscripted number denotes the number of ligands thought to be associated with the aluminum in solution. For K_s involving Al(OH)₄⁻, the constant is preceded by an asterisk (* K_{s4}), indicating that a hydrogen ion (or proton) was liberated during the reaction. Values for solubility constants or activities of ions are given as pK_s or pAl , etc., where the p represents the negative logarithm of the particular constant or activity, or as exponents (*e.g.*, $10^{-35.67}$ *etc.*).

Calculation of ΔF_R° . The ΔF_R° was calculated from the solubility constant by the Nernst equation which, at 25°C, with substitution for R and converting to common logarithms, reduces to the following:

$$\Delta F_R^\circ = -1.3641 \log K_s \text{ (in kilocalories)}$$

$$(1) \Delta F_R^\circ = 1.364 pK_s.$$

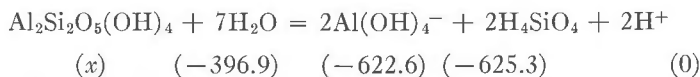
Likewise:

$$(2) \Delta F_R^\circ = \sum \Delta F_f^\circ \text{ products} - \sum \Delta F_f^\circ \text{ reactants.}$$

The ΔF_f° 's of most solution products used in our calculations were chosen from other independent measurements, Table 4.

The value for silicic acid (H₄SiO₄) was revised, however, in accordance with the heat of formation of quartz determined by Weise, *et al.* (1962), and evidence that the K_s for quartz is probably about $10^{-4.0}$ (Morey, Fournier, and Rowe, 1962). Using the general procedure of Siever (1957), the ΔF_f° for silicic acid was calculated to be -312.65 kcal/mole. Wagman, *et al.*, (1966) published another value, -314.7 kcal, after our results were in manuscript.

To illustrate our calculations an example is taken from the first run of Keokuk kaolinite (bulk sample). Since the pH of the solution was 8.1, $\text{Al}(\text{OH})_4^-$ was considered to be the major ionic species of aluminum in solution. Numbers in parentheses below the equation are the ΔF_f° 's of the ions directly above them.



For the reaction:

$$*K_{s4} = [\text{Al}(\text{OH})_4^-]^2 [\text{H}_4\text{SiO}_4]^2 [\text{H}^+]^2$$

Analysis of the kaolinite solution yielded the following concentrations of ions expressed in terms of the element:

$$\text{Al} = .025 \text{ ppm} = 10^{-6.05} \text{ moles/liter} = [\text{Al}(\text{OH})_4^-]$$

$$\text{Si} = 1.70 \text{ ppm} = 10^{-4.22} \text{ moles/liter} = [\text{H}_4\text{SiO}_4]$$

$$\text{H} = 10^{-8.1} \text{ moles/liter}$$

$$p^*K_{s4} = 2p\text{Al}(\text{OH})_4^- + 2p\text{H}_4\text{SiO}_4 + 2p\text{H} = 12.10 + 8.44 + 16.20 \\ = 36.74$$

$$\Delta F_R^\circ = 1.364p^*K_{s4} = 50.11 \text{ kcal}$$

$$\sum \Delta F_f^\circ \text{ products} = (-622.6) + (-625.3) = -1247.9 \text{ kcal}$$

$$\sum \Delta F_f^\circ \text{ reactants} = \Delta F_f^\circ \text{ kaolinite} + (-396.9)$$

$$\Delta F_f^\circ \text{ kaolinite} = -1247.9 - (-396.9) - (\Delta F_R^\circ) \\ = -851.0 - (\Delta F_R^\circ) = -901.11 \text{ kcal/mole}$$

We have calculated free energies of formation from 311 analyzed samples processed over a period of about three years. Considerable experience preparing samples and improving techniques gained during the study has given us a basis for ranking the analyses and consequently the calculations in terms of quality. For one example, the necessary length of time for centrifuging to clear a suspension varies with the kind of clay mineral as well as its dispersibility. As another example, we first ground the clays with water in a mechanically driven mortar, thinking this would expedite dissolution. Later we learned that the disordering of clay mineral crystals caused by grinding affected dissolution results adversely, which was corrected only by long standing and solution of the clay, accompanied by "rehealing" of clay surfaces. Simply shaking the disaggre-

