

Thermochemical Approximations for Clay Minerals

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Abstract

The Gibbs energies of formation for clay minerals have been approximated by a model which assumes that these minerals are formed by the combination of silicon hydroxide with metal hydroxides. The change in free energy during the polymerization of hydroxides to form silicates plus water is shown to be generally small and has been represented by a correction term. The dispersion between the predicted and the experimental data of better than ± 2.0 kcal mol⁻¹ is comparable to the total uncertainty in the experimentally determined constants. The approximated free energies of formation for vermiculites and ferromagnesium chlorites are presented.

Introduction

The study of the chemical constraints which predicate the environments of formation (or alteration) of clay minerals has been hindered by the sparsity of relevant thermochemical constants. Although several workers have determined the Gibbs free energy of formation (ΔG_f°) for kaolinite (*e.g.*, see Polzer and Hem, 1965; Kittrick, 1969; Reesman and Keller, 1968; Huang and Keller, 1973), few (if any) ΔG_f° for the other clay minerals are available. The recently reported ΔG_f° for montmorillonites and illites (Reesman and Keller, 1968; Helgeson, 1969; Huang and Keller, 1973) pertain to specific or idealized minerals and may be of limited geochemical applicability. The ΔG_f° for ferromagnesium chlorites and vermiculites remain to be determined.

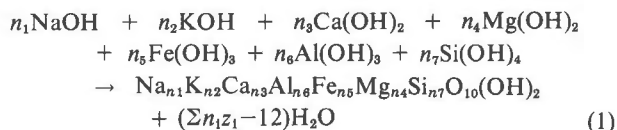
This report presents a method for approximating the ΔG_f° for clay minerals with an accuracy which is adequate for many geochemical calculations. It is intended as a first step towards developing better methods for approximating the ΔG_f° for these minerals; the gambit will undoubtedly be modified and extended as accurate experimental data become available. Obviously there is a need for methods to estimate the ΔG_f° values for clay minerals. The experimental determinations are difficult, and many have considerable room for improvement. Clay minerals show considerable variations in composition, and it is unlikely that the ΔG_f° for every one of them will ever be determined experimentally.

The Predictive Method

The predictive method employed in this report considers the clay minerals to be formed by the com-

ination ("polymerization") of simple metal hydroxides with silicon hydroxide, Si(OH)₄. The change in free energy during the polymerization of the hydroxides to form clay minerals is usually small and has been approximated by a one parameter correction term. The model in its present form is essentially heuristic and the validity for its use rests chiefly on the good agreement between the predicted and experimental data.

The mechanics of the procedure may be illustrated by considering the formation reaction of a typical montmorillonite:



where n_i is the reaction coefficient of the i -th hydroxide and z_i is the charge on the i -th cation (including Si). Usually n_i corresponds to the amount of the i -th cation (or silicon) in the formula unit for the clay mineral. The free energy of formation for the clay mineral whose formation is described by the above reaction is calculated by the expression:

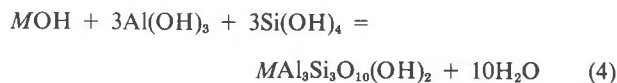
$$\Delta G_f^\circ (\text{Montm.}) = \sum n_i \Delta G_f^\circ (r_i) - (\sum n_i z_i - 12)\Delta G_f^\circ (\text{H}_2\text{O}) - Q \quad (2)$$

where $\Delta G_f^\circ (r_i)$ is the free energy of formation of the i -th hydroxide component and Q is an empirical correction factor defined as

$$Q = \sigma(n_i z_i - 12) \quad (3)$$

i.e., Q is expressed as a function of the number of moles of water released during the reaction.

The free energy data for the hydroxide components are given in Table 1. It became apparent that the published ΔG_f^0 values for solid alkali metal hydroxides resulted in predicted data which were consistently higher than the experimental results. The strategy was therefore adopted (I thank Professor R. M. Garrels for the suggestion) to derive the necessary free energies for KOH and NaOH from the published ΔG_f^0 values for muscovite and paragonite. The following reactions were considered:



Where M is K or Na. Employed in these calculations were ΔG_f^0 (muscovite) = -1330 kcal (Zen, Set 2, 1972; Robie and Waldbaum, 1968) and ΔG_f^0 (paragonite) = -1318 kcal (Zen, Set 2, 1972). The ΔG_f^0 for KOH and NaOH so derived are shown in Table 1.

