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EVALUATION OF STANDARD FREE ENERGIES OF FORMATION OF CLAY MINERALS BY AN IMPROVED REGRESSION METHOD

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Abstract—An improved regression method for the evaluation of standard free energies of formation (ΔG°_f) of clay minerals is here proposed in an attempt to remove some of the limitations of the earlier method (Chen, 1975). Particularly, this method suggests a procedure for the assignment of rankings for $\Sigma\ \Delta G^\circ_{f,\,i}$ values. Moreover, an iterative least-squares fitting technique is applied to solve the exponential equation to obtain the estimated ΔG°_f. The estimated ΔG°_f data for the various standard clay minerals are derived and compared with data available in the literature; in general, there is good agreement between the values. It is also shown how the regression method can be extended to clay minerals of variable composition. The ΔG°_f's for several such minerals have been evaluated; a large number of combination equations required for such computations have been listed, so that for other similar minerals the process of evaluation of ΔG°_f is greatly simplified.

Key Words—Clay minerals, Free energies of formation, Regression method.

INTRODUCTION

Experimental methods for the determination of free energies of formation of clay minerals by calorimetry, solubility measurements, or hydrofluoric acid dissolution are both complex and time consuming. Clay minerals having variable compositions present even greater difficulties since the free energy of formation must be determined for each individual composition. The laborious nature of the experimental process, therefore, limits the availability of free energy data to a few select mineral species, thereby limiting the general applicability of thermodynamics, in practice, to a relatively small number of clay mineral systems.

Development of theoretical and empirical methods for the evaluation of free energies of formation are invaluable, in that they provide a relatively simple and rapid means of obtaining such values with a fair degree of accuracy. One such theoretical method (Slaughter, 1966) utilizes various crystal constants to obtain free energy values. The inherent difficulty with this method, however, is the nonavailability of accurate crystal energy parameters. In another empirical method (Tardy and Garrels, 1974), free energies of silicates are represented as sums of their oxide and hydroxide components, which are assumed to have fixed values for all silicates, but which differ from those of the pure oxide/hydroxide phases. Free energies of formation have also been evaluated (Nriagu, 1975) by applying a small correction term to the total free energy change accompanying the combination of silicon hydroxide with metal hydroxides. However, the average difference between the predicted and experimental data was observed to be about ±9.5 kcal/mole. This model was further refined (Mattigod and Sposito, 1978) with a consequent increase in accuracy of the data to about 2.6 kcal/mole. Recently, solid-solution concepts in various forms have been used to derive solubility constants as well as stability fields of clay minerals (Aagaard and Helgeson, 1983; Fritz, 1985; Lippman, 1977, 1981; Tardy and Fritz, 1981; Tardy *et al.,* 1987; Varadachari, 1992).

Of the various empirical procedures suggested so far, the method used for silicate minerals in general, by Karpov and Kashik (1968) and further refined by Chen (1975), is both versatile and promising. It can be applied to any kind of clay mineral whose chemical composition is known; the basic input data required for the calculations are readily available in the literature. Moreover, the results show good agreement with experimental data; in general, the calculated values deviate from the experimental ones by an average of less than 0.2% (on the order of 2 kcal/mole). However, this method, which may be termed "the regression method" has further room for improvement. For example, the process for assignment of the rank "x" is quite arbitrary, although choice of this value is critical for obtaining ΔG°_f (standard free energy of formation). A suitable method for solving the complex exponential equation also needs to be outlined. Moreover, this method has so far only been applied to a few standard silicate minerals whose free energies of formation are already available. Its utility for nonstoichiometric clay minerals has not yet been explored.

The object of this study is to present an improved regression method for the evaluation of standard free energies of formation and to extend this to nonstoichiometric clay minerals. More precisely, this work includes 1) a process for the assignment of "x" rankings, 2) a process for computation of ΔG°_f using an iterative, least-squares fitting of data, and 3) evaluation of ΔG°_f of non-stoichiometric clays and tabulation of numerous combination equations required for such computation.

METHODOLOGY

Details of the regression method have been explained by Chen (1975). Briefly, the procedure consists in first, representing the mineral in question in the form of combinations of various compounds. Thus kaolinite, $Al_2Si_2O_5(OH)_4$ may be written as $Al_2O_3 + 2SiO_2 + 2H_2O$, $Al_2SiO_5 + SiO_2 + 2H_2O$, $2AlO(OH) + 2SiO_2 + H_2O$, etc. For each combination, the ΔG°_f of the individual component minerals are added to give the sum $\Sigma\ \Delta G^\circ_{f,i}$. All the values of ΔG°_f used here are obtained from Helgeson *et al.* (1978); the value of ΔG°_f for water is taken from Robie *et al.* (1978). Various possible combinations for each mineral are constructed and the $\Sigma\ \Delta G^\circ_{f,i}$ values obtained therefrom. The values of $\Sigma\ \Delta G^\circ_{f,i}$ are then arranged in descending order and each is assigned an integral value, x, which represents the rank of the $\Sigma\ \Delta G^\circ_{f,i}$. Utilizing the values of $\Sigma\ \Delta G^\circ_{f,i}$ and x, a regression equation of the form:

$$\Sigma\ \Delta G^\circ_{f,i} = ae^{bx} + c \qquad (1)$$

is derived where a, b, and c are constants and the value of c gives the ΔG°_f of the mineral.

Fitting for the above exponential equation is, however, not simple. One method consists of applying a logarithmic transformation to the data to obtain a linear function and then determining the least-squares solution for the transformed data. Such transformation, however, results in a distortion of the error field associated with the variable and thus causes a biased least-squares fit.

