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FREE ENERGY OF FORMATION OF KAOLINITE FROM SOLUBILITY MEASUREMENTS[1]

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ABSTRACT

The free energy of formation of seven kaolinite samples ranged from −902.5 to −903.8 kcal per mole, in general agreement with x-ray diffraction indications of crystallinity. Measurements were made over a wide range of common ion activities and are in relatively good agreement with those based upon heat of solution measurements and estimations from natural relationships. Ion activities supported by a few kaolinite samples appear to be controlled by relatively soluble small particles that can be removed by chemical extractions or centrifuging.

INTRODUCTION

In the clay and fine silt size fractions of soils and sediments one normally observes a series of mineral assemblages whose composition is dependent upon weathering intensity (Jackson *et al.*, 1948). Where weathering has been relatively severe, one of the most abundant of these minerals is kaolinite. Since a close correspondence is usually observed between natural mineral assemblages and the environment of their occurrence, and those predicted from free energy data (Garrels, 1957), reliable free energy data can be crucial to an understanding of the weathering of soils and sediments.

Garrels also postulated that kaolinite formed from gibbsite at an aqueous concentration of approximately 10 ppm SiO_2. From this, a standard free energy of formation, ΔG_f^0 of kaolinite may be computed as -900 ± 2 kcal per mole. The first experimental ΔG_f^0 for kaolinite was determined by Barany and Kelley (1961) from heat of solution measurements and the entropy determined by King and Weller (1961), giving ΔG_f^0 (kaolinite) as -903.1 ± 0.7 kcal per mole.

A solubility approach to the ΔG_f^0 of kaolinite would serve as an independent check on the above values, utilizing different kaolinite samples, procedures, assumptions and thermodynamic values. The latter is particularly important, considering the disturbingly ephemeral nature of some thermodynamic data. A case in point is the ΔG_f^0 values for kaolinite given in the previous paragraph. The values given are recalculations[2] using more recent thermodynamic values for quartz and gibbsite.

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[2] Calculations of the free energy of formation of kaolinite.

From kaolinization of gibbsite at 10 ppm SiO_2. Consider the reaction:

Perhaps the most important advantage of the solubility approach is that experimentally it is a solution-precipitation process and is likely to have many features in common with actual weathering processes. Disadvantages are the possible introduction of metastable phases and extremely long equilibration times.

EXPERIMENTAL

Kaolinite samples[1] were selected from various commercial sources on the basis of purity as determined by *x*-ray diffraction, ethylene glycol sorption measurements (to indicate high surface area impurities), and chemical analyses where available.

In general, 10.0 g samples were given 5 centrifuge washes with 200 ml of 0.001 *N* HCl to remove soluble substances. Samples from undersaturation were suspended in 200 ml of 0.001 *N* HCl in 250 ml polyethylene bottles, and the pH adjusted to 3.00 with HCl. Samples were agitated on

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$$2Al(OH)_{3(c)} + 2Si(OH)_{4(aq)} = Al_2Si_2O_5(OH)_{4(c)} + 5H_2O_{(l)} \qquad (1)$$

where $Si(OH)_{4(aq)}$ is 1.7×10^{-4} m/l. This fixes the equilibrium constant K at $[Si(OH)_4]^{-2}$ or $10^{7.54}$ where brackets denote activity. The standard free energy of reaction, $\Delta G_R{}^0 = -RT\ln K = -1.36 \log 10^{7.54} = -10.3$ kcal. From (1), $\Delta G_R{}^0 = \Delta G_f{}^0(\text{kaolinite}) + 5\Delta G_f{}^0(H_2O) - 2\Delta G_f{}^0\ (\text{gibbsite}) - 2\Delta G_f{}^0\ (Si(OH)_4)$. Taking $\Delta G_f{}^0$ (gibbsite) as -273.5 kcal per mole (Barany and Kelley, 1961) and $\Delta G_f{}^0\ (Si(OH)_{4(aq)})$ as -313.1 kcal per mole (computed from the data of van Lier *et al.*, 1960; Wise *et al.*, 1963), $\Delta G_f{}^0\ (\text{kaolinite}) = -10.3 - 5(-56.7) + 2(-273.5) + 2(-313.1) = -900$ kcal per mole.