The expression for Q is *empirical*. According to Equation (1), the hydroxides polymerize to form silicate + water, and Q may be envisaged as the sum of the dehydration energies of the water molecules split out. In other words, the dehydration of the hydroxides during the formation of silicates may be analogous to the splitting out of water during the formation of a polymer. It was found during the study that the best fit between the experimental and predicted data was obtained when σ was assigned a constant value of 0.39. Thus $Q = 0.39 \times$ (the number of moles of water liberated). Attempts to fit the experimental data with Q terms which were functions of mole fractions (see also Nriagu, 1974; Nriagu and Dell, 1974) resulted in dispersions which were either larger or comparable to those obtained with Equation (3).

TABLE 1. Thermodynamic Constants for Ions and Compounds Used in the Calculation of the Free Energy Data for Clay Minerals*

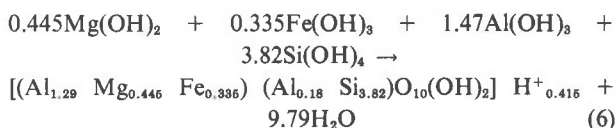
Ion, compound	ΔG_f^0 , kcal mol ⁻¹	Source
H ₂ O	-56.69	Wagman et al., 1968
KOH	-114.6	See text
NaOH	-102.6	See text
Ca(OH) ₂	-214.22	Garrels and Christ, 1965
Mg(OH) ₂	-202.12	Helgeson, 1969
Al(OH) ₃	-274.2	Kittrick, 1969
Fe(OH) ₂	-118.5	See, Nriagu and Dell, 1974
Fe(OH) ₃	-166.5	Wagman et al., 1969
H ₄ SiO ₄ (amorphous)	-318.6	Wagman et al., 1968

* These data have been found to give the least deviation between the predicted and experimentally determined free energies of formation.

For the kaolinite group of minerals, $\Sigma n_i z_i = 14$. For the other groups of clay minerals, the relation

$$\Sigma n_i z_i = 22 \quad (5)$$

is generally true, *i.e.*, the sum of the hydroxyl ions of the constitutive metal hydroxides is 22. Where there is a charge imbalance in the reported compositions of the clay mineral ($\Sigma n_i z_i < 22$ in most cases), the clay mineral has been assumed to be in the H⁺ form. The composition for Aberdeen montmorillonite reported by Kittrick (1971) serves to illustrate the calculative procedure for clay minerals in H⁺ form:



Since $\Delta G_f^0(H^+) = 0$, therefore

$$\Delta G_f^0(\text{Aberdeen montm.}) = \Sigma n_i \Delta G_f^0(r_i) \\ - 9.79 \Delta G_f^0(H_2O) - Q, \text{ with } Q = 0.39 \times 9.79 \quad (7)$$

Although H⁺ does not figure in the free energy calculation, it must be considered in the calculation of activity products.

Finally, the calculative procedure is illustrated explicitly by considering the formation reaction for kaolinite:



$$\Delta G_f^0(\text{kaolinite}) = 2(-274.2) + 2(-318.6) - 5(-56.69) \\ - 5 \times 0.39 = -904.1 \quad (9)$$

This value is shown in Table 2 along with the predicted ΔG_f^0 values for other clay minerals.

Discussion

Table 2 compares the predicted and experimental ΔG_f^0 values for the various clay minerals. The error bounds for the predicted ΔG_f^0 data have been assessed by means of the expression:

Error range

$$= \left[\frac{(\Delta G_{f(\text{experimental})} - \Delta G_{f(\text{predicted})})^2}{m} \right]^{1/2} \quad (10)$$

where m is the number of listed data for the particular group of clay minerals.