The method adopted here, utilizes an iterative least squares technique (Draper and Smith, 1981; van Heeswijk and Fox, 1988). Briefly this method may be described as follows (Scarborough, 1976):

Suppose an equation of the generalized form

$$y = f(x, a, b, c) \qquad (2)$$

contains two variables, x and y, and three unknowns, a, b, and c. First, some initial values of the unknowns are assumed as a_0, b_0, and c_0. Let α, β, and γ be the values by which these values differ from the actual values a, b, c. Then

$$\begin{aligned} a &= a_0 + \alpha \\ b &= b_0 + \beta \\ c &= c_0 + \gamma \end{aligned} \qquad (3)$$

If $x_1, x_2, \ldots, x_p$ and $y_1, y_2, \ldots, y_p$ are the experimentally observed values of x and y, then, by substituting a_0, b_0, c_0 values in Eq. 2, we obtain

$$y'_n = f(x_n, a_0, b_0, c_0) \qquad (4)$$

where n ranges from 1 to p. Eq. 4 is an approximation curve with a residual r_n where,

$$y'_n = y_n + r_n \qquad (5)$$

Thus, r_n gives the difference between the approximated value and the observed value of y. However, this observed value y_n differs from the value obtained from the best representative curve. This residual, termed ϵ_n, is related as

$$\epsilon_n = f(x_n, a, b, c) - y_n \qquad (6)$$

Combining Eqs. 3 and 6 gives

$$\epsilon_n + y_n = f(x_n, a_0 + \alpha, b_0 + \beta, c_0 + \gamma) \qquad (7)$$

On expanding in Taylor series as a function of a, b, c and ignoring higher order terms, we get

$$\begin{aligned} \epsilon_n + y_n = f(x_n, a_0, b_0, c_0) + \alpha(\delta f/\delta a)_0 \\ + \beta(\delta f/\delta b)_0 + \gamma(\delta f/\delta c)_0 \end{aligned} \qquad (8)$$

However, since $y'_n = f(x_n, a_0, b_0, c_0)$ and $r_n = y'_n - y_n$, this Eq. 8 may be rewritten as

$$\begin{aligned} \epsilon_n = \alpha(\delta f_n/\delta a)_0 + \beta(\delta f_n/\delta b)_0 \\ + \gamma(\delta f_n/\delta c)_0 + r_n \end{aligned} \qquad (9)$$

These equations are linear in α, β, and γ. Furthermore, according to the method of least squares, the best representative values of a, b, and c are those for which $\Sigma^p_{n=1}\ \epsilon^2$ is a minimum.

Eq. 8 can be easily solved for α, β, and γ by the least-squares technique if an initial estimate of a_0, b_0, c_0 is provided for the first iteration. At the completion of each iteration, the values a_0, b_0, c_0 are replaced by revised values derived from Eq. 2, and the whole procedure is repeated again by replacing the zero subscripts by 1 (e.g., a_1, b_1, c_1). This will lead to another set of revised estimates of a_2, b_2, c_2 and so on. The iterative process is continued until the solution converges, that is until, α, β, γ reach selected small values. At each stage of the iterative procedure, $\Sigma\ \epsilon^2_n$ is evaluated to see if a reduction in its value is actually achieved.

In some instances, convergence may occur very slowly or convergence may not occur at all. To combat this, it is suggested (Draper and Smith, 1981) that the parameter increments α, β, γ are halved or doubled.

In the particular case of the Eq. 1, $\Sigma\ \Delta G^\circ_{f,i} = ae^{bx} + c$ which has the form

$$f(x) = ae^{bx} + c \qquad (10)$$

the partial derivatives are

$$\delta f/\delta a = e^{bx} \qquad (11)$$

$$\delta f/\delta b = ax\ e^{bx} \qquad (12)$$

$$\delta f/\delta c = 1 \qquad (13)$$

The procedure for iteration is the same as described above. Here, the initial approximate estimates a_0, b_0, c_0 were obtained by solving Eq. 1 using logarithmic transformation or by graphical means.

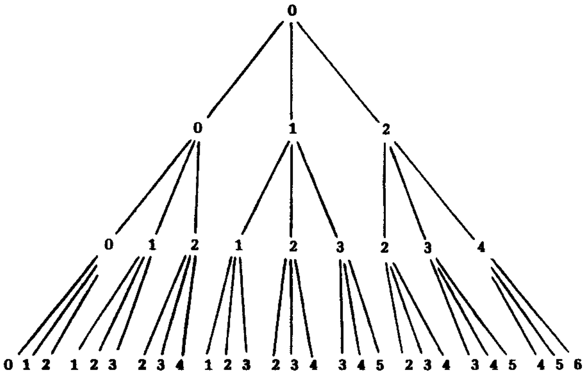

Figure 1. "Tree" diagram for obtaining the various possible combinations of x for a set of four data.

On substituting Eqs. 11–13 in Eq. 9, we obtain the equation

$$\epsilon_n = \alpha\, e^{b_0 x_n} + \beta a_0 x_n\, e^{b_0 x_n} + \gamma + r_n \qquad (14)$$

or

$$\epsilon_n = \alpha\, e^{b_0 x_n} + \beta a_0 x_n\, e^{b_0 x_n} + \gamma + a_0\, e^{b_0 x_n} + c_0 - y_n \qquad (15)$$

By substituting values of n, we obtain p linear equations. These equations can be solved by the usual linear least-squares inversion technique (Draper and Smith, 1981) utilizing matrix algebra.

Calculations were done on a VAX 11/780 mainframe computer using a Fortran subroutine CURVEFIT provided by van Heeswijk and Fox (1988). The two sets of input data required are computed values of $\Sigma\ \Delta G^\circ_{f,i}$ and corresponding assigned values of rankings x. Assignment of the x values may lead to erroneous results if done by visual examination of the data, as is the usual practice. Difficulties usually arise since one has the choice of assigning the rank of the (i + 1)th ΔG°_f with the same value as that of the ith $\Sigma\ \Delta G^\circ_f$, or with a higher value. In this work, it has been possible to provide x assignments by choosing that combination of x that gives the best fitting curve. For a set of $\Sigma\ \Delta G^\circ_{f,i}$, it is possible that several values of $\Sigma\ \Delta G^\circ_{f,i}$ may have the same value of x; alternatively, a particular x within the series may not have a corresponding value of $\Sigma\ \Delta G^\circ_{f,i}$, thereby leaving a missing value of x in the arrangement. In order to obtain the curve with the best fitting values of x, curve fitting is done for every possible combination of x values. Thus, each set of $\Sigma\ \Delta G^\circ_{f,i}$ for a mineral can be assigned several sets of probable rankings, x, from which one such set is chosen which produces a curve fit with the lowest residual error ($\Sigma\ \epsilon^2$). Without any limitation on the values that x may assume, the total number of combinations is infinite. However, certain conditions may be imposed based on the characteristics of the exponential curves. It is, thereby, possible to obtain a finite number of x combinations. The conditions are as follows:

1) The $\Sigma\ \Delta G^\circ_{f,i}$ having the lowest numerical value is assigned a rank x equal to zero.
2) Rankings of subsequent $\Sigma\ \Delta G^\circ_{f,i}$ may either be zero or greater than zero.
3) When the $\Sigma\ \Delta G^\circ_{f,i}$ are arranged in order of increasing absolute numerical value, the ranking of the (i + 1)th $\Sigma\ \Delta G^\circ_f$ is either equal to or greater than the ranking of the ith $\Sigma\ \Delta G^\circ_f$, i.e., x value for $\Sigma\ \Delta G^\circ_{f,i+1} \geq$ x value for $\Sigma\ \Delta G^\circ_{f,i}$. This logic is derived from the nature of the exponential curve.
4) A minimum of three different rankings is required to construct the exponential curve.
5) The rankings of adjacent $\Sigma\ \Delta G^\circ_{f,i}$ may have a missing value. Effectively, it means that the rankings for the (i + 1)th and ith $\Sigma\ \Delta G^\circ_f$ may have a difference of 0, 1 or 2, i.e., $x_{i+1} - x_i = 0$, 1 or 2. Thus, two adjacent $\Sigma\ \Delta G^\circ_{f,i}$ may have the same rank, x, or their x's may differ by a value of 1 or 2; in the latter case, the $\Sigma\ \Delta G^\circ_{f,i}$ of higher absolute numerical value has a higher corresponding rank x. Such an example can be seen in Table 2 where the rankings of $\Sigma\ \Delta G^\circ_{f,i}$ for kaolinite are 0, 1, 3, 5, 7 instead of 0, 1, 2, 3, 4. Such a situation may arise from the fact that one can miss out constructing equations for intermediate $\Sigma\ \Delta G^\circ_{f,i}$, thereby leaving gaps in the x value.

Conditions (1) to (4) are fundamental to the regression method as suggested by Chen (1975). Condition (5) has been incorporated because it has been found to improve curve-fitting, i.e., further minimize $\Sigma\ \epsilon^2$ as compared to one in which the possibility of a missing value has not been considered. The possibility of two and more missing ranks, x, is practically impossible to compute at this stage because the total possible combinations for assignment of x becomes infinite. However, it has been observed in practice that if a sufficient number of equations are constructed, the aforesaid ranking rules are sufficient to provide very good curve fits.

The various possible means of assigning x values to a set of $\Sigma\ \Delta G^\circ_{f,i}$ data have been computed based on the graph theory-tree method (Harary, 1972). An example of such a construction is shown in Figure 1 for a system containing 4 values of $\Sigma\ \Delta G^\circ_{f,i}$. The combinations are obtained by following the branches beginning from the top 0 and following the lines downward.

However, from this set, combinations that contain less than three different values of x are deleted, e.g., 0000, 0001, etc. Thus, the following combinations are obtained from Figure 1: 0012, 0013, 0023, 0024, 0112, 0113, 0122, 0123, 0124, 0133, 0134, 0135, 0223, 0224, 0233, 0234, 0235, 0244, 0245, 0246. A combination such as 0012 refers to the fact that when the $\Sigma\ \Delta G^\circ_{f,i}$ values are arranged serially in order of increasing numerical value, then the lowest value $\Sigma\ \Delta G^\circ_{f,i}$ has a rank

Table 1. Comparative values for the standard free energy of formation of some clay minerals.

Mineral	ΔG°_f (kcal/mole)	
Kaolinite $Al_2Si_2O_5(OH)_4$	−905.121[2]	
	−905.614[1]	(Helgeson *et al.*, 1978)
	−910.0[1]	(Zen, 1972)
	−908.048[1]	(Robie *et al.*, 1978)
	−904.0[1]	(Reesman and Keller, 1968)
	−903.5[1]	(Kittrick, 1971b)
	−902.59[2]	(Chen, 1975)
	−888.1[1]	(Barany and Kelley, 1961)
Pyrophyllite $Al_2Si_4O_{10}(OH)_2$	−1257.550[2]	
	−1255.997[1]	(Helgeson *et al.*, 1978)
	−1260.0[1]	(Zen, 1972)
	−1259.383[1]	(Robie *et al.*, 1978)
	−1258.7[1]	(Reesman and Keller, 1968)
	−1256.95[2]	(Chen, 1975)
	−1250.1[2]	(Slaughter, 1966)
	−1259.8[2]	(Sposito, 1986)
Talc $Mg_3Si_4O_{10}(OH)_2$	−1328.558[2]	
	−1320.188[1]	(Helgeson *et al.*, 1978)
	−1323.115[1]	(Robie *et al.*, 1978)
	−1320.0[1]	(Bricker *et al.*, 1973)
	−1319.3[2]	(Slaughter, 1966)
Phlogopite $KAlMg_3Si_3O_{10}(OH)_2$	−1395.221[2]	
	−1396.187[1]	(Helgeson *et al.*, 1978)
	−1402.679[1]	(Mukherjee, 1979)
	−1400.7[2]	(Tardy and Garrels, 1974)
Muscovite $KAl_3Si_3O_{10}(OH)_2$	−1337.991[2]	
	−1336.301[1]	(Helgeson *et al.*, 1978)
	−1340.0[1]	(Zen, 1972)
	−1338.56[1]	(Robie *et al.*, 1978)
	−1330.5[2]	(Chen, 1975)
	−1327.5[2]	(Karpov and Kashik, 1968)
	−1327.0[1]	(Reesman and Keller, 1968)
Biotite $KAlFe_3Si_3O_{10}(OH)_2$	−1135.497[2]	
	−1147.156[1]	(Helgeson *et al.*, 1978)
Chlorite $Mg_5Al_2Si_3O_{10}(OH)_8$	−1953.276[2]	
	−1961.703[1]	(Helgeson *et al.*, 1978)
	−1974.0[1]	(Zen, 1972)
	−1952.2[2]	(Chen, 1975)
Sepiolite $Mg_2Si_3O_6(OH)_4$	−1021.729[2]	
	−1020.5[1]	(Christ *et al.*, 1973)
or $Mg_4Si_6O_{15}(OH)_2(H_2O)_2 \cdot 4H_2O$	−2213.492[2]	
	−2211.192[1]	(Helgeson *et al.*, 1978)

[1] Derived by experimental methods.

[2] Derived by theoretical/empirical methods.

x = 0; the next $\Sigma \Delta G^\circ_{f,i}$ also has rank x = 0; the third $\Sigma \Delta G^\circ_{f,i}$ has x = 1 and the highest $\Sigma \Delta G^\circ_{f,i}$ has x = 2. For systems containing more than four $\Sigma \Delta G^\circ_{f,i}$ values, the "branches" of the tree shown in Figure 1 are extended further, on the same principle.