From heat of solution. Consider:

$$2Al_{(c)} + 2SiO_{2(c)} + 5H_2O_{(l)} = Al_2Si_2O_5(OH)_{4(c)} + 3H_{2(g)} \qquad (2)$$

By the consideration of 5 reactions where the standard enthalpy of formation, $\Delta H_f{}^0$, was measured, $\Delta H_R{}^0$ for (2) was computed for two kaolinite samples by Barany and Kelley (1961) to be -202.6 ± 0.7 kcal. Taking $\Delta H_f{}^0$ of water to be -68.3 kcal per mole and quartz to be -217.8 kcal per mole (Wise, *et al.*, 1963), $\Delta H_f{}^0\ (\text{kaolinite}) = \Delta H_R{}^0 + 5\Delta H_f{}^0 H_2O + 2\Delta H_f{}^0\ (SiO_2) = -202.6 + 5(-68.3) + 2(-217.8) = -979.7$ kcal per mole.

Next, to obtain the standard entropy S^0, of kaolinite, consider the equation

$$2Al_{(c)} + 2Si_{(c)} + 2H_{2(g)} + \frac{9}{2}O_{2(g)} = Al_2Si_2O_5(OH)_{4(c)} \qquad (3)$$

The S^0 for $Al_{(c)} = 6.7$, $Si_{(c)} = 4.5$, $H_{2(g)} = 31.2$, and $O_{2(g)} = 49.0$ cal deg.$^{-1}$ mole^{-1}. For kaolinite, S^0 has been determined from low temperature heat capacities by King and Weller (1961) as 48.5 cal deg.$^{-1}$ mole^{-1}. From (3), $\Delta S_R{}^0$ and $\Delta S^0\ (\text{kaolinite}) = 48.5 - 9/2(49.0) - 2(31.2) - 2(4.5) - 2(6.7) = -257.0$ cal deg.$^{-1}$ mole^{-1}. Since $\Delta G_f{}^0\ (\text{kaolinite}) = \Delta H_f{}^0 - T\Delta S^0$, then $\Delta G_f{}^0\ (\text{kaolinite}) = -979.7 - (298.15)(-0.257) = -903.1$ kcal per mole.

[1] Kaolinite from North Carolina, South Carolina (API H-5) and New Mexico (API H-9) were obtained from Wards Natural Science Establishment. The kaolinite from England is No. 3 Colloidal from Hammill and Gillespie Inc., and the kaolinite from Florida is from the Edgar Plastic Kaolin Co. Georgia 1 is No. 600 Washed Kaolin and Georgia 3 is No. 27 Washed Kaolin from Southern Clays Inc. Georgia 2 is Pioneer Air Floated Clay from the Georgia Kaolin Co., and the Idaho kaolinite was collected north of Moscow, Idaho.

a shaker for approximately the first two months. *X*-ray diffraction analysis of samples before and after equilibration did not reveal any mineralogical changes. Room temperature during analysis periods was determined by thermometer readings to be between 23 and 25° C. Preliminary experiments with autoclaving indicated that microorganisms did not interfere.

Aliquots for analysis were removed from the supernatant liquid after centrifuging. Absence of suspended kaolinite was checked with a Tyndall beam. Silica was determined as the blue silicomolybdate (*Standard Methods*, 1960, p. 228). Early aluminum determinations were with 8-hydroxyquinoline (Margerum *et al.*, 1953), in good agreement with later determinations with aluminon (Hsu, 1963). All colorimetric determinations were made on the Bausch and Lomb Spectronic 20 colorimeter. Final pH measurements were made on the Heath EUW-301 Recording Electrometer. The machine was calibrated to within ±0.02 units of three buffers prior to determinations. Agreement between duplicate determinations of pAl, pSi and pH was generally ±0.03 or better. Activities for Al^{3+} were computed from the Debye-Hückel equation (Klotz, 1950, p. 329).