It is seen (Table 2) that the predicted ΔG_f^0 value for kaolinite agrees quite well (± 0.6 kcal fw⁻¹; fw = formula weight) with the experimental data. The agreement between the predicted and experimental data for montmorillonites of ± 2.0 kcal fw⁻¹ should be considered excellent. The consistently poorer agree-

TABLE 2. Predicted and Experimental Free Energy Values for Clay Minerals

Clay Mineral	Chemical Composition	Predicted ΔG_f^0 , kcal/fw	Reported ΔG_f^0 , kcal/fw
Kaolinite	$Al_2Si_2O_5(OH)_4$	- 903.8	- 903.0 (Baranay and Kelly, 1961) - 903.6 (Polzer and Hem, 1965) - 903.8 (Kittrick, 1969) - 902.9 (Robie and Waldbaum, 1968) - 904.0 (Reesman and Keller, 1968) - 902.87 (Zen, 1972) - 902.7 (Huang and Keller, 1973)
Georgian kaolinite	$Al_{1.98}Mg_{0.03}Si_2O_5(OH)_4$	- 904.3	- 903.5 "
Arizona montmorillonite	$(Ca_{0.19}Na_{0.02}K_{0.02})(Al_{1.52}Fe_{0.14}^{3+}Mg_{0.33})(Si_{3.93}Al_{0.07})O_{10}(OH)_2$	-1253.1	-1252.1 "
Wyoming montmorillonite	$(Ca_{0.1}Na_{0.27}K_{0.02})(Al_{1.52}Fe_{0.19}^{3+}Mg_{0.22})(Si_{3.94}Al_{0.06})O_{10}(OH)_2$	-1252.6	-1248.2 " -1251.6 (R.M. Garrels, Pers. Comm.)
Aberdeen montmorillonite	$(Al_{1.29}Mg_{0.445}Fe_{0.335}^{3+})(Al_{0.18}Si_{3.82})O_{10}(OH)_2$	-1224.6	-1225.2 (Kittrick, 1971)
Mg-montmorillonite	$Mg_{0.20}(Si_{3.81}Al_{1.71}Fe_{0.22}^{3+}Mg_{0.29})O_{10}(OH)_2$	-1254.7	-1255.8 (Weaver et al., 1971)
Mg-montmorillonite (beidellite)	$Mg_{0.67}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	-1278.8	-1275.3 (Helgeson, 1969)
Ca-montmorillonite (beidellite)	$Ca_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	-1280.8	-1279.2 (Helgeson, 1969)
K-montmorillonite (beidellite)	$K_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	-1282.5	-1279.6 "
Na-montmorillonite (beidellite)	$Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	-1279.5	-1277.8 " -1278.8 (M.E. Thompson, Pers. Comm.)
Beavers Bend illite	$(K_{0.60}Na_{0.04})(Al_{1.43}Fe_{0.42}^{3+}Mg_{0.16})(Si_{3.48}Al_{0.52})O_{10}(OH)_2$	-1254.6	-1250.5 (Huang and Keller, 1973)
Beavers Bend illite	$K_{0.53}(Al_{1.66}Fe_{0.2}^{3+}Mg_{0.13})(Si_{3.62}Al_{0.38})O_{10}(OH)_2$	-1269.2	-1267.6 (Routson and Kittrick, 1971)
Fithian illite	$K_{0.64}(Al_{1.54}Fe_{0.29}^{3+}Mg_{0.19})(Si_{3.51}Al_{0.49})O_{10}(OH)_2$	-1270.0	-1270.6 "
Goose Lake illite	$K_{0.59}(Al_{1.58}Fe_{0.24}^{3+}Mg_{0.15})(Si_{3.65}Al_{0.35})O_{10}(OH)_2$	-1266.1	-1265.3 "
Illite	$K_{0.6}Mg_{0.25}Al_{2.30}Si_{3.50}O_{10}(OH)_2$	-1301.5	-1301.0 (Helgeson, 1969)
Mg-chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8$	-1955.4	-1954.8 "
Chlorite	$Fe_{0.2}^{2+}Mg_{4.8}Al_2Si_3O_{10}(OH)_8$	-1938.2	-
	$Fe_{0.5}^{2+}Mg_{4.5}Al_2Si_3O_{10}(OH)_8$	-1912.7	-
	$Fe_{2}^{2+}Mg_4Al_2Si_3O_{10}(OH)_8$	-1870.3	-

ment between the predicted data and the experimental results of Huang and Keller (1973) should be noted; without their data, the agreement between the predicted and experimental results is better than 2 kcal fw⁻¹. Illites show the same disparity (± 2.0 kcal

fw⁻¹) between the predicted and experimental ΔG_f^0 values as do montmorillonites. It should have been recognized that the "predictability" of the ΔG_f^0 data for these minerals is comparable to the accuracy with which these constants are experimentally "known."

