AN EXAMINATION OF STANDARD ENTHALPIES OF FORMATION OF SELECTED MINERALS IN THE SYSTEM SiO₂–Al₂O₃–Na₂O–K₂O–H₂O
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ABSTRACT. Thermodynamic calculations based on equilibrium experiments involving univariant hydrothermal reactions indicate that $\epsilon_{\text{corundum}} - \epsilon_{\text{muscovite}} = 9800$ cal (+350), where the $\epsilon$'s denote the errors in the standard enthalpies of formation tabulated in Robie and Waldbaum (1968). Methods of estimating entropies and heat capacities are discussed. From a critical survey of the literature, self-consistent thermodynamic data independent from the standard enthalpies of formation of corundum, the aluminosilicate polymorphs, and muscovite have been established for several minerals and aqueous species and are $G_r^\circ(\text{Al}^{+++}) = -116.0$ kcal mole$^{-1}$, $G_r^\circ[\text{Al(OH)}_2]^-$ = $-310.2$, $G_r^\circ(\text{H}_2\text{SiO}_3) = -312.56$, $G_r^\circ(\text{amorphous silica}) = -202.8$, $G_r^\circ(\text{gibbsite}) = -274.16$, $G_r^\circ(\text{bayerite}) = -273.67$, $G_r^\circ(\text{diaspore}) = -219.05$, and $G_r^\circ(\text{boehmite}) = -216.85$ kcal mole$^{-1}$. Using these data and data from the literature for quartz, kaolinite, alkali feldspars, sodium montmorillonite, and water, together with the constraint $\epsilon_{\text{quartz}} = 9800$ cal, independent calculations of $H_r^\circ(\text{aluminosilicate})$ based on hydrothermal reactions result in two mutually exclusive sets of standard enthalpies of formation for corundum, the aluminosilicate polymorphs, paragonite, and muscovite. Each is supported by independent evidence, but the two sets have been checked against soil, diagenetic and certain hydrothermal mineral assemblages, and against their associated interstitial solutions. The following values of enthalpies were adopted: $H_r^\circ(\text{corundum}) = -391.9$ kcal mole$^{-1}$, $H_r^\circ(\text{muscovite}) = -1422.48$, $H_r^\circ(\text{paragonite}) = -1412.05$, $H_r^\circ(\text{pyrophyllite}) = -1342.42$, $H_r^\circ(\text{aluminosilicate}) = -610.89$, $H_r^\circ(\text{silimanite}) = -610.15$, $H_r^\circ(\text{kyanite}) = -611.43$, and $H_r^\circ(\text{mullite}) = -1604.4$ kcal mole$^{-1}$, which provide an internally consistent set that best explains the geological observations. The question of inconsistencies will only be settled by new calorimetric determinations of enthalpies of key minerals.

INTRODUCTION

The behavior of reactions and the stability relations of mineral assemblages are governed by thermodynamic quantities, and so a knowledge of entropies and enthalpies is a basic requirement for every geochemical calculation. Thermodynamic data are available for many minerals, but the tabulated values are not always consistent internally with phase equilibrium data. In many instances, new determinations show drastic departures from previously reported figures. A case in point is provided by the history of the standard enthalpy of quartz, which was found as recently as 1962 to be about 7 kcal more negative than the older value of $-210$ kcal mole$^{-1}$ (Rossini and others, 1952).

Thermodynamic properties have been measured or estimated for most of the important minerals in the system SiO₂–Al₂O₃–K₂O–Na₂O–H₂O (for example, Robie and Waldbaum, 1968; Reesman and Keller, 1968; Wagman and others, 1968; Helgeson, 1969; Zen, 1972; Parks, 1972), but inconsistencies, especially in the standard enthalpies of formation of some minerals, have been pointed out several times (for example, Flood

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and Knapp, 1957; Kay and Taylor, 1960; Pankratz and Kelley, 1964b; Zen, 1969a, 1972). The purpose of this paper is to determine a set of internally consistent standard enthalpies of formation for the minerals in the system SiO₂- Al₂O₃–K₂O–Na₂O–H₂O based on an analysis of available phase equilibrium and calorimetric data and to consider these values in terms of the mineralogy found in soils and in diagenetic assemblages.

