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Gibbs Free Energies of Formation Calculated from Dissolution Data Using Specific Mineral Analyses. III. Clay Minerals

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Abstract

Gibbs free energies of formation ($\Delta G°_f$) were calculated for representative clay minerals equilibrated in aqueous solution using specific chemical compositions, and taking into account the different species of hydrated Al and Fe species produced during reaction. Results in kcal/mole are: Bueker flint clay, −893.8; Keokuk kaolinite, −902.7; Georgia kaolinite, −903.5, but −902.5 for ideal structural formula; Wyoming (Na-rich) montmorillonite, −1248.2; Arizona (Ca-rich) montmorillonite, −1252.1; Beavers Bend (Na-rich) illite, −1250.5; Fithian (Ca-rich) illite, −1282.1.

Ca-rich varieties of certain clay minerals, plagioclases, and pyroxenes had higher negative $\Delta G°_f$ values than did Na-rich varieties.

Introduction

Although numerous Gibbs free energies of formation ($\Delta G°_f$) for kaolinite have been calculated from calorimetric data (Barany and Kelley, 1961) and from aqueous solubility data (Kittrick, 1966, 1970), few $\Delta G°_f$ are reported for clay minerals other than kaolinite (Reesman and Keller, 1967, 1968). Using aqueous solubility data to calculate $\Delta G°_f$, it has generally been assumed that at pH values about 6.70 (isoelectric point), $Al(OH)_4^-$ is the major Al species present in the system, and at pH of 6.70 to below 3.0, the dominant ion is assumed to be $Al(OH)_2^+$. However, in a recent paper Huang and Keller (1972a) show that different species of hydrated Al^{3+}—for example, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, and $Al(OH)_4^-$—can be present in varying proportions in an aqueous solution depending upon the pH (see Figure 1, Huang and Keller, 1972a). Hence the calculation of $\Delta G°_f$ from aqueous solubility data on aluminum silicate minerals should be based on the proportion of different Al species in the calculation. The purpose of this paper is (1) to calculate standard free energies of formation ($\Delta G°_f$) for representative clay minerals from analytical data for an equilibrated reaction that considers the different Al (or Fe) hydrated species in the system, and (2) to compare results for Ca-rich clays and silicates with their Na-rich counterparts.

Laboratory Dissolution

Two grams of finely dispersed, 2μm diameter (or less) clay minerals—namely: Bueker flint clay (kaolinite), Keokuk and Georgia kaolinites, Wyoming and Arizona montmorillonites, and Beavers Bend and Fithian illites—were equilibrated in deionized water at room temperature for periods of up to 102 days. The detailed experimental procedure and results were reported in an earlier paper (Huang and Keller, 1971). The laboratory results show that the most rapid dissolution of framework cations of clay minerals occurs with the first 24 hours, begins to slow down in the 5-day interval, and approaches a constant value which is apparently nearly achieved after 102 days (see Figure 1, Huang and Keller, 1971). Although *complete* equilibrium can not be established, the concentrations of ions at 102 days which were used for the calculation of $\Delta G°_f$ may be taken as "apparently" equilibrated or near-equilibrated concentrations, and the solubilities (K_s) calculated from these apparently equilibrated concentrations as "apparent" solubilities.

Assumptions and Calculations

The necessary steps and assumptions in calculation of $\Delta G°_f$ discussed earlier (Huang and Keller, 1972b; Huang and Kiang, 1973) include (1) the determination of species concentration in the equilibrated solution, (2) the calculation of activity coefficients (using the

Debye-Hückel method) of individual ions from analytical concentrations, (3) the calculation of solubility constants (K_s) from the activities of dissolved species, (4) the calculation of Gibbs free energies of reaction by the equation, $\Delta G^\circ_r = -1.364 \log K_s$, and (5) the determination of Gibbs free energy of formation (ΔG°_f) for the minerals from an equation in which $\Delta G^\circ_r = \Sigma \Delta G^\circ_f$ (products) $- \Sigma \Delta G^\circ_f$ (reactants), using known ΔG°_f of other species in the equation (see Table 1, Huang and Kiang, 1973).