TABLE 2, Continued

Vermiculite	$(\text{Mg}_{2.71}\text{Fe}_{0.02}^{2+}\text{Fe}_{0.46}^{3+}\text{Ca}_{0.06}\text{K}_{0.10})$ $(\text{Si}_{2.91}\text{Al}_{1.14})\text{O}_{10}(\text{OH})_2$	-1326.9 *	-
	$(\text{Mg}_{2.82}\text{Fe}_{0.02}^{2+}\text{Fe}_{0.43}^{3+}\text{Ca}_{0.03}\text{K}_{0.01})$ $(\text{Si}_{2.91}\text{Al}_{1.14})\text{O}_{10}(\text{OH})_2$	-1327.6 *	-
Vermiculite (idealized formula)	$(\text{Mg}_3\text{Fe}_{0.5}^{3+})(\text{Si}_{2.95}\text{Al}_{1.1})\text{O}_{10}(\text{OH})_2$	-1367.9	-
'Average' montmorillonite	$\text{K}_{0.4}(\text{Mg}_{0.34}\text{Fe}_{0.17}^{3+}\text{Fe}_{0.04}^{2+}\text{Al}_{1.50})$ $(\text{Al}_{0.17}\text{Si}_{3.83})\text{O}_{10}(\text{OH})_2$	-1261.4	-1260.6 **
'End member' illite	$\text{K}_{0.4}(\text{Mg}_{0.34}\text{Fe}_{0.17}^{3+}\text{Fe}_{0.04}^{2+}\text{Al}_{1.50})$ $(\text{Al}_{0.17}\text{Si}_{3.83})\text{O}_{10}(\text{OH})_2$	-1289.0	-1291.8 **

* These compositions correspond approximately to those of Libby (Montana) vermiculites reported by Boettcher (1968).

** Predicted by the method of Tardy and Garrels (1974).

The agreement between the predicted and experimental ΔG_f° shown by the data in Table 2 is rather remarkable considering (a) the wide range in composition of the clay minerals represented and (b) the differences in experimental techniques used to obtain the listed data. There are also differences in the methods of data interpretation. For example, Kittrick (1971), Routson and Kittrick (1971), and Weaver, Jackson, and Syers (1971) assumed that Fe^{3+} was conserved in their system as hematite. On the other hand, Huang and Keller (1973) believed that most of the iron remained in solution as ferric hydroxide complexes. In this regard, it is worth mentioning that Helgeson (1969) compiled his ΔG_f° values for the idealized clay minerals from the solubility data in the literature. The small deviations between the predicted and experimental data (differences in methodology notwithstanding) lend considerable support to the suggested method for approximating the ΔG_f° values for clay minerals.

Few solubility measurements have been reported from which ΔG_f° for chlorites or vermiculites may be derived. The ΔG_f° of magnesium chlorite calculated by Helgeson (1969) from the reported solubilities of chlorite and kaolinite in seawater is in good agreement with the value predicted by the present method. The ΔG_f° values for ferromagnesium chlorites have been predicted and are shown in Table 2. Also given in Table 2 are the ΔG_f° values for vermiculites with chemical compositions which are similar to the samples from Libby, Montana (see Boettcher, 1968). Unfortunately there are no experimental data to check these predicted constants. Notice however that the substitution of Fe^{2+} for Mg^{2+} in chlorite causes a sub-

stantial decrease in the ΔG_f° of the resultant chlorite phase.