Utilizing each combination of x, the least-squares fit regression curve is computed as described earlier and the residual error is obtained. That combination which shows the best curve fitting, i.e., smallest residual error, is selected. The corresponding value of c in Eq. 1 gives the required value of the standard free energy of formation, ΔG°_f.

RESULTS AND DISCUSSION

General

Values of ΔG°_f derived here for some standard layer silicates are shown in Table 1, together with ΔG°_f values obtained from the literature; Figure 2 shows the corresponding exponential curves. The chemical combination equations, $\Sigma \Delta G^\circ_{f,i}$ values and rankings x, which were utilized in deriving the ΔG°_f values, are listed in Table 2. From Table 1, it may be observed that, in general, data obtained by the regression method are close to those obtained by Helgeson *et al.* (1978). Since

Table 2. $\Sigma\Delta G^\circ_{f,i}$ and the rankings of the combinations for some clay minerals.

Clay minerals and their combinations	$\Sigma\Delta G^\circ_{f,i}$ [kcal/mole] (average value)	Rank [x]
Kaolinite $Al_2Si_2O_5(OH)_4$		
1. $Al_2O_3 + 2SiO_2 + 2H_2O$	−897.496	0
2. $Al_2SiO_5 + SiO_2 + 2H_2O$	−898.613	1
3. $2AlO(OH) + 2SiO_2 + H_2O$	−900.482	3
4. $0.5Al_2SiO_5 + Al(OH)_3 + 1.5SiO_2 + 0.5H_2O$	−901.775	5
5. $Al(OH)_3 + AlO(OH) + 2SiO_2$	−902.710	7
Regression equation: $\Sigma\Delta G^\circ_{f,i} = 7.6414e^{-0.165062x} - 905.1208$		
Muscovite $KA_3Si_3O_{10}(OH)_2$		
1. $Al_2O_3 + KAlSiO_4 + 2SiO_2 + H_2O$	−1322.556	0
2. $KAlSiO_4 + Al_2SiO_5 + SiO_2 + H_2O$	−1323.673	1
3. $KAlSi_2O_6 + 2AlO(OH) + SiO_2$	−1326.484	3
4. $0.5Al_2Si_4O_{10}(OH)_2 + KAlSiO_4 + AlO(OH)$	−1326.999	4
5. $0.5Al_2Si_2O_5(OH)_4 + KAlSi_2O_6 + 0.5Al_2O_3$	−1327.557	4
6. $0.5Al_2Si_2O_5(OH)_4 + KAlSi_2O_6 + AlO(OH) - 0.5H_2O$	−1329.050	6
7. $Al_2Si_2O_5(OH)_4 + KAlSiO_4 - H_2O$		
Regression equation: $G^\circ \Sigma\Delta = 15.51422e^{-0.093371x} - 1337.991$		
Phlogopite $KAlMg_3Si_3O_{10}(OH)_2$		
1. $3MgSiO_3 + 0.5K_2O + 0.5Al_2O_3 + H_2O$	−1329.420	0
2. $KAlSi_3O_8 + 3MgO + H_2O$	−1360.175	1
3. $KAlSiO_4 + 3Mg(OH)_2 + 3SiO_2 - 2H_2O$	−1376.600	2
4. $Mg_3Si_2O_5(OH)_4 + KAlSiO_4 - H_2O$	−1389.931	4
Regression equation: $\Sigma\Delta G^\circ_{f,i} = 65.8053e^{-0.630062x} - 1395.221$		
Biotite $KAlFe_3Si_3O_{10}(OH)_2$		
1. $0.5K_2O + 0.5Al_2O_3 + 3FeO + 3SiO_2 + H_2O$	−1076.859	0
2. $0.5K_2O + 0.5Al_2SiO_4 + 3FeO + 2.5SiO_2 + H_2O$	−1077.417	0
3. $0.5K_2O + 0.5Al_2Si_2O_5(OH)_4 + 3FeO + 2SiO_2$	−1080.918	0
4. $0.5K_2O + Fe_2SiO_4 + FeO + H_2O + 0.5Al_2SiO_5 + 1.5SiO_2$	−1082.250	0
5. $0.5K_2O + Fe_2SiO_4 + 0.5Al_2SiO_5 + SiO_2 + H_2O$	−1084.665	0
6. $0.5K_2O + 3FeSiO_3 + AlO(OH) + 0.5H_2O$	−1085.603	0
7. $KAlSi_2O_6 + 3Fe(OH)_2 + SiO_2 - 2H_2O$	−1121.808	2
8. $KAlSi_2O_6 + 3FeO + SiO_2 + H_2O$	−1123.269	2
9. $KAlSiO_4 + 3Fe(OH)_2 + 2SiO_2 - 2H_2O$	−1126.562	3
10. $KAlSi_2O_6 + Fe_2SiO_4 + FeO + H_2O$	−1127.612	3
11. $KAlSiO_4 + 3FeO + 2SiO_2 + H_2O$	−1128.023	3
12. $KAlSi_3O_8 + 3Fe(OH)_2 - 2H_2O$	−1130.894	4
13. $KAlSi_3O_8 + 3FeO + H_2O$	−1132.355	4
14. $KAlSiO_4 + 0.5Fe_3Si_4O_{10}(OH)_2 + 1.5FeO + 0.5H_2O$	−1135.191	6
15. $KAlSiO_4 + 1.5Fe_2SiO_4 + 0.5SiO_2 + H_2O$	−1135.268	6
Regression equation: $\Sigma\Delta G^\circ_{fi} = 54.1834e^{-0.6753} - 1135.497$		
Pyrophyllite $Al_2Si_4O_{10}(OH)_2$		
1. $Al_2O_3 + 4SiO_2 + H_2O$	−1250.098	0
2. $Al_2SiO_5 + 3SiO_2 + H_2O$	−1251.215	1
3. $0.5Al(OH)_3 + 0.75Al_2SiO_5 + 3.25SiO_2 + 0.25H_2O$	−1252.796	3
4. $2AlO(OH) + 4SiO_2$	−1253.084	3
5. $0.5Al_2Si_2O_5(OH)_4 + 0.5Al_2O_3 + 3SiO_2$	−1254.154	5
6. $0.5Al_2Si_2O_5(OH)_4 + 0.5Al_2SiO_5 + 2.5SiO_2$	−1254.716	6
Regression equation: $\Sigma\Delta G^\circ_{f,i} = 7.443719e^{-0.1593382x} - 1257.550$		
Talc $Mg_3Si_4O_{10}(OH)_2$		
1. $MgO + 4SiO_2 + H_2O$	−1283.385	0
2. $Mg_2SiO_4 + Mg(OH)_2 + 3SiO_2$	−1305.524	2
3. $1.5Mg_2SiO_4 + 2.5SiO_2 + H_2O$	−1306.215	2
4. $2MgSiO_3 + 2SiO_2 + Mg(OH)_2$	−1306.798	2
5. $0.5Mg_3Si_2O_5(OH)_4 + 1.5MgSiO_3 + 1.5SiO_2$	−1312.799	3
6. $Mg_3Si_2O_5(OH)_4 + 2SiO_2 - H_2O$	−1317.473	4
Regression equation: $\Sigma\Delta G^\circ_{f,i} = 45.17277e^{-0.3511567x} - 1328.558$		
Chlorite $Mg_5Al_2Si_3O_{10}(OH)_8$		
1. $5MgO + Al_2O_3 + 3SiO_2 + 4H_2O$	−1895.707	0
2. $Al_2Si_2O_5(OH)_4 + MgSiO_3 + 4MgO + 2H_2O$	−1912.072	1
3. $Al_2SiO_5 + 2MgSiO_3 + 3MgO + 4H_2O$	−1913.318	1