KAOLINITE DISSOLUTION. Consider the dissolution of kaolinite under conditions where it is the stable phase, so that

$$6H^+ + Al_2Si_2O_5(OH)_4 = 2Al^{3+} + 2Si(OH)_4 + H_2O \tag{1}$$

At equilibrium, the concentrations of Al and Si in solution should be equal. Such a situation is shown for the kaolinite from North Carolina in Fig. 1. Kaolinite dissolves slowly under these conditions (approximately 4 years elapsed between initial and final analyses), with Si initially going into solution more rapidly than Al. However, when extrapolated to infinite time (where the system is presumably at equilibrium), the concentrations of Al and Si are essentially equal at $1 \times 10^{-3.65}$ m/l.

In the remaining kaolinites, the concentration of $Si(OH)_4$ exceeded that of Al^{3+}, ranging from a factor of approximately 2 for the kaolinite from South Carolina, up to a factor of approximately 200 for the kaolinite from Idaho. The work on kaolinite dissolution by Polzer and Hem (1965) indicates the excess $Si(OH)_4$ is probably contributed by impurities in the sample. Though undesirable, such impurities are not ruinous unless they prevent kaolinite from controlling the activity of at least one of its common ions. In fact, the North Carolina kaolinite that gave congruent dissolution showed considerable mica impurity by *x*-ray diffraction analysis. Since it is the control by kaolinite of a common ion rather than the source of the common ion that is important, dissolution of the 2–5 μ fraction of kaolinite Georgia 3 was allowed to proceed in 0.0100 *M* $AlCl_3$ in order to obtain a wider range in Al^{3+} values (Table 1).

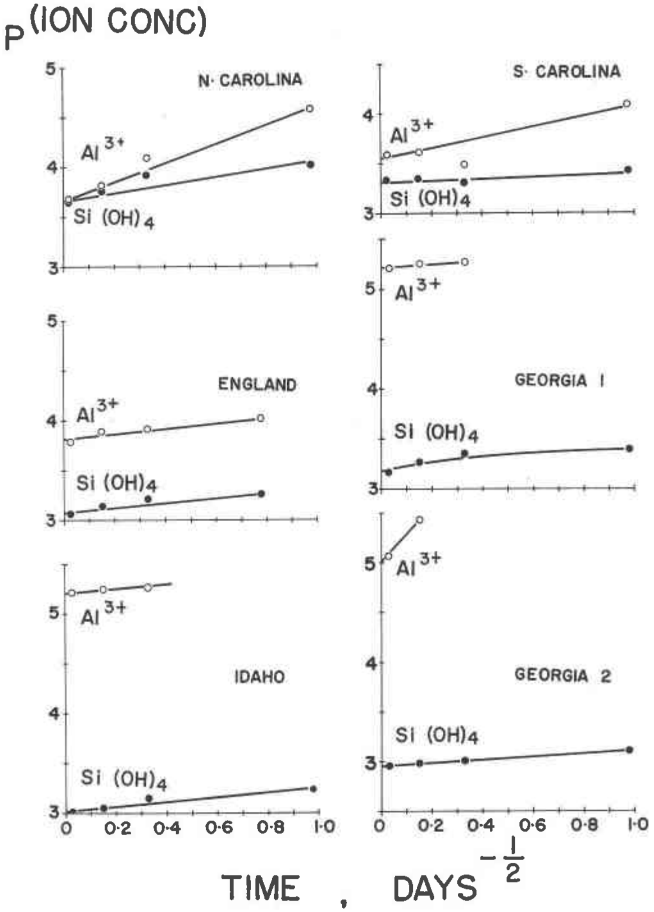

FIG. 1. Concentrations of Al and Si in the supernatant liquid equilibrated with six crystalline kaolinites as a function of $1/\sqrt{\text{equilibration time}}$. Analyses were taken (from right to left) at 1, 9, 43, and 1.38×10^3 days respectively.