TABLE 5. FREE ENERGIES OF FORMATION CALCULATED FROM SOLUTION DATA

Material	Calculated F_f°	Previous F_f°
Dickite	$-904.4 \pm .7$ kcal/fw	$-902.3 \pm .5$ (Barany and Kelley, 1961)
Kaolinite (in ball clay)	$-904.0 \pm .2$ kcal/fw	$-903.0 \pm .5$ (Barany and Kelley, 1961) -903.1 ± 0.4 (Kittrick, 1966)
"Fire clay mineral"	-900 to 904 (variable)	
Halloysite	-899 ± 1.0 kcal/fw	$-898.6 \pm .5$ (Barany and Kelley, 1961)
Endellite	$-902.3 \pm .7$ kcal/ $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	
Montmorillonite (Cheto)	$-1275.4 \pm .6$ kcal/fw	
Montmorillonite (Clay Spur)	-1270 ± 1.2 kcal/fw	
Gibbsite	$-550.3 \pm .4$ kcal/ $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	$-547.0 \pm .4$ (Barany and Kelley, 1961)
Boehmite	$-435.2 \pm .5$ kcal/ $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	-435.0 (Rossini, <i>et al.</i> 1952)
Diaspore	$-437.2 \pm .8$ kcal/ $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	-439.0 (Fyfe and Hollander, 1965)
Pyrophyllite	$-1258.7 \pm .8$ kcal/fw	
Muscovite	-1327 (only 1 sample run)	-1330.1 ± 1.3 (Barany, 1964)

Sources of Barany and Kelley's samples: dickite, San Juanito, Mexico, halloysite, Bedford, Ind, kaolinite, Murfreesboro, Ark., and Alta, N. Mexico.

gated clay fractions yielded results of less variability. Other handling of materials between initial suspension and final analyses was improved.

Using these experiences, and by evaluating strictly the 311 analyses, we have taken what we consider our best values from about 150 analyses to be, with uncertainties, as listed in Table 5.

DISCUSSION OF PROBLEMS AND OBSERVATIONS ENCOUNTERED IN THE DISSOLUTION STUDY

Special problems. Two problems, each of which singly gave serious concern to the possible meaning of our dissolution experiments, contributed eventually to a favorable resolution of both. One was the almost certainty that grinding of clay minerals during disaggregation of samples would disrupt and disorder their crystallinity leading to the following probable adverse results. Owing to the input of mechanical energy into the clay crystals during grinding of them, their solubilities would be increased, or modified, sufficiently that a valid K_s truly representative of the intact mineral, per se, could not be derived from the data.

The second problem was the achievement of equilibrium, or very near equilibrium, between mineral crystals and solution, and equally necessary to insure usefulness of the data, some independent evidence of preferably reversible crystallization which would be objectively convincing. We believe that both of these problems have been resolved but wish to discuss them further.

Evidence as to the extent of increase in solubility due to grinding comes from an experiment with the Keokuk-geode kaolinite. Extraordinarily high crystallinity in the Keokuk kaolinite, as demonstrated by a nearly "complete" X-ray diffractogram (Hayes, 1963; Keller, Pickett, and

Reesman, 1966) is diminished to that of "ordinary" kaolinite by grinding with a mortar and pestle for only a few minutes by hand. It is more drastically reduced to a high content of apparently X-ray-amorphous material by dry grinding in a mechanical mortar for a few hours (Keller, Pickett, and Reesman, 1966). We found the solubility constant for Keokuk-geode kaolinite dry-ground for 12 hours to be $10^{-33.26}$ whereas that of bulk Keokuk kaolinite crystals simply shaken in water was $10^{-37.22}$, an energy difference of more than 5.40 kcal.

In passing, it was noted that drastic chemical treatment (energy) of diaspore with HF or hot concentrated NaOH (to destroy associated mineral impurities) also increased the solubility of the diaspore.

Pulverized clay minerals were washed with distilled water, and washings discarded, before dissolution processing began. Nevertheless, solubility began at a high value, and declined for a period of time, but declined too rapidly, in our opinion, to have dissolved all of the considerable amount of clay disordered during grinding. We interpret the rapid decline in solubility to be caused by a restoration, or "rehealing," of disrupted crystal edges and faces, and further interpret this effect to mean that saturation-equilibrium had been reached between clay crystals and liquid. This effect, plus the reasonably close agreement between our ΔF_f° values and those of Barany and Kelley, and others, strengthens confidence that our dissolution data are from systems at, or very near, equilibrium.