Because the distribution of each ion of Al, Fe, Mg, or Ca in aqueous solution depends on pH and the total analytical concentration of the ions, their proportions can be calculated from the equilibrium constants, as typified by the calculation of each Al species in the solution as follows (Huang and Keller, 1972a):

(1) $[H^+][OH^-] = 10^{-14.0}$

(2) $[H^+]^4[Al(OH)_4^-] = 10^{-23.5}[Al^{3+}]$

(3) $[H^+][Al(OH)^{2+}] = 10^{-4.89}[Al^{3+}]$

(4) $[H^+]^2[Al(OH)_2^+] = 10^{-8.56}[Al^{3+}]$

(5) $[H^+]^2[Al_2(OH)_2^{4+}] = 10^{-6.6}[Al^{3+}]^2$

(6) $[Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2^+] + [Al(OH)_4^-] + 2[Al_2(OH)_2^{4+}] = \Sigma C_{Al}$

An IBM 306/65 computer was used to solve the above six simultaneous equations for Al species. The results of the calculations of Al, Fe, Mg, and Ca species are given in Table 1.

Results and Discussion

(A) ΔG°_f *Based on Aqueous Solubility Data*

The mineral formulas of the clay minerals, which were derived from the bulk analyses as obtained from the literature (see Grim, 1968) and unpublished data for Wyoming montmorillonite (Keller, unpublished), are shown below in the dissolution reaction of the minerals in deionized water at 25°C, 1 atmosphere.

(I) *Flint clay* (Bueker flint clay-kaolinite)

$Al_2Si_2O_5(OH)_4 + 5\,H_2O = 1.78\,Al(OH)_2^+ + 0.22\,Al(OH)_4^- + 2\,H_4SiO_4 + 1.56\,OH^-$ $K_s = [Al(OH)_2^+]^{1.78}[Al(OH)_4^-]^{0.22}[H_4SiO_4]^2[OH^-]^{1.56}$

By substituting activities of individual species from Table 1,

Then, $\log K_s = -29.26$

Since $\Delta G^\circ_r = \Sigma \Delta G^\circ_f$ (products) $- \Sigma \Delta G^\circ_f$ (reactants)

$\Delta G^\circ_f = -853.85 - \Delta G^\circ_f$ (Bueker flint clay)

Since $\Delta G^\circ_r = -1.364 \log K_s$

Then, ΔG°_f (Bueker flint clay) $= -853.85 + 1.364 \log K_s = -893.8$ kcal/mole. Our data on ΔG°_f for Bueker flint clay (-893.8 kcal/mole) is considerably larger than the reported data of -900 to -904 kcal/mole by Reesman and Keller (1968). The difference in ΔG°_f for the sample may be attributed to consideration of the proportion of different Al species at pH = 6.82 in our calculations.

(II) *Kaolinites*

(A) Keokuk kaolinite

$Al_2Si_2O_5(OH)_4 + 7\,H_2O = 2\,Al(OH)_4^- + 2\,H_4SiO_4 + 2H^+$

Then ΔG°_f (Keokuk kaolinite) $= -902.7$ kcal/mole; where $K_s = 10^{-37.80}$

(B) Georgia kaolinite

1) ΔG°_f of Georgia kaolinite from the specific mineral formula.

$(Al_{1.98}Mg_{0.03})Si_2O_5(OH)_4 + 5\,H_2O = 0.04\,Al(OH)^{2+} + 1.84\,Al(OH)_2^+ + 0.10\,Al(OH)_4^- + 0.03\,Mg^{2+} + 2\,H_4SiO_4 + 1.88\,OH^-$

Then, ΔG°_f (Georgia kaolinite) $= -903.5$ kcal/mole; where $K_s = 10^{-38.24}$

2) ΔG°_f of Georgia kaolinite in terms of the ideal structural formula.