CALCULATION OF STANDARD ENTHALPIES AND FREE ENERGIES
FROM HYDROTHERMAL EQUILIBRIUM CURVES

Much experimental information has been gathered on reactions under various pressures and temperatures, simulating conditions occurring in natural rock systems. Consider the equilibrium between kaolinite and pyrophyllite, which may be represented by

\[
\text{Al}_2\text{Si}_3\text{O}_9\text{(OH)}_4 + 2\text{H}_4\text{SiO}_4\text{(aq)} \rightleftharpoons \text{Al}_2\text{Si}_4\text{O}_{10}\text{(OH)}_2 + 5\text{H}_2\text{O}
\]

(kaolinite) (pyrophyllite)

The fluid phase can be a chloride solution or pure water. Equilibrium conditions are fixed when P, T, and the concentrations of aqueous species are measured. The same reaction can be studied in a more restricted way with pure water as the initial fluid phase and quartz present:

\[
1 \text{ kaolinite} + 2 \text{ quartz} \rightleftharpoons 1 \text{ pyrophyllite} + 1 \text{ H}_2\text{O},
\]

where equilibrium conditions are known simply by measuring P and T.

Studies of the second type have been performed extensively (compare, Fyfe, 1960, for a discussion). We will call them buffered hydrothermal reactions, as opposed to the first type of non-buffered hydrothermal experiments (for example, the ones studied by Hemley, 1967).

Evaluation of hydrothermal synthesis data.—When standard enthalpies of formation are calculated from reversed hydrothermal curves in P-T space, errors in the experimental set-up are transmitted to the thermodynamic quantities.

For reversed hydrothermal experiments in which kinetic barriers have been overcome, it is probably safe to assume that the T-P brackets obtained represent true equilibria (compare, Fyfe, 1960; Turner, 1968, p. 92 and following). Differences of only several hundred calories per mole in the \( H_f^\circ \) of a mineral can shift the equilibrium P-T curve by several tens of degrees and/or several hundreds (or even thousands) of bars. Hydrothermal techniques can detect equilibrium points within a few tens of degrees and a few hundred bars and are therefore able to determine very small differences in \( H_f^\circ \) or \( G_f^\circ \). For instance, experiments by Althaus (1969) could detect shifts in the kyanite–sillimanite reaction in the P-T dimensions when starting materials of slightly different composition were used.

In short, phase equilibrium data are sensitive enough so that thermodynamic data calculated from them can be as reliable as data determined calorimetrically.
Methods of calculation.—Once equilibrium curves are experimentally determined, thermodynamic quantities can be derived from individual data points or smoothed curves (Robie and Stout, 1963; Orville and Greenwood, 1965; Weisbrod, 1968; Zen, 1969a, 1971, and 1972; and Fisher and Zen, 1971).

In the present analysis, rather than using smoothed curves (as proposed by Orville and Greenwood and by Weisbrod) we shall consider each experimental equilibrium point on its own merit, as suggested by Robie and Stout (1963), Robie (1965), Helgeson (personal commun.), Apps (1968), and Zen (1971).

Our approach is similar to that of Robie (1965), but instead of using \((H_r^o - H_{298}^o)\) and \((S_r^o - S_{298}^o)\), calculations are carried out with the equation

\[
\Delta G(T,P) = \sum n_i H_r^o(T_r, P_r) + \sum n_i \int_{T_r}^{T} C_{P_i} dT - \left( \sum n_i S_1^o \right) \cdot T - \left[ \sum n_i \int_{T_r}^{T} \frac{C_{P_i}}{T} dT \right] \cdot T + \Delta V_s^o \cdot \Delta P + \int_{P_r}^{P} n_i V_{f_i} dP \quad (1)
\]

where \(C_p\) is a known function of the temperature. At equilibrium, \(\Delta G(T,P) = 0\). The change in volume of the solids can be considered constant below 10 kbar as discussed by Waldbaum (1965), Helgeson (1969), and Zen (1969a, 1971) and is substantiated by coefficients of thermal expansion and compressibility given by Birch (1966) and Skinner (1966). Pressure effects on the Gibbs energy of water, represented by the last term in equation 1, have been obtained from the tabulation of Burnham, Holloway, and Davis (1969). Molar volumes of minerals, enthalpies, and entropies are from the references mentioned earlier. Heat capacity coefficients are from Kelley (1960) and other publications of the Bureau of Mines.

Equation 1 represents the equilibrium condition for a reaction in \(P\)-\(T\) space and can therefore be used to calculate the equilibrium curve.