Table 2. Continued.

Clay minerals and their combinations	$\Sigma\Delta G^{\circ}_{f,i}$ [kcal/mole] (average value)	Rank [x]
4. $0.5Mg_3Si_4O_{10}(OH)_2 + Mg_2SiO_4 + 1.5MgO + 2AlO(OH) + 2.5H_2O$	−1931.442	3
5. $2.5Mg_2SiO_4 + Al_2O_3 + 0.5SiO_2 + 4H_2O$	−1931.577	3
6. $Mg_2SiO_4 + 3Mg(OH)_2 + 2Al(OH)_3 + 2SiO_2 - 2H_2O$	−1938.254	4
7. $Mg_3Si_2O_5(OH)_4 + Al_2SiO_5 + 2Mg(OH)_2$	−1944.750	6
8. $1.5Mg_3Si_2O_5(OH)_4 + 0.5MgO + 2AlO(OH)$	−1949.825	8
9. $Mg_3Si_2O_5(OH)_4 + MgAl_2O_4 + MgSiO_3 + 2H_2O$	−1950.142	9
Regression equation: $\Sigma\Delta G^{\circ}_{f,i} = 57.07883e^{-0.32814x} - 1953.276$		
Sepiolite $Mg_2Si_3O_6(OH)_4$		
1. $2MgO + 3SiO_2 + 2H_2O$	−999.49	0
2. $Mg_2SiO_4 + 2SiO_2 + 2H_2O$	−1014.236	2
3. $2MgSiO_3 + SiO_2 + 2H_2O$	−1015.886	3
4. $0.5Mg_3Si_2O_5(OH)_4 + 0.5Mg(OH)_2 + 2SiO_2 \quad 0.5H_2O$	−1019.895	5
5. $0.5Mg_3Si_4O_{10}(OH)_2 + 0.5Mg(OH)_2 + SiO_2 + H_2O$	−1021.253	7
Regression equation: $\Sigma\Delta G^{\circ}_{f,i} = 22.16086e^{-0.4969167x} - 1021.729$		

Note: Sepiolite formulated as $Mg_4Si_6O_{15}(OH)_2(H_2O)_3 \cdot 3H_2O$ is the same as the above formula multiplied by 2 with 3 moles of H_2O added, i.e., $2 \times Mg_2Si_3O_6(OH)_4 + 3H_2O = Mg_4Si_6O_{15}(OH)_2(H_2O)_3 \cdot 3H_2O$. The "c" value for the latter formula may be modified accordingly.

the basic data used for these computations were obtained from Helgeson *et al.* (1978), it would be more reasonable to limit the comparisons of our ΔG°_f data with those of Helgeson *et al.* (1978). The other data (Table 1) are only to show the wide variation in ΔG°_f values that is obtained by different methods. It is seen here, that ΔG°_f for talc, chlorite, and biotite show large differences from the values obtained by Helgeson *et al.* (1978). For biotite, this is to be expected since equations of sufficient complexity utilizing iron silicates (Table 2) could not be constructed due to non-availability of basic ΔG°_f data. It appears, therefore, that the regression method can be applied to biotite only when more data on ΔG°_f of complex iron-rich silicates are made available. In the case of talc and chlorite, the differences are, however, difficult to explain since the regression curves themselves show good curve fitting (Figure 2). More up-to-date experimental data on ΔG°_f of these two minerals are needed to verify the results and ascertain if indeed such error is present. For all other minerals, deviations are within 0.5 to 2.3 kcal/mole and are also in better agreement with the values

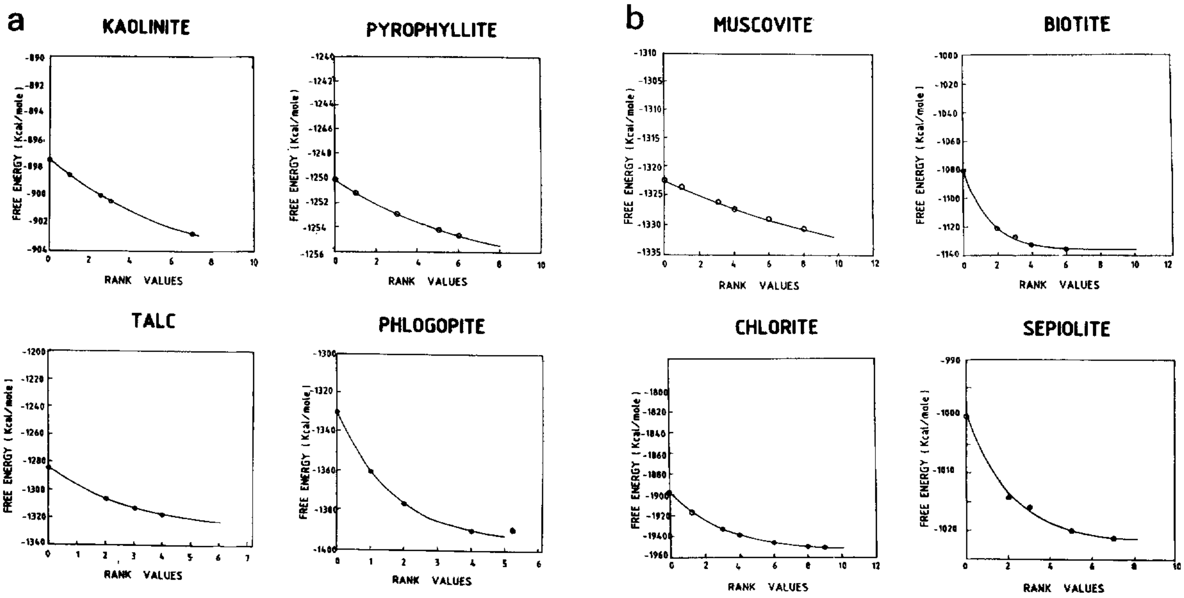

Figure 2. Regression of $\Sigma\ \Delta G^{\circ}_{f,i}$ values for some standard clay minerals.