$Al_2Si_2O_5(OH)_4 + 5\,H_2O = 0.04\,Al(OH)^{2+} + 1.86\,Al(OH)_2^+ + 0.10\,Al(OH)_4^- + 2\,H_4SiO_4 + 1.85\,OH^-$

Then, ΔG°_f (ideal) $= -902.5$ kcal/mole; where $K_s = 10^{-37.82}$

The difference in ΔG°_f for Georgia kaolinite by the two calculations is 1.0 kcal/mole. The ΔG°_f for Keokuk kaolinite (-902.7 kcal/mole) and for Georgia kaolinite (-903.5 or -902.5 kcal/mole) agree well with those values of ΔG°_f -902.5 to -903.8 kcal/mole for kaolinites calculated by Kittrick (1966) and with the value of ΔG°_f -902.9 kcal/mole for kaolinite reported by Robie and Waldbaum (1968) ,but differ slightly from the value ΔG°_f -904.0 ± 0.2 kcal/mole calculated by Reesman and Keller (1968). Nevertheless, the reasonably good agreement in ΔG°_f for kaolinite seems to corroborate the validity of our calculations.

(III) *Montmorillonites*

(A) Wyoming montmorillonite (Clay spur, *Na-rich* montmorillonite)

$(Na_{0.27}Ca_{0.10}K_{0.02})(Al_{1.52}Fe^{3+}{}_{0.19}Mg_{0.22})(Si_{3.94}Al_{0.06})O_{10}(OH)_2 + 10.46\ H_2O = 0.27\ Na^+ + 0.10\ Ca^{2+} + 0.02\ K^+ + 1.58\ Al(OH)_4^- + 0.19\ Fe(OH)_2^+ + 0.22\ Mg^{2+} + 3.94\ H_4SiO_4 + 0.46\ H^+$

Then $\Delta G°_f$ (Wyoming montmorillonite) $= -1248.2$ kcal/mole; where $K_s = 10^{-30.53}$

(B) Arizona montmorillonite (Cheto, *Ca-rich* montmorillonite)

$(Ca_{0.19}Na_{0.02}K_{0.02})(Al_{1.52}Fe^{3+}{}_{0.14}Mg_{0.33})(Si_{3.93}Al_{0.07})O_{10}(OH)_2 + 10\ H_2O = 0.19\ Ca^{2+} + 0.02\ Na^+ + 0.02\ K^+ + 0.94\ Al(OH)_2^+ + 0.65\ Al(OH)_4^- + 0.14\ Fe(OH)_2^+ + 0.33\ Mg^{2+} + 3.93\ H_4SiO_4 + 1.51\ OH^-$

Then $\Delta G°_f$ (Arizona montmorillonite) $= -1252.1$ kcal/mole; where $K_s = 10^{-36.08}$

The values of $\Delta G°_f$ for both Wyoming and Arizona montmorillonites differ by about 20 kcal/mole from the values (−1270 for Wyoming and −1274.4 for Arizona) reported by Reesman and Keller (1968). The difference in $\Delta G°_f$ is due to (1) the consideration of the proportion of different Al species, and (2) the Fe species included in our calculations. The value of $\Delta G°_f$ (−1248.2 kcal/mole) for Wyoming montmorillonite, however, is slightly larger than the value of $\Delta G°_f$ (−1234.3 kcal/mole) calculated from solubility data by Kittrick (1971). The difference may be due to the Na, Ca, and K species included in our calculations but omitted in his.

(IV) *Illites*

(A) Beavers Bend illite

$(K_{0.60}Na_{0.04})(Al_{1.43}Fe^{3+}{}_{0.42}Mg^{2+}{}_{0.16})(Si_{3.48}Al_{0.52})O_{10}(OH)_2 + 10\ H_2O = 0.60\ K^+ + 0.04\ Na^+ + 1.03\ Al(OH)_2^+ + 0.92\ Al(OH)_4^- + 0.42\ Fe(OH)_2^+ + 0.16\ Mg^{2+} + 3.48\ H_4SiO_4 + 1.49\ OH^-$

Then, $\Delta G°_f = -1250.5$ kcal/mole; where $K_s = 10^{-43.31}$

(B) Fithian illite

$(K_{0.59}Na_{0.02}Ca_{0.01})(Al_{1.54}Fe^{3+}{}_{0.29}Mg_{0.23})(Si_{3.47}Al_{0.53})O_{10}OH_2 + 10.03\ H_2O = 0.59\ K^+ + 0.02\ Na^+ + 0.01\ Ca^{2+} + 1.08\ Al^{3+} + 0.23\ Al(OH)^{2+} + 0.76\ Al(OH)_2^+ + 0.22\ Fe(OH)^{2+} + 0.07$