Table 3 compares the predicted and experimental ΔG_f° data for other layer silicates. Except for the results of Beane (1973), the predicted data are in good agreement with the experimental ΔG_f° values. The "predictability" of the free energy data for these minerals is about $2.0 \text{ kcal mol}^{-1}$, which is the same as for the clay minerals. For greenalite and ferric minnesotaite, the present model gives results which differ from those calculated by the method of Tardy and Garrels (1974); such a disparity is discussed below.

The free energy data predicted by the present method should be used as first approximations, to be corrected as more experimental data become available. It cannot be used to obtain the various ΔG_f° for minerals with the same formula; for example, it cannot discriminate between the ΔG_f° values for kaolinite, nacrite, and dickite. In spite of the short-coming, the dispersion of the data in Table 2 indicates that the predicted ΔG_f° values are adequate for: (a) evaluating the relative stabilities of clay minerals; (b) assessing the diagenetic modifications of clay minerals in soils and sediments.

In a recent paper, Tardy and Garrels (1974) have presented another method for estimating the ΔG_f° for layer silicates. Their method is based on the assumption that each silicate can be represented as an ideal solid solution of oxide and hydroxide components which possess Gibbs energies of formation within the silicate structures which are constant but may differ from ΔG_f° values assigned to the components as separate phases. Their model thus essentially operates on the oxides and does not include the cor-

TABLE 3. Comparison of Experimental and Predicted Free Energies of Formation for Silicate Minerals

Mineral Name	Chemical composition	Predicted ΔG_f° kcal.mol ⁻¹	Reported ΔG_f° , kcal.mol ⁻¹
Microcline	KAlSi ₃ O ₈	- 892.8	- 892.817 (Robie and Waldbaum, 1968)
Minnesotaite	Fe ₃ ²⁺ Si ₄ O ₁₀ (OH) ₂	-1070.1	-1069.9 (Mel'nik, 1972)
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	-1321.0	-1319.0 (Hostetler et al., 1971) -1320.0 (Bricker et al., 1973) -1324.486 (Robie and Waldbaum, 1968) -1323.28 (Mel'nik, 1972)
Annite	KFe ₃ ²⁺ AlSi ₃ O ₁₀ (OH) ₂	-1135.6	-1145.8 (Beane, 1973)
	KFe _{0.3} ²⁺ Fe _{2.7} AlSi ₃ O ₁₂ H _{1.7}	-1151.2	-1148.2 (Zen, 1973)
Phlogopite	KMg ₃ AlSi ₃ O ₁₀ (OH) ₂	-1388	-1407.4 (Beane, 1973)
Sepiolite	Mg ₂ Si ₃ O ₆ (OH) ₂	-1023.8	-1020.5 *
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	- 963.8	- 965.77 (Mel'nik, 1972) - 962.08 (Bricker et al., 1973) - 964.92 (Hostetler and Christ, 1968)
Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	-1261.9	-1260.0 (Zen, Set 1, 1972)
Greenalite	Fe ₃ ²⁺ Si ₂ O ₅ (OH) ₄	- 713.0	-720 **
Ferric minnesotaite	Fe ₂ ³⁺ Si ₄ O ₁₀ (OH) ₂	-1046.5	-1055.0 **

* Recalculated by Tardy and Garrels (1974) from the data of Christ et al., 1973.

** Predicted by Tardy and Garrels (1974) with their method.

reaction (*i.e.*, Q) term. On the other hand, my model basically demonstrates that the change in free energy during the combination of metal hydroxides to form silicates plus water is usually small (except for the alkali metal hydroxides).

Superficially, it would appear that the major difference between the two models involves the replacement of the "silication" energies of Tardy and Garrels (1974) by "hydroxylation" energies in the

present model. Thus one could write



$$\begin{aligned} \Delta G_b^0(\text{Al}_2\text{O}_3) \\ = 2\Delta G_f^0[\text{Al}(\text{OH})_3] - 3\Delta G_f^0(\text{H}_2\text{O}) - Q \\ = -379.5 \text{ kcal} \end{aligned} \quad (12)$$

where ΔG_b^0 is the Gibbs energy of Al_2O_3 bound in the mineral lattice. By definition,

$$\Delta G_{\text{hydroxylation}}^0 = \Delta G_b^0 - \Delta G_f^0, \quad (13)$$

so that

$$\Delta G_{\text{hydroxylation}}^0 = -379.5 - (-378.1) \quad (14)$$

$$\Delta G_{\text{hydroxylation}}^0 = -1.4$$

The $\Delta G_f^0(\text{Al}_2\text{O}_3)$ is taken from Tardy and Garrels (1974). Table 5 summarizes the calculated hydroxylation energies for the other metal oxides. It becomes immediately apparent that the difference between the two models is deeper than the mere replacement of the silication energy by hydroxylation energy.