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1 List of symbols: \(a, b, c,\) coefficients of heat capacity functions; \(C_r,\) heat capacity at constant pressure; \(\Delta G(T,P),\) Gibbs free energy of a reaction at \(T\) and \(P;\) \(G_r^o,\) standard Gibbs energy of formation from the elements at \(T_r = 25^\circ C\) and \(P_r = 1\ atm;\) \(\Delta H_r^o(T,P),\) enthalpy change in a reaction at \(T\) and \(P;\) \(H_r^o,\) standard enthalpy of formation from the elements, at \(T_r\) and \(P_r;\) \(K(T,P),\) equilibrium constant of a reaction at \(T, P;\) \(n, n_i,\) coefficients of equations or chemical reactions; \(P_r,\) reference pressure, 1 atm; \(P,\) pressure; \(S_r^o,\) third-law entropy; \(\Delta S_r^o(T,P),\) entropy change of a reaction at \(T\) and \(P;\) \(T_r,\) reference temperature, 298.15 K; \(T,\) temperature in degrees Kelvin; \(V,\) molar volume; \(\Delta V_s,\) change of volume of solids across a reaction; Subscripts: \(c, s, g,\) crystalline, solid, gaseous; \(w,\) water; \(aq,\) aqueous. Superscript \(^o\) refers to standard state.
Conversely, if points on the curve are known experimentally, the standard enthalpy of formation of any one mineral in the reaction can be calculated from the equilibrium points, provided that the rest of the thermodynamic data are available. This assumes a previous knowledge of the third-law entropy and heat capacity equation of the mineral whose enthalpy of formation is being calculated. For many geologically important minerals, this is the case, but in other instances, no such data are available. Fortunately, there are several methods by which a fair estimate can be attempted; a discussion is given in the following paragraphs.

Estimation of heat capacity power functions; errors involved.—Heat capacities are well represented by the function \( C_p = a + b \, T + c \, T^{-2} \) (Maier and Kelley, 1932). Helgeson (1969), among others, indicates that a summation method gives satisfactory estimates of the heat capacity of a mineral. The method assumes that the heat capacity function is equal to the summation of those of the oxide components; structural water is represented with a constant \( C_p \) of 9 cal K\(^{-1}\) mole\(^{-1}\). In equation 1 the estimated heat capacity function of the mineral whose enthalpy of formation is being calculated appears in two integrals, \( \int \frac{C_p}{T} \, dT \) and \( \int \frac{C_p}{T} \, dT \), one related to enthalpy and the other to entropy. If one assumes that a certain error \( \varepsilon \) is associated with the estimation of the \( C_p \) function, the total error due to a faulty estimate is therefore

\[
\Delta_{\text{total}} = n_i \int \varepsilon \, dT - (n_i \int \varepsilon / T \, dT) \cdot T
\]  

(2)

as derived from equation 1.

One way of checking possible uncertainties due to the oxide summation estimate is to compare experimental heat capacities against estimated ones. For that purpose, several silicates from various structural groups with known \( C_p \) functions were chosen, and the following values calculated at different temperatures at atmospheric pressure: heat capacity, entropy, enthalpy of formation, and total error as expressed in equation 2. In figure 1 the results are represented as differences between the "observed" and the "calculated" values, the "observed" value being the one calculated with the \( C_p \) function derived from experimental data, and the "calculated" figure the value obtained by means of the oxide summation estimate. \( C_p \)'s were taken from Kelley (1960), Helgeson (1969), Pankratz and Kelley (1964a, gehlenite), Pankratz (1968, \( \alpha \)-leucite); other figures are from Robie and Waldbaum (1968). For most minerals the deviation from experimental values remains within moderate limits at low temperatures. Maximum deviations were found in estimating \( C_p \) of microcline. Disregarding that case, at 700\(^\circ\)C the deviations are: in \( C_p \)'s, from \(-6\) to about 0.0 cal K\(^{-1}\) mole\(^{-1}\); in entropies, from \(-4\) to 0.0 cal K\(^{-1}\) mole\(^{-1}\), and in enthalpies, from \(-3000\) to 0.0 cal mole\(^{-1}\) (fig. 1A to C). However, since enthalpies and the entropy contribution in equation 2 have opposing sign, the total error is considerably reduced: again at 700\(^\circ\)C, total error is usually well below 1 kcal mole\(^{-1}\) (fig. 1D). In the worst possible case, that of microcline, total error is
Fig. 1. Thermodynamic quantities calculated from observed and estimated $C_p$ functions to illustrate errors introduced by estimation procedure. A = albite; Cl = clinoenstatite; F = forsterite; G = gehlenite; J = jadeite; L = leucite; M = microcline; Mu = muscovite.
A. Heat capacity calculated with an experimental ("observed") function and with an estimated one. Plotted as deviations $[C_p ("observed") - C_p (estimated)]$ versus temperature.
B. Entropy calculated from "observed" $C_p$ functions versus entropy calculated from the estimated function plotted as deviations $[S ("observed") - S (estimated)]$ versus temperature.
C. High-temperature enthalpy $[H(T) - H(288)]$ estimates from $C_p$ functions plotted as deviations $[\delta = \Delta H ("observed") - \Delta H (estimated)]$ versus temperature.
D. Total error versus temperature. Total error is $\epsilon = \delta - \Delta S \times T$ where $\delta$ is defined in (C), and $\Delta S$ is represented in (B).
around 1600 cal mole\(^{-1}\) for that temperature. Taking these results as indicative of a general trend, it can be said that the oxide summation method—although generally overestimating thermodynamic properties—permits a reasonably accurate estimate of enthalpies of formation with the approach described in the text.