TABLE. 1. Analytical Data and Activities of Dissolved Species in the Dissolution of Clay Minerals

Species	Moles/liter	Activity	Log act.
(I) BUEKER FLINT CLAY			
pH = 6.82; ionic strength = 5.91×10^{-5}			
$Al(OH)_2^+$	0.103×10^{-4}	0.102×10^{-4}	-4.99
$Al(OH)_4^-$	0.127×10^{-5}	0.120×10^{-5}	-5.92
H_4SiO_4	0.114×10^{-3}	0.114×10^{-3}	-3.94
OH^-		$10^{-7.18}$	-7.18
(II) KAOLINITES			
(A) Keokuk kaolinite; pH = 8.19; ionic strength = 9.76×10^{-4}			
$Al(OH)_4^-$	0.130×10^{-5}	0.125×10^{-5}	-5.90
H_4SiO_4	0.155×10^{-4}	0.155×10^{-4}	-4.81
OH^-		$10^{-5.81}$	-5.81
(B) Georgia kaolinite; pH = 5.37, ionic strength = 6.05×10^{-6}			
$Al(OH)_2^+$	0.862×10^{-6}	0.858×10^{-6}	-6.07
$Al(OH)_4^-$	0.464×10^{-7}	0.427×10^{-7}	-7.37
$Al(OH)^{2+}$	0.185×10^{-7}	0.171×10^{-7}	-7.77
Mg^{2+}	0.206×10^{-6}	0.203×10^{-6}	-6.69
H_4SiO_4	0.160×10^{-4}	0.160×10^{-4}	-4.80
OH^-		$10^{-8.63}$	-8.63
(III) MONTMORILLONITES			
(A) Wyoming montmorillonite; pH = 8.20; ionic strength = 1.01×10^{-3}			
Na^+	0.170×10^{-2}	0.164×10^{-2}	-2.79
Ca^{2+}	0.823×10^{-5}	0.1716×10^{-5}	-5.15
K^+	0.169×10^{-4}	0.163×10^{-4}	-4.79
$Al(OH)_4^-$	0.371×10^{-5}	0.358×10^{-5}	-5.45
$Fe(OH)_2^+$	0.287×10^{-4}	0.249×10^{-4}	-4.60
Mg^{2+}	0.393×10^{-4}	0.342×10^{-4}	-4.47
H_4SiO_4	0.161×10^{-3}	0.161×10^{-3}	-3.79
OH^-		$10^{-5.80}$	-5.80
(B) Arizona montmorillonite; pH = 7.28; ionic strength = 1.74×10^{-4}			
Ca^{2+}	0.594×10^{-4}	0.559×10^{-4}	-4.25
Na^+	0.154×10^{-4}	0.151×10^{-4}	-4.82
K^+	0.200×10^{-4}	0.194×10^{-4}	-4.71
$Al(OH)_2^+$	0.503×10^{-5}	0.493×10^{-5}	-5.31
$Al(OH)_4^-$	0.349×10^{-5}	0.347×10^{-5}	-5.46
$Fe(OH)_2^+$	0.448×10^{-6}	0.420×10^{-6}	-6.37
Mg^{2+}	0.163×10^{-4}	0.154×10^{-4}	-4.81
H_4SiO_4	0.289×10^{-3}	0.289×10^{-3}	-3.54
OH^-		$10^{-6.72}$	-6.72
(IV) ILLITES			
(A) Beavers Bend illite; pH = 6.79; ionic strength = 7.11×10^{-5}			
K^+	0.335×10^{-5}	0.332×10^{-5}	-5.48
Na^+	0.913×10^{-4}	0.905×10^{-4}	-4.04
$Al(OH)_2^+$	0.128×10^{-5}	0.126×10^{-5}	-5.90
$Al(OH)_4^-$	0.113×10^{-5}	0.112×10^{-5}	-5.95
$Fe(OH)_2^+$	0.663×10^{-6}	0.632×10^{-6}	-6.20
Mg^{2+}	0.954×10^{-5}	0.918×10^{-5}	-5.04
H_4SiO_4	0.858×10^{-4}	0.858×10^{-4}	-4.07
OH^-		$10^{-7.21}$	-7.21
(B) Fithian illite; pH = 4.21; ionic strength = 1.85×10^{-4}			
K^+	0.361×10^{-4}	0.355×10^{-4}	-4.45
Na^+	0.870×10^{-5}	0.856×10^{-5}	-5.07
Ca^{2+}	0.389×10^{-4}	0.366×10^{-4}	-4.44
Al^{3+}	0.251×10^{-5}	0.245×10^{-5}	-5.61
$Al(OH)^{2+}$	0.530×10^{-6}	0.512×10^{-6}	-6.29
$Al(OH)_2^+$	0.178×10^{-5}	0.178×10^{-5}	-5.75
$Fe(OH)^{2+}$	0.323×10^{-5}	0.303×10^{-5}	-5.52
$Fe(OH)_2^+$	0.108×10^{-5}	0.981×10^{-6}	-6.01
Mg^{+2}	0.219×10^{-4}	0.206×10^{-4}	-4.69
H_4SiO_4	0.798×10^{-4}	0.798×10^{-4}	-4.10
OH^-		$10^{-9.79}$	-9.79