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From (1), the equilibrium constant $K=[Al^{3+}]^2[Si(OH)_4]^2/[H^+]^6$ where brackets denote ion activities. The activities of kaolinite and water are assumed to be unity. Taking negative logarithms, $pK=2p[Al^{3+}]+2p[Si(OH)_4]-6p[H^+]$. For the North Carolina kaolinite (Table 1—notice that the ion activity correction changes the pAl of 3.65 to $p[Al^{3+}]$ of 3.82) as an example, $pK=2(3.82)+2(3.65)-6(3.72)=-7.38$. $\Delta G_R{}^0=-RT\ln K=-(1.36)(7.38)=-10.04$ kcal. From (1), $\Delta G_f{}^0$ (kaolinite) $=-\Delta G_R{}^0+2\Delta G_f{}^0(Si(OH)_4)+\Delta G_f{}^0(H_2O)-6\Delta G_f{}^0(H^+)$.

TABLE 1. ION CONCENTRATIONS AND ΔG_f^0 VALUES FOR RELATIVELY CRYSTALLINE KAOLINITES[1]

Sample	pAl	pSi(OH)$_4$	p[H$^+$]	ΔG_f^0 kcal per mole
England	3.80	3.07	3.46	−903.8
Georgia 1	5.22	3.17	3.99	−903.6
Georgia 2	5.00	2.95	3.87	−903.4
Idaho	5.21	3.02	4.02	−902.9
N. Carolina	3.65	3.65	3.72	−902.9
Georgia 3	2.00	3.80	3.38	−902.7
S. Carolina	3.55	3.30	3.62	−902.5

Average $\Delta G_f^0 \pm$ave. deviation $= -903.1 \pm 0.4$ kcal per mole.

[1] Samples were equilibrated approximately 4 years. In general, pH values were not a straight-line function of time, so that values given are those of the last sampling. Values for Al and Si are from straight-line infinite-time extrapolations, which, however, were within experimental error of values for the last sampling.

Ionic strength values (estimated from initial pH and indicated ion analyses) ranged from 0.0013 to 0.0018, except for Georgia 3, where ionic strength was determined by the addition of 0.0100 *M* $AlCl_3$.

The ΔG_f^0 of $Si(OH)_4$ is -313.1 kcal per mole (computed from the data of van Lier *et al.*, 1960, and Wise *et al.*, 1963) and taking the ΔG_f^0 of Al^{3+}, H_2O and H^+ as -115.0, -56.7, and 0.0 kcal per mole respectively,[1] ΔG_f^0 (kaolinite) $= 10.0 + 2(-115.0) + 2(-313.1) + (-56.7) = -902.9$ kcal per mole. If (1) is rewritten assuming pH = pKw-pOH, solving for pKw one finds the effective sample temperature to have been 25.3° C., assuming no error in ΔG_f^0 values and taking $\Delta G_f^0(OH^-)$ to be -37.6 kcal per mole.

The ΔG_f^0 of the North Carolina kaolinite is in good agreement with the value of -903.1 kcal per mole computed previously from calorimetry and heat capacity measurements and work on the dissolution of a Lewiston, Montana, kaolinite by Polzer and Hem (1965). It is also in good agreement with a number of other kaolinite samples from diverse localities (Table 1). Lack of congruent dissolution appears to have had no effect other than to help demonstrate the application of solubility product principles to the kaolinite system, agreement in Table 1 having been achieved over a four-fold range in H^+, an eight-fold range in $Si(OH)_4$, and a 1500-fold range in Al^{3+} concentrations.

Because of the long equilibration times, the relatively straight-line extrapolations to infinite time, and the good agreement with completely

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[1] The source of thermodynamic values not otherwise indicated is Appendix 2, Garrels and Christ (1965).