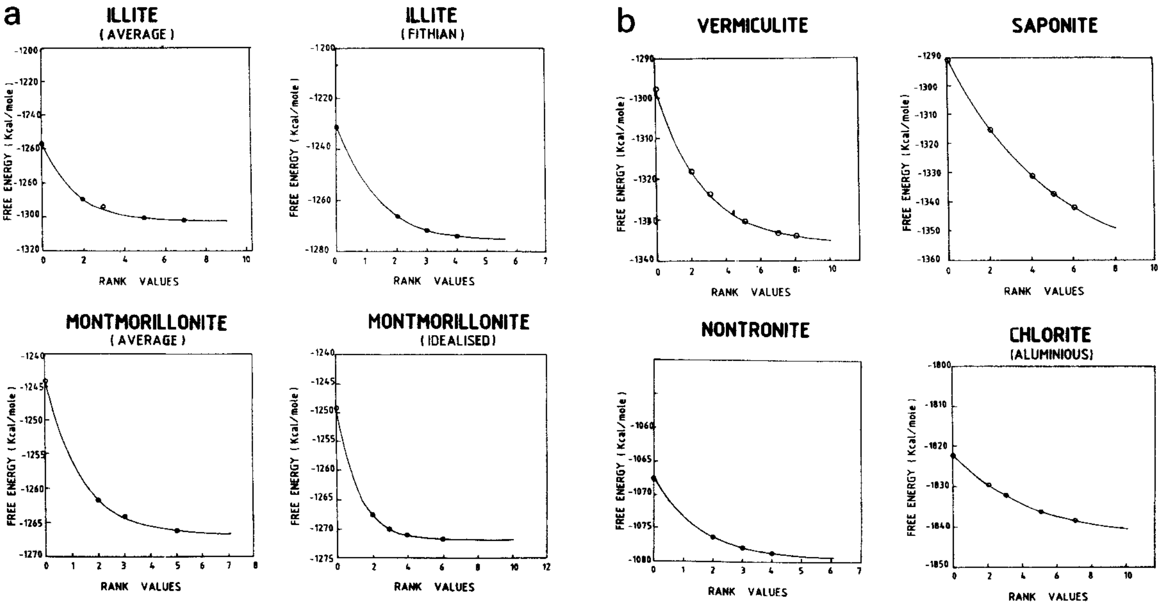

Figure 3. Regression of $\Sigma\ \Delta G°_{f,i}$ values for some non-stoichiometric clay minerals.

obtained by Helgeson *et al.* (1978) than those obtained by any other theoretical or experimental means (Table 1).

Standard free energy of formation of clay minerals of variable composition

Free energies of formation of several clay minerals of variable composition, which have been derived here, are shown in Table 3. The various combinations used for these derivations as well as their $\Sigma\ \Delta G°_{f,i}$ values are represented in Table 4. The corresponding regression curves may be seen in Figure 3.

Formulae for the minerals have been taken from the following sources: Montmorillonite, average (Tardy and Garrels, 1974); montmorillonite, idealized (Grim, 1968); illite, Fithian (Nriagu, 1975); illite, average (Weaver and Pollard, 1973); nontronite (Grim, 1968); saponite (Grim, 1968); and vermiculite and aluminous chlorite (Jackson, 1965). The $\Delta G°_f$ for various montmorillonites (in kcal/mole), which have been obtained from the literature for comparative study, are as follows: −1270.0*, −1234.25* and −1254.3¶ for Clay Spur (Kittrick, 1971a; Reesman and Keller, 1968; Sposito, 1986); −1230.6*, −1228.3¶ and −1245.7¶ for Aberdeen (Kittrick, 1971b; Sposito, 1986; Tardy and Garrels, 1974); −1248.2* and −1257.6¶ for Wyoming and −1274.4*, −1252.1* and −1261.0¶ for Arizona (Huang and Keller, 1973; Reesman and Keller, 1968; Sposito, 1986). It is obvious that widely different values are obtained for montmorillonites of different compositions and sometimes even for montmorillonites of the same origin.

For illites, the variation in the data is not very wide. Thus, values (in kcal/mole) such as −1270.0¶ (Nriagu, 1975), −1277.7* (Rouston and Kittrick, 1971), −1278.8¶ (Tardy and Garrels, 1974), −1282.1* (Huang

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* Derived by experimental methods.

¶ Derived by theoretical/empirical methods.

Table 3. Standard free energies of formation (c), a, and b values evaluated for some clay minerals of variable composition.

Mineral	ΔG_f [kcal/mole]	a	b
Illite (average) $K_{0.55}Na_{0.15}Al_{2.18}Mg_{0.26}Si_{3.56}O_{10}(OH)_2$	−1302.349	45.14204	−0.640779
Illite (Fithian) $K_{0.62}Al_{2.03}Fe_{0.29}Mg_{0.19}Si_{3.51}O_{10}(OH)_2$	−1274.734	43.72045	−0.806652
Vermiculite $Al_{1.4}Fe_{0.35}Mg_{2.675}Si_{2.85}O_{10}(OH)_2$	−1335.828	38.30339	−0.377853
Montmorillonite (average) $K_{0.4}Al_{1.67}Fe_{0.17}Mg_{0.38}Si_{3.83}O_{10}(OH)_2$	−1266.625	22.36392	−0.751450
Montmorillonite (idealised) $K_{0.33}Al_{1.67}Mg_{0.33}Si_4O_{10}(OH)_2$	−1271.772	22.43354	−0.853461
Saponite $K_{0.33}Al_{0.33}Mg_3Si_{3.67}O_{10}(OH)_2$	−1362.875	72.23858	−0.206231
Nontronite $K_{0.33}Al_{0.33}Fe_2Si_{3.67}O_{10}(OH)_2$	−1079.522	11.92548	−0.681420
Chlorite (aluminous) $Al_{4.8}Si_{3.4}O_{10}(OH)_8$	−1842.694	20.58559	−0.215571

Table 4. $\Sigma\Delta G^{\circ}_{f,i}$ and the rankings of the combinations for some clay minerals of variable composition.