$Fe(OH)_2^+ + 3.47\ H_4SiO_4 + 6.06\ OH^-$
Then, $\Delta G^\circ_f = -1282.1$ kcal/mole; where $K_s = 10^{-90.92}$. Our values for both illites (−1250.5 and −1282.1 kcal/mole) again exceed those (−1307.7 and 1318.0 kcal/mole) reported by Reesman and Keller (1968) who did not differentiate hydrated Al species.

(B) *ΔG°_f Based on Equilibrium with Secondary Phase*

The analyses of extracted solutions (Table 1) show that the concentration of Al or Fe^{3+} in the solution is less than that of Si in the mineral formula. This suggests that a secondary Al- or Fe^{3+}-hydroxide could form during the dissolution of a clay mineral. As in the case of the dissolution of plagioclase feldspars (Huang and Kiang, 1973), a secondary phase such as gibbsite, microcrystalline gibbsite, or amorphous Al- or Fe^{3+}-hydroxide ($\Delta G^\circ_f = -166.0$ kcal/mole for amorphous $Fe(OH)_3$, Latimer, 1952) may be assumed in the equilibrium equation from which ΔG°_f for the clay mineral is calculated. The results of such calculations are as follows:

(I) *Flint clay* (Bueker flint clay-kaolinite)

$Al_2Si_2O_5(OH)_4 + 5\ H_2O = 0.18\ Al(OH)_2^+ + 0.02\ Al(OH)_4^- + 2\ H_4SiO_4 + 0.160\ H^- + 1.80\ Al(OH)_3$
Then, ΔG°_f (Bueker flint clay) = −895.2 kcal/mole (with respect to equilibrium with amorphous $Al(OH)_3$).

The results of ΔG°_f for flint clay and other clay minerals, calculated with respect to microcrystalline gibbsite, or gibbsite, are shown in Table 2.

TABLE 2. Comparison of ΔG°_f Obtained from Different Calculations

	ΔG°_f based on aqueous solubility data	ΔG°_f based on equilibrium with secondary phase*			
		A	B	C	D
Flint clay (Bueker)	-893.8	-895.2	-897.0	-900.0	-902.4
Kaolinites					
Keokuk	-902.7	-900.6	-902.5	-905.4	-908.0
Georgia	-903.5	-899.0	-900.9	-903.9	-906.5
Georgia (ideal)	-902.5	-898.0	-899.9	-902.9	-905.5
Montmorillonites					
Wyoming (Na-)	-1248.2	-1242.1	-1243.6	-1245.9	-1248.0
Arizona (Ca-)	-1252.1	-1252.8	-1254.3	-1256.6	-1258.7
Illites					
Beavers Bend	-1250.5	-1251.1	-1253.0	-1255.9	-1258.5
Fithian	-1282.1	-1274.6	-1276.4	-1279.5	-1282.1