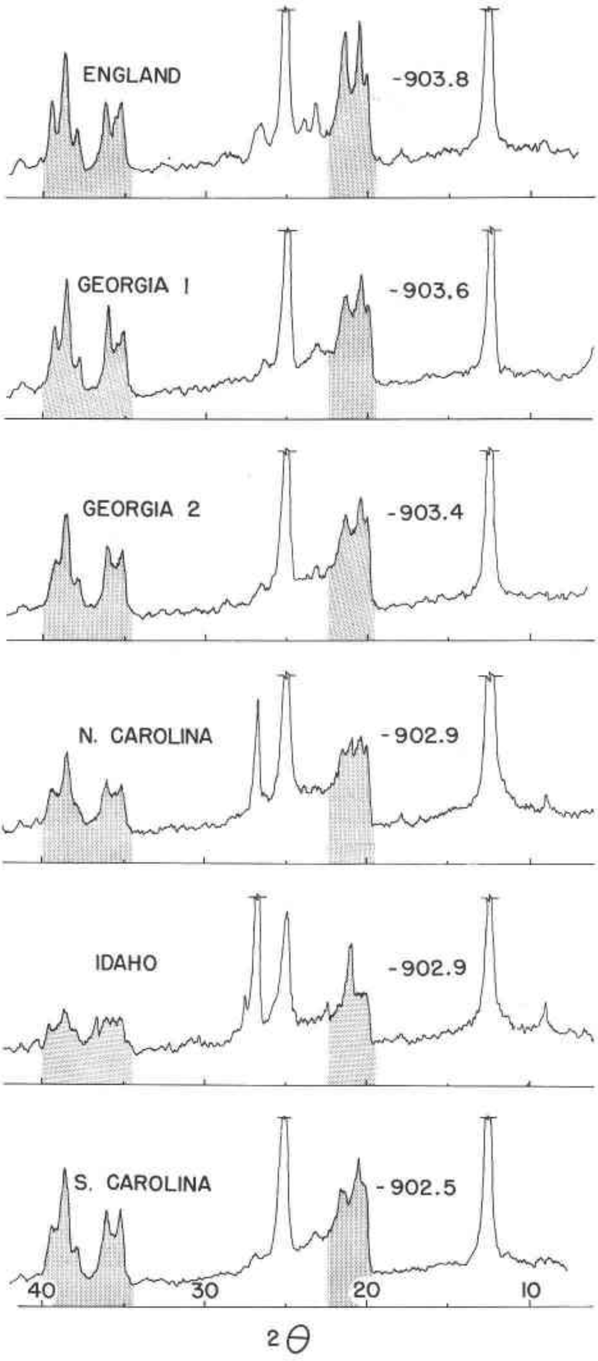
ENGLAND
-903.8
GEORGIA I
-903.6
GEORGIA 2
-903.4
N. CAROLINA
-902.9
IDAHO
-902.9
S. CAROLINA
-902.5
40
30
20
10
2θ

TABLE 2. ION CONCENTRATIONS AND ΔG_f^0 VALUES FOR RELATIVELY SOLUBLE KAOLINITES[1]

Sample	pAl	$pSi(OH)_4$	$p[H^+]$	ΔG_f^0 kcal per mole
Florida	4.87	3.50	4.55	−899.2[2]
New Mexico	3.68	2.97	3.75	−900.8
Georgia 3	1.71	3.65	3.45	−901.4
Georgia 3	4.96	3.51	4.30	−901.1

[1] Samples equilibrated approximately 4 years. Infinite-time extrapolations similar to those in Fig. 1 indicated the samples to be essentially at equilibrium. Ionic strengths are estimated from initial pH and indicated ion analyses and ranged from 0.004 to 0.12.

[2] This value appears to be in agreement with a value of −899.6 kcal per mole obtained for a Missouri kaolinite by Reesman and Keller (Progr. Abs. 14th North Am. Clay Minerals Conf. and Second Meet. Clay Minerals Soc., Aug. 23–26, 1965, Berkeley, Calif.).

independent calorimetric measurements and natural relations, one feels relatively assured that the samples were at equilibrium.

EFFECT OF CRYSTALLINITY

The kaolinite samples of Fig. 1 were *x*-rayed by the random powder method and are arranged in Fig. 2 in descending order of ΔG_f^0. Brindley *et al.*, (1963) find resolution in certain triple-peak areas to be an indicator of kaolinite crystallinity. By this criteria, there is a crystallinity decrease among the kaolinites in Fig. 2 that corresponds in a general way to an increasingly positive ΔG_f^0. Although the kaolinite from South Carolina appears to be more crystalline than its rather positive ΔG_f^0 would suggest, the sample components producing the *x*-ray patterns in Fig. 2 generally appear to control the solubility characteristics of the sample.