Clay minerals and their combinations	$\Sigma\Delta G^{\circ}_{f,i}$ [kcal/mode] (average value)	Rank [x]
Illite (average) $K_{0.55}Na_{0.15}Al_{2.18}Mg_{0.26}Si_{3.56}O_{10}(OH)_2$		
1. $1.09Al_2O_3 + 0.26MgO + 3.56SiO_2 + 0.275K_2O + 0.075Na_2O + H_2O$	−1257.102	0
2. $0.26MgSiO_3 + 0.55KAlSi_2O_6 + 0.15NaAlSiO_4 + 2.05SiO_2 + 0.74Al_2O_3 + H_2O$	−1290.140	2
3. $0.26MgSiO_3 + 0.55KAlSi_3O_8 + 0.815Al_2SiO_5 + 0.835SiO_2 + 0.075Na_2O + H_2O$	−1290.666	2
4. $0.26MgO + 0.075Na_2O + 0.55KAlSi_3O_8 + 0.28SiO_2 + 0.815Al_2Si_2O_5(OH)_4 - 0.63H_2O$	−1294.241	3
5. $0.55KAl_3Si_3O_{10}(OH)_2 + 0.26MgSiO_3 + 0.15NaAlSiO_4 + 0.19Al_2O_3 + 1.5SiO_2 + 0.45H_2O$	−1300.314	5
6. $0.15NaAlSi_3O_8 + 0.55KAl_3Si_3O_{10}(OH)_2 + 0.26MgSiO_3 + 0.19Al_2Si_2O_5(OH)_4 + 0.82SiO_2 + 0.07H_2O$	−1302.478	7
Illite (Fithian) $K_{0.62}Al_{2.03}Fe_{0.29}Mg_{0.19}Si_{3.51}O_{10}(OH)_2$		
1. $1.015Al_2O_3 + 0.145Fe_2O_3 + 0.19MgO + 0.31K_2O + 3.51SiO_2 + H_2O$	−1231.020	0
2. $0.62KAlSiO_4 + 0.705Al_2SiO_5 + 0.145Fe_2O_3 + 0.095Mg_2SiO_4 + 2.09SiO_2 + H_2O$	−1264.930	2
3. $0.62KAlSi_3O_8 + 0.705Al_2O_3 + 0.145Fe_2O_3 + 0.19MgSiO_3 + 1.46SiO_2 + H_2O$	−1266.985	2
4. $0.62KAlSi_3O_8 + 0.705Al_2Si_2O_5(OH)_4 + 0.24SiO_2 + 0.145Fe_2O_3 + 0.19MgO - 0.41H_2O$	−1271.150	3
5. $0.62KAl_3Si_3O_{10}(OH)_2 + 0.085Al_2O_3 + 0.19MgSiO_3 + 0.145Fe_2O_3 + 1.46SiO_2 + 0.38H_2O$	−1272.821	4
Vermiculite $Al_{1.4}Fe_{0.35}Mg_{2.675}Si_{2.85}O_{10}(OH)_2$		
1. $2.85SiO_2 + 0.7Al_2O_3 + 0.175Fe_2O_3 + 2.675MgO + H_2O$	−1297.515	0
2. $0.7Al_2SiO_5 + 1.3375Mg_2SiO_4 + 0.175Fe_2O_3 + 0.8125SiO_2 + H_2O$	−1318.020	2
3. $0.7Al_2Si_2O_5(OH)_4 + 1.3375Mg_2SiO_4 + 0.175Fe_2O_3 + 0.1125SiO_2 - 0.4H_2O$	−1322.920	3
4. $0.5Mg_3Si_4O_{10}(OH)_2 + 0.7Al_2O_3 + 0.175Fe_2O_3 + 0.5875Mg_2SiO_4 + 0.2625SiO_2 + 0.5H_2O$	−1323.277	3
5. $0.5Mg_3Si_2O_5(OH)_4 + 0.7Al_2SiO_5 + 0.175Fe_2O_3 + 0.5875Mg_2SiO_4 + 0.5625SiO_2$	−1323.931	3
6. $0.5Mg_5Al_2Si_3O_{10}(OH)_8 + 0.2Al_2O_3 + 0.175Fe_2O_3 + 0.175MgO + 1.35SiO_2 - H_2O$	−1330.391	5
7. $0.535Mg_5Al_2Si_3O_{10}(OH)_8 + 0.175Fe_2O_3 + 0.165Al_2SiO_5 + 1.08SiO_2 - 1.14H_2O$	−1332.876	7
8. $0.535Mg_5Al_2Si_3O_{10}(OH)_8 + 0.175Fe_2O_3 + 0.165Al_2Si_2O_5(OH)_4 + 0.915SiO_2 - 1.47H_2O$	−1334.031	8
Montmorillonite (average) $K_{0.4}Al_{1.67}Fe_{0.17}Mg_{0.38}Si_{3.83}O_{10}(OH)_2$		
1. $0.835Al_2Si_4O_{10}(OH)_2 + 0.19Mg_2SiO_4 + 0.2K_2O + 0.085Fe_2O_3 + 0.3SiO_2 + 0.165H_2O$	−1243.456	0
2. $1.67Al(OH)_3 + 0.38MgSiO_3 + 0.085Fe_2O_3 + 0.2K_2O + 3.45SiO_2 - 1.505H_2O$	−1245.059	0
3. $0.4KAlSi_3O_8 + 0.635\ Al_2Si_4O_{10}(OH)_2 + 0.38MgO + 0.085Fe_2O_3 + 0.09SiO_2 + 0.365H_2O$	−1261.673	2
4. $0.4KAlSi_3O_8 + 0.635Al_2SiO_5 + 0.085Fe_2O_3 + 0.38MgSiO_3 + H_2O + 1.615SiO_2$	−1261.752	2
5. $0.4KAlSiO_4 + 0.635Al_2Si_2O_5(OH)_4 + 0.19Mg_2SiO_4 + 0.085Fe_2O_3 + 1.97SiO_2 - 0.27H_2O$	−1264.066	3
6. $0.4KAlSi_3O_8 + 0.635Al_2Si_2O_5(OH)_4 + 0.085Fe_2O_3 + 0.38MgSiO_3 + 0.98SiO_2 - 0.27H_2O$	−1266.198	5
Montmorillonite (idealised) $K_{0.33}Al_{1.67}Mg_{0.33}Si_4O_{10}(OH)_2$		
1. $1.67AlO(OH) + 4SiO_2 + 0.33MgO + 0.165K_2O + 0.165H_2O$	−1248.368	0
2. $0.5Al_2Si_2O_5(OH)_4 + 0.335Al_2SiO_5 + 2.665SiO_2 + 0.165K_2O + 0.33MgO$	−1250.308	0
3. $0.835Al_2SiO_5 + 3.265SiO_2 + 0.165K_2O + 0.33MgO + H_2O$	−1267.272	2
4. $0.67Al_2Si_4O_{10}(OH)_2 + 0.33KAlSi_3O_8 + 0.33MgO + 0.33SiO_2 + 0.33H_2O$	−1268.141	2
5. $0.33KAl_3Si_3O_{10}(OH)_2 + 0.165Mg_2SiO_4 + 0.34Al_2SiO_5 + 2.505SiO_2 + 0.67H_2O$	−1270.108	3
6. $0.11Mg_3Si_2O_5(OH)_4 + 0.33KAlSi_2O_6 + 0.67Al_2Si_4O_{10}(OH)_2 + 0.44SiO_2 + 0.11H_2O$	−1270.755	4
7. $0.33MgSiO_3 + 0.33KAlSi_3O_8 + 0.5Al_2Si_2O_5(OH)_4 + 0.17Al_2SiO_5 + 1.51SiO_2$	−1271.143	4
8. $0.34Al_2Si_4O_{10}(OH)_2 + 0.165Mg_2SiO_4 + 0.33KAl_3Si_3O_{10}(OH)_2 + 1.485SiO_2 + 0.33H_2O$	−1271.733	6
Saponite $K_{0.33}Al_{0.33}Mg_3Si_{3.67}O_{10}(OH)_2$		
1. $0.165Al_2O_3 + 3MgO + 3.67SiO_2 + 0.165K_2O + 2H_2O$	−1290.559	0
2. $0.165Al_2SiO_5 + 3MgSiO_3 + 0.165K_2O + 0.505SiO_2 + H_2O$	−1315.337	2
3. $1.5Mg_2SiO_4 + 0.33KAlSi_3O_8 + 1.18SiO_2 + H_2O$	−1330.992	4
4. $0.5Mg_3Si_4O_{10}(OH)_2 + 0.33KAlSiO_4 + 0.75Mg_2SiO_4 + 0.59SiO_2 + 0.5H_2O$	−1336.831	5
5. $Mg_3Si_2O_5(OH)_4 + 0.33KAlSiO_4 + 1.34SiO_2 - H_2O$	−1341.384	6
6. $0.5Mg_3Si_4O_{10}(OH)_2 + 0.5Mg_3Si_2O_5(OH)_4 + 0.33KAlSiO_4 + 0.34SiO_2 - 0.5H_2O$	−1342.742	6
Nontronite $K_{0.33}Al_{0.33}Fe_2Si_{3.67}O_{10}(OH)_2$		
1. $0.11KAl_3Si_3O_{10}(OH)_2 + Fe_2O_3 + 0.11K_2O + 3.34SiO_2 + 0.89H_2O$	−1067.595	0
2. $0.33KAlSiO_4 + 3.34SiO_2 + 2FeO(OH)$	−1076.495	2
3. $0.33KAlSi_3O_8 + 2FeO(OH) + 2.68SiO_2$	−1077.925	3
4. $0.33KAlSi_3O_8 + 2.68SiO_2 + Fe_2O_3 + H_2O$	−1078.770	4
Chlorite (aluminous) $Al_{4.8}Si_{3.4}O_{10}(OH)_8$		
1. $2.4Al_2O_3 + 3.4SiO_2 + 4H_2O$	−1822.134	0
2. $4.8AlO(OH) + 3.4SiO_2 + 1.6H_2O$	−1829.300	2
3. $0.85Al_2Si_4O_{10}(OH)_2 + 3.1AlO(OH) + 1.6H_2O$	−1831.776	3
4. $1.7Al_2Si_2O_5(OH)_4 + 0.7Al_2O_3 + 0.6H_2O$	−1835.935	5
5. $1.7Al_2Si_2O_5(OH)_4 + 1.4AlO(OH) - 0.1H_2O$	−1838.025	7