For *clay minerals*, the two models give results which are quite comparable (see Table 4). The ΔG_f^0 values for greenalite and ferric minnesotaite obtained by the two methods differ appreciably (see Tables 3 and 4). For each of the two minerals, the dis-

TABLE 4. Comparison of the Free Energy Data (For Silicate Minerals) Predicted in This Report with Those Calculated by the Method of Tardy and Garrels (1974)*

Mineral Name	ΔG_f° , kcal.fw ⁻¹		
	This report**	Tardy and Garrels (1974)	Experimental
Fithian illite	-1277.1	-1278.8	-1277.7
Beavers Bend illite	-1276.3	-1276.2	-1274.7
Goose Lake illite	-1272.8	-1273.4	-1272.1
Aberdeen montmorillonite	-1229.7	-1228.3	-1230.6
Belle Fourche montm. [†]	-1234.1	-1236.4	-1240.6
Average montmorillonite	-1267.2	-1266.5	-
End member montm.	-1296.2	-1299.0	-
Clinchlore	-1962.4	-1958.7	1961.8
Annite	-1154.7	-1149.1	-1151.7
Greenalite	- 713.0	- 720.0	-
Ferric minnesotaite	-1046.5	-1055.0	-

* The chemical formulae for these minerals are given in Tables 2 and 3, unless specified otherwise.

** A correction of -3.5 kcal. per mole of Al has been made for species containing aluminum; Tardy and Garrels used this correction factor for their model and in their recalculation of the published experimental results (listed in the Table).

† Based on structural formula of $\text{H}_{0.28}^{+3}[\text{Al}_{1.515}\text{Fe}_{0.225}\text{Mg}_{0.29}](\text{Al}(\text{Al}_{0.065}\text{Si}_{3.935}\text{O}_{10}(\text{OH})_2)]$

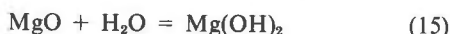
TABLE 5. Hydroxylation and Silication Energies for the Metal Oxides*

	$\Delta G^\circ_{\text{hydroxylation}}$ (per 20H)	$\Delta G^\circ_{\text{silication}}$
K ₂ O	-95.9	-111.0
Na ₂ O	-58.7	-72.6
MgO	-9.7	-13.1
FeO	-2.1	-4.0
CaO	-13.5	-
Al ₂ O ₃	-1.4 (-8.4)**	-4.3
Fe ₂ O ₃	+13.6	0.0
SiO ₂	-1.4	0.0
H ₂ O	0	-2.5

* The silication energies listed are from Tardy and Garrels (1974). The hydroxylation energies are based on the ΔG°_f data for the metal hydroxides listed in Table 1.

** The value in brackets includes the correction factor of 3.5 kcal for each mole of Al(OH)₃.

parity in the predicted data is about twice the difference between the silication and hydroxylation energies for MgO in Table 5. It may be recalled, however, that Tardy and Garrels assumed *a priori* that the hydroxyl ions of the layer silicates were derived from Mg(OH)₂. Where there is insufficient or no Mg in the mineral composition to account for the hydroxyl ions, their model calls for the appropriate amount of water molecules to be included in the formation reaction. Such a strategy may lead to inconsistencies as evidenced by substituting the listed values for $\Delta G^\circ_{f(\text{silicated})}$ of Mg(OH)₂ and MgO into the following equation



The resulting $\Delta G^\circ_{f(\text{silicated})}$ for water is -54.1 kcal, which may be compared with the value of -59.2 used in their calculation. Obviously experimental data will be needed to decide as to which set of the predicted ΔG°_f values for greenalite and ferric minnesotaite is more nearly correct.

Acknowledgments

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