*A: Equilibrium with amorphous $Al(OH)_3$ (ΔG°_f = -271.3 kcal/mole)
B: Equilibrium with microcrystalline gibbsite (ΔG°_f = -272.3 kcal/mole)
C: Equilibrium with gibbsite (ΔG°_f = -273.9 kcal/mole)
D: Equilibrium with gibbsite (ΔG°_f = -275.3 kcal/mole)

(II) *Kaolinites*

(A) Keokuk kaolinite
$Al_2Si_2O_5(OH)_4 + 0.16\ H^- + 5\ H_2O = 0.16\ Al(OH)_4^- + 2\ H_4SiO_4 + 1.84\ \underline{Al(OH)_3}$
Then, ΔG°_f (Keokuk kaolinite) = −900.6 kcal/mole (with respect to equilibrium with amorphous $Al(OH)_3$).

(B) Georgia kaolinite
(1) ΔG°_f of Georgia kaolinite calculated from the specific mineral formula.
$(Al_{1.98}Mg_{0.03})Si_2O_5(OH)_4 + 5\ H_2O = 0.10\ Al(OH)_2^+ + 0.03\ Mg^{2+} + 2\ H_4SiO_4 + 0.15\ OH^- + 1.87\ \underline{Al(OH)_3}$
Then ΔG°_f (Georgia kaolinite) = −899.0 kcal/mole (with respect to equilibrium with amorphous $Al(OH)_3$).
(2) ΔG°_f of Georgia kaolinite in terms of ideal structural formula. $Al_2Si_2O_5(OH)_4 + 5\ H_2O = 0.10\ Al(OH)_2^+ + 0.01\ Al(OH)_4^- + 2\ H_4SiO_4 + 0.09\ OH^- + 1.89\ \underline{Al(OH)_3}$
Then, ΔG°_f (ideal) = −898.0 kcal/mole (with respect to equilibrium with amorphous $Al(OH)_3$.

(III) *Montmorillonites*

(A) Wyoming montmorillonite
$(Na_{0.27}Ca_{0.10}K_{0.02})(Al_{1.52}Fe^{3+}_{0.19}Mg_{0.22})(Si_{3.94}Al_{0.06})O_{10}(OH)_2 + 0.42\ Fe(OH)_3 + 10\ H_2O = 0.27\ Na^+ + 0.10\ Ca^{2+} + 0.02\ K^+ + 0.22\ Mg^{2+} + 0.61\ Fe(OH)^+_2 + 0.09\ Al(OH)_4^- + 3.94\ H_4SiO_4 + 1.45\ OH^- + 1.49\ \underline{Al(OH)_3}$
Then, ΔG°_f (Wyoming montmorillonite) = −1242.1 kcal/mole (with respect to equilibrium with amorphous $Al(OH)_3$).

(B) Arizona montmorillonite
$(Ca_{0.19}Na_{0.02}K_{0.02})(Al_{1.52}Fe^{3+}_{0.14}Mg_{0.23})(Si_{3.93}Al_{0.07})O_{10}(OH)_2 + 10\ H_2O = 0.19\ Ca^{2+} + 0.02\ Na^+ + 0.02\ K^+ + 0.23\ Mg^{2+} + 0.01\ Fe(OH)_2^+ + 0.07\ Al(OH)_2^+ + 0.04\ Al(OH)_4^- + 3.93\ H_4SiO_4 + 1.12\ OH^- + 0.13\ \underline{Fe(OH)_3} + 1.48\ \underline{Al(OH)_3}$
Then, ΔG°_f (Arizona montmorillonite) = −1252.8 kcal/mole (with respect to equilibrium with amorphous $Al(OH)_3$)

(IV) *Illites*

(A) Beavers Bend illite $(K_{0.60}Na_{0.04})(Al_{1.43}Fe^{3+}_{0.42}Mg_{0.16})(Si_{3.48}Al_{0.52})O_{10}(OH)_2 + 10\ H_2O = 0.60\ K^+ + 0.04\ Na^+ + 0.16\ Mg^{2+} + 0.03\ Fe(OH)_2^+ + 0.05\ Al(OH)_2^+ + 0.05\ Al(OH)_4^- + 3.48\ H_4SiO_4 + 0.99\ OH^- + 0.39\ \underline{Fe(OH)_3} + 1.85\ \underline{Al(OH)_3}$