and Keller, 1973) and −1319.7* (Reesman, 1974) have been obtained for Fithian illite; −1272.1* and −1273.4¶ for Goose Lake illite (Rouston and Kittrick, 1971; Tardy and Garrels, 1974); and −1250.0*, −1274.7* and −1276.2¶ for Beavers Blend illite (Huang and Keller, 1973; Rouston and Kittrick, 1971; Tardy and Garrels, 1974). In spite of compositional variations even amongst the Fithian illite samples used by the various workers, the ΔG°_{f} value calculated in this study is well within the range of values obtained experimentally. Moreover, the ΔG°_{f} of illite (average) evaluated in this study by the regression method, i.e., −1302.349 kcal/mole, is very close to that of a similar mineral studied by Helgeson (1969) and Nriagu (1975), the values obtained by them being −1300.98* and −1301.05¶ kcal/mole, respectively. Experimental data for the other minerals such as saponite, nontronite, etc., are not yet available for comparative analysis.

In order to derive the ΔG°_{f} of other clay minerals, the combinations shown in Tables 2 and 4 may be easily utilized. Appropriate balancing of equations must be done. Care must be taken to ensure that composition of the mineral gives a net charge of zero; if cationic charge differs from the anionic charge by even a small fraction, then the equations cannot be balanced. Necessary adjustments, in the composition, may be made before further computation can be done.

In conclusion, it appears that this method provides a fairly reliable and rapid means of evaluating ΔG°_{f} of clay minerals. Its greatest advantage is its extreme versatility; it can be utilized for any kind of clay mineral, and all that is needed is a knowledge of its chemical composition. In cases where experimental determinations are not convenient, the regression method provides a handy tool for obtaining very important thermodynamic data.

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