In Table 2 are data from several kaolinite samples that gave considerably more positive ΔG_f^0 values than those shown in Table 1. Since *x*-ray patterns of these samples (not shown) did not indicate a correspondingly lesser degree of crystallinity than the other kaolinites, the presence of a more soluble component with poor diffraction characteristics was suspected. A minor amount of such material might not be detected by *x*-ray diffraction, yet if it occurred as small particles, its solubility characteristics could dominate the system.

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FIG. 2. Random powder *x*-ray diffraction patterns of several kaolinites with experimentally derived ΔG_f^0 values in kcal per mole. Resolution of peaks in shaded areas indicates degree of crystallinity. Standard Philips holders were filled from the back with 0.15 g kaolinite. $CuK\alpha$, Ni filter, 1° 2θ per min.

To determine if a minor amount of amorphous material could dominate the solubility characteristics of a kaolinite sample, separate samples of kaolinite Georgia 3 were subjected to extraction treatments with two reagents and a centrifuge size separation (Table 3). Each treatment made the ΔG_f^0 of the sample more negative, with the ΔG_f^0 of material $>2\mu$ equivalent spherical diameter remaining after 9 centrifugings corresponding to one of the more crystalline of the kaolinites of Table 1. The more negative ΔG_f^0 was then in much better agreement with the apparent crystallinity of the sample as indicated by the *x*-ray diffraction pattern (which was not changed by the treatment).

TABLE 3. EFFECT OF SAMPLE TREATMENT ON ION CONCENTRATIONS AND ΔG_f^0 VALUES FOR KAOLINITE GEORGIA 3

pAl	pSi(OH)$_4$	p[H$^+$]	ΔG_f^0 kcal per mole	Treatment
2.40	3.52	3.40	−902.6	12 centrifuge washes with 0.0010 *N* HCl
4.13 4.39	3.32 3.30	3.73 3.87	−903.0 −902.4	13 extractions with 8-hydroxyquinoline[1]
4.02	3.60	3.77	−903.3	$<2\mu$ and $>5\mu$ material removed with 9 centrifugings

Samples were equilibrated approximately 4 years from undersaturation. Ionic strengths for all samples were estimated from initial pH and indicated ion analyses and ranged from 0.0006 to 0.024.

[1] Forty g of Georgia 3 was extracted with 0.10 *M* 8-hydroxyquinoline in chloroform until the rate of Al removal was negligible. This required 10 extractions at pH 5.1 and then 3 extractions at pH 2.0.

It would appear then that the steady-state solubility characteristics of the kaolinites in Table 2 were dominated by particles $<2\mu$ equivalent spherical diameter, probably of poor crystallinity, which dissolve faster than crystalline kaolinite precipitates. Further, it would appear that the most negative ΔG_f^0 of Table 1 (−903.8 kcal per mole for the kaolinite from England) more nearly corresponds to the ΔG_f^0 of crystalline kaolinite than any of the others individually, or their collective average.

ERROR

Given an estimated error in p[ion] measurements of ±0.03 and assuming the errors in each are independent, the maximum relative error in pK would be ten (from the coefficients of the ions in equation 1, that is, $2+2+6$) times 0.03 or ±0.30. This is equivalent to an error of ±0.41

kcal per mole in ΔG_f^0, which is exactly the average deviation found in Table 1. The fact that the average deviation found equaled the maximum error expected from ion analyses, suggests the presence of deviations outside that of ion analysis. The most likely source of such deviation is variation in kaolinite crystallinity as discussed in the previous section. Probably a better indicator of the normal variation to be expected from analysis errors is the average deviation of ±0.15 kcal per mole found for duplicate samples of kaolinite Georgia 3 in Table 2.

If errors in ΔG_f^0 of Al^{3+} and $Si(OH)_4$ were negligible, the above maximum relative error would also be the maximum absolute error. However, the error in $\Delta G_f^0(Al^{3+})$ is usually given as ±0.1 kcal (and may be larger; see Plumb, 1962) and that of $\Delta G_f^0(Si(OH)_4)$ is determined by the error in ΔG_f^0 (quartz) which is ±0.34 kcal per mole (Wise *et al.*, 1963). The maximum absolute error in ΔG_f^0 (kaolinite) can then be estimated as $0.15 + 0.1 + 0.34 = \pm 0.5$ kcal per mole.

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