Then, $\Delta G°_f$ (Beavers Bend illite) = −1251.1 kcal/mole (with respect to equilibrium with amorphous $Al(OH)_3$)

(B) Fithian illite $(K_{0.59}Na_{0.02}Ca_{0.01})(Al_{1.54}Fe^{3+}_{0.29}Mg_{0.23})(Si_{3.47}Al_{0.53})O_{10}(OH)_2 + 10.03\ H_2O = 0.59\ K^+ + 0.02\ Na^+ + 0.01\ Ca^{2+} + 0.23\ Mg^{2+} + 0.13\ Fe(OH)^{2+} + 0.04\ Fe(OH)_2^+ + 0.11\ Al^{3+} + 0.02\ Al(OH)^{2+} + 0.08\ Al(OH)_2^+ + 3.47\ H_4SiO_4 + 1.84\ OH^- + 0.12\ \underline{Fe(OH)_3} + 1.86\ \underline{Al(OH)_3}$

Then, $\Delta G°_f$ = −1274.6 kcal/mole (with respect to equilibrium with amorphous $Al(OH)_3$).

As shown in Table 2, $\Delta G°_f$ calculated for each mineral on the basis of equilibrium with secondary phase is somewhat different from $\Delta G°_f$ calculated from aqueous solubility data.

Conclusions

(1) Our values for $\Delta G°_f$ for flint clay, montmorillonites, and illites of specific mineral formulas are higher than the values reported by Reesman and Keller (1968). The difference in $\Delta G°_f$ is due to (1) inclusion of Fe species in our calculations but not in theirs, and/or (2) the consideration of the proportion of different Al (and Fe) hydrated species in our calculation (rather than by assuming a species in our calculation). Nevertheless, $\Delta G°_f$ values calculated from dissolution data for kaolinites agree reasonably well with values determined by other procedures. Table 2 suggests that the probable errors in our calculation are low, and add confidence to $\Delta G°_f$ values obtained by our calculation. Further discussion in the uncertainties and possible sources of error were reported in an earlier paper (Huang and Keller, 1972).

(2) Thus, it is noteworthy that Na-rich varieties have larger $\Delta G°_f$ values than Ca-rich varieties for the following minerals, the parenthesized values for $\Delta G°_f$ being in kcal/mole: (a) Montmorillonites, from Wyoming (−1248.2) *vs* Ca-rich from Arizona (−1252.1); (b) Plagioclases, albite, $Ab_{95}An_1Or_4$ (−897.1) *vs* bytownite, $Ab_{12}An_{86}Or_2$ (−959.4); (c) Illites, Beavers Bend, $K_{0.60}Na_{0.04}$ (−1250.5) *vs* Fithian, $K_{0.59}Na_{0.02}Ca_{0.01}$ (−1282.1); and (d) Pyroxenes, jadeite, $NaAlSi_2O_6$, (−677.2) *vs* Ca–Al pyroxene, $CaAl_2SiO_6$ (−745.1). The data on plagioclase and pyroxene are taken from Huang and Kiang (1973) and Robie and Waldbaum (1968), respectively.

TABLE 3. A Comparison of Gibbs Free Energies of Formation for Clay Minerals (kcal/mole)

Mineral	Huang and Keller (1973)	Others
Flint clay		
(Bueker)	-893.8	
Kaolinites*		-902.9 (Robie and Waldbaum, 1968)
Keokuk	-902.7	
Georgia	-903.5	
Georgia (ideal)	-902.5	
Montmorillonites		
Wyoming (Na-)	-1248.2	-1270 (Reesman and Keller, 1968) -1234.3 (Kittrick, 1971)
Arizona (Ca-)	-1252.1	-1274.4 (Reesman and Keller, 1968)
Illites		
Beavers Bend	-1250.5	-1307.7 (Reesman and Keller, 1967)
Fithian	-1282.1	-1318.0 (Reesman and Keller, 1967)

* -902.5 -- -903.8 kcal/mole (Kittrick, 1966)

* -904.0 ± 0.2 kcal/mole (Reesman and Keller, 1968)

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