All alumino-silicate minerals used in this study showed incongruent dissolution, which is to be expected. The concept of the solubility constant has no restrictions as to congruency, only that the product of the activities of the component ions should remain constant. Aluminum activity in solution may be controlled by the ability of aluminum to form as a separate high-alumina mineral phase. Chemical bonding in the sheet structure minerals varies in the different structural sites, thereby allowing for differential rates of dissolution—the basis for Osthaus' (1956) determination of octahedral and tetrahedral aluminum.

Buffer capacities of solutions equilibrated with high alumina and alumino-silicate minerals are very low. Variations in pH of solutions-equilibrated with the minerals of this study often show strong pH dependence upon minor carbonate or sulfide mineral phases. In nature, the presence of pH controlling mineral phases are probably very important in causing the relatively rapid supersaturation of ions necessary for the formation of such metastable mineral phases such as boehmite, allophane, and endellite.

The high-alumina minerals. Solubility data for the three high alumina

minerals, gibbsite, diaspore, and boehmite, indicate that in the presence of water, the stabilities of gibbsite and diaspore are about equal and both are more stable than boehmite. The preferred ΔF_f° for diaspore, as determined by solubility data, is -218.5 kcal/mole (HAlO_2), which is 1.0 kcal above the value found by Fyfe and Hollander (1965). The calculated ΔF_f° for gibbsite of -550.28 kcal/ $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ from solubility data seems to be in better agreement with geologic occurrence of gibbsite than the value of -547.0 kcal/mole as determined by Barany and Kelley (1961) from HF solution calorimetry. The ΔF_f° of boehmite (-435.2 kcal/ $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) is in good agreement with the ΔF_f° value of Rossini, *et al.*, (1952), but this is to be expected, because the ΔF_f° of the aqueous ions of aluminum $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_4^-$ are based upon the ΔF_f° of boehmite.

Kaolin minerals. Kaolinite samples, including *b*-axis disordered "fire clay" minerals, showed variations in pKs_2 from 37.0 to 40.5. Most samples that received strong mechanical disaggregation showed a tendency to reheat and yield lower *Ks* with increasing equilibration time. Evidence is inconclusive, but highly suggestive, that more-disordered kaolinites are less stable than are the better crystalline samples. This idea was suggested by Kittrick (1966) and is supported by variation in dehydroxylation peak temperatures that range from 560° to 600°C in most kaolinites, to 690° for the Keokuk kaolinite (Keller, *et al.*, 1966).

Most consistent *Ks* for kaolinite were obtained with solutions processed with Keokuk kaolinite and with kaolinitic ball clay from Kentucky. Flint clays (kaolin rich) varied with geographic occurrence. Missouri flint clays were lighter in color and "purer" in kaolinite; non-Missouri flint clays contain more carbon, siderite, and pyrite which darken them, and are probably tougher. Chemically, the Missouri flint clays gave pH values from 6.6 to 7.2, whereas the other flint clays gave pH values from about 4.0 to 5.4. Available solubility data indicate that the Missouri flint clays are probably more stable, but there might be a larger quantity of disordered material in the non-Missouri flint clays that had been produced by mechanical disaggregation, and which did not have sufficient time to re-stabilize.

For well-crystallized kaolinite, a ΔF_f° of -904.0 kcal/formula wt. is the best estimate from solubility data. Variation in solubility data among the tough, *b*-axis disordered "fire clay" kaolin is probably valid and inherent, and a probable range in ΔF_f° from $-900.$ to $-904.$ kcal/fw in them is likely.

A rather wide range in pKs_2 (from 37.5 to 41.9) for dickites makes uncertain the appraisal of the relative stabilities of dickite and kaolinite.

Variability in K_s of dickite might be related to impurities in the sample, because bulk samples yielded higher solubility constants. Dickites yielded lower concentrations of silicon into solution than did kaolinite, which might indicate that silicon is more tightly bound in dickite, that reaction rates are slower for the dissolution of dickite, or that the differences in silicon might be related to the degree of mechanical disruption of the clay lattice.

A pK_{s_2} of about 40.4, and a ΔF_f° of -904.4 kcal/fw, are thought to be most nearly representative for dickite. If so, dickite should be slightly more stable than kaolinite, which is opposite to the findings of Barany and Kelley (1961) who found a ΔF_f° of -903.0 for kaolinite and -902.4 for dickite.

Endellite and halloysite also showed variations in K_s , but it appears that endellite has the lower K_s . Re-hydration of halloysite sample (62) and the corresponding lowering of the K_s are bases for this statement (see Table 3), and the generally lower values of K_s of endellite samples (64) and (65), as compared with halloysite sample (64), seem also to reinforce this belief. The stability of endellite in an aqueous environment is in agreement with the requirement of reducing the activity of water, or partial pressure of water vapor, in order to dehydrate endellite and form halloysite.

A ΔF_f° of -901.8 kcal/ $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ for endellite and -899.4 kcal/fw for halloysite seem to be consistent with the solubility data of these minerals. The ΔF_f° for halloysite is slightly greater than the -900.1 kcal/ $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ for allophane (Keller, *et al.*, 1967), which was also determined from solubility data.

Pyrophyllite. The ΔF_f° calculated for pyrophyllite was surprisingly negative—about 5.5 kcal below its oxides. These data would indicate that it is possible for pyrophyllite to form at standard temperatures and pressures, unless there are kinetic difficulties in its genesis. A slight amount of 9.16Å material observed in X-ray diffractograms of several Missouri fire clay samples, dubiously identified as mica, might be pyrophyllite(?).

Solution data from pyrophyllite sample (1) show very strikingly the effects of mechanical disorder, whereas pyrophyllite sample (2), which was disaggregated much more carefully, yields a calculated ΔF_f° of -1258.7 kcal/fw. Pyrophyllite (1) showed a drop in silicon from 31 ppm to 1.12 ppm over a period of about fourteen months.

Montmorillonite. Solubility constants for the Cheto, Arizona montmorillonite were interpreted from the montmorillonite formula of the Chambers, Arizona—the same bentonite body—(A.P.I., reference mineral,

Kerr, *et. al.*, 1950), whereas the Clay Spur, Wyoming material was based upon the mineral formula of Osthau (1956). Formulae used for these minerals are given in Table 3.

The montmorillonites used in this study seem to be rather unstable with respect to kaolinite and quartz, but they may represent the stable clay phase in the presence of sodium, calcium, and magnesium in the system. Apparent instability of these montmorillonites may result from inferior analytical values because of incomplete removal of ultra-fine colloidal material from solution.

Appraisal of the aqueous dissolution approach to determination of ΔF_f° . Determination of ΔF_f° of complex silicate minerals by means of aqueous dissolution is a relative newcomer compared to measurements by solution calorimetry and entropy data. Lacking refinements and testing through time, it inspires less confidence than do the older methods, but calorimetry is also not infallible—note the recent change in ΔF_f° of quartz from -196.9 to -204.71 kcal/fw, a change of some 4 percent of what had been regarded a dependable value. We have tried to develop a set of K_s and ΔF_f° of clay minerals that are consistent within the group and can be applied to geologic problems.

CONCLUSIONS

1. Dissolution techniques, if carefully applied, can provide useful solubility information that can be utilized in determining the free energy of formation.
2. Disruption of mineral surfaces, produced either mechanically or chemically, causes an increase in the amount of ions dissolved in solution. Consequent abnormally high solubility constants, resulting from increased dissolution, tend to decrease with increasing time, because the mineral surfaces tend to restabilize. Although removal of easily soluble material as aliquots for chemical analysis must play a part in the apparent restabilization, the very minor amount of material removed for analysis plays a very subordinate role in surface stabilization.
3. The effects of surface readjustments provide the best evidence of reversibility for these reactions. Restabilization of disordered surfaces is as much a reversible approach to equilibrium as would be the concentration of an equilibrated solution that was maintaining equilibrium during the concentration process. Reordering within a short time indicates that there is a sufficient quantity of material leaving and returning to the surfaces, at the near-equilibrium conditions, to allow for the restabilization.
4. The rapid response of mechanically disordered samples to near-

equilibrium conditions, and the process of restabilization over rather short periods of time indicate that effective equilibration has occurred in most clay minerals within a matter of weeks.

5. Colloidal particles, not removed from solution, tend to increase the quantity of analytically determined ions.

6. All aluminosilicates observed in this study showed incongruent dissolution. Except for Ouray dickite sample (2), silicon was taken into solution preferentially over aluminum.

7. The lower silicon values for equilibrated dickite, rather than kaolinite, solutions indicate that the silicon may be more tightly bound in the dickites than in the kaolinites.

8. The very low buffer capacity of solutions equilibrated with high alumina and aluminosilicate minerals indicates that variation in pH imposed by other minerals may be the most important factor in producing the degree of supersaturation necessary for the formation of metastable mineral phases such as boehmite, allophane, and endellite.

9. Stability data calculated for the various kaolinite samples suggest a possible variation that may be dependent upon crystallinity.

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