**Estimation of third-law entropies.**—Entropies can be estimated by using additivity rules and other methods (Latimer, 1951; Fyfe, Turner, and Verhoogen, 1958; Helgeson, 1969; Drozin, 1961, listed in Ivanov and Gusynin, 1970; Fonarev, 1967; and Zen, 1971).

In the phyllosilicates, a good estimate can be obtained by a slight variation of the oxide additivity rule by incorporating Mg as brucite and the non-tetrahedral Al as gibbsite, insofar as water in the structure allows it. As an example, the entropies of muscovite (two non-tetrahedral Al) and talc (three Mg) can be estimated by adding the entropies of 0.5 K\(_2\)O, 0.667 Al(OH)\(_3\), 1.167 Al\(_2\)O\(_3\), 3 SiO\(_2\), and 1 Mg(OH)\(_2\), 2 MgO, 4 SiO\(_2\), respectively. Corrections to entropies can be performed by a relationship of the type: \(S = S' + n' k (V_{\text{obs}} - V_{\text{calc}})\) (compare Fyfe, Turner, and Verhoogen, 1958), where the index \(n'\) is a normalizing factor, equal to the number of non-tetrahedral Al or Mg atoms not incorporated as gibbsite or brucite (for example, in muscovite and talc, \(n' = 1.334\) and 2.0, respectively), \(S'\) is the uncorrected oxide-hydroxide summation entropy, \(k' = 0.65\) on the average, \(V_{\text{obs}}\) is the experimental molar volume, and \(V_{\text{calc}}\) the oxide-hydroxide summation volume. Estimates for phyllosilicates are usually close to the observed entropies, especially since the volume calculated by oxide-hydroxide addition is also close to the observed volume (table 1).

**CRITICAL SURVEY OF THE THERMODYNAMIC PROPERTIES OF SOLUTION SPECIES**

Standard thermodynamic properties of minerals and aqueous species can be calculated from hydrothermal synthesis studies (Hemley, 1959; Hemley and Jones, 1964; and others) and from solubility measurements.

**Table 1**

Estimation of entropies of phyllosilicates by oxide-hydroxide summation

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Observed values</th>
<th>Oxide summation</th>
<th>Oxide-hydroxide summation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>S(_{\text{uncor}})</td>
<td>S(_{\text{vol-cor}})</td>
</tr>
<tr>
<td>Dickite</td>
<td>94.20</td>
<td>198.60</td>
<td>101.48</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>97.06</td>
<td>199.04</td>
<td>101.48</td>
</tr>
<tr>
<td>Halloysite</td>
<td>97.20</td>
<td>198.60</td>
<td>101.48</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>56.60</td>
<td>126.60</td>
<td>61.10</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>76.40</td>
<td>149.91</td>
<td>75.70</td>
</tr>
<tr>
<td>Muscovite</td>
<td>69.00</td>
<td>140.71</td>
<td>68.56</td>
</tr>
<tr>
<td>Talc</td>
<td>62.34</td>
<td>136.25</td>
<td>68.24</td>
</tr>
</tbody>
</table>

\(S = \) Entropy in cal K\(^{-1}\) mole\(^{-1}\); \(V = \) molar volume in cc. 
S\(_{\text{uncor}}\) = Uncorrected entropy; S\(_{\text{vol-cor}}\) = volume-corrected entropy; V\(_{\text{calc}}\) = calculated molar volume.

For n' see text.

Entropy of pyrophyllite from King and Weller (1970); rest of the data from Robie and Waldbaum (1968).
(for example, Kittrick, 1966a, 1966b; Apps, ms). A revision of some of the most important solution species and adoption of a consistent set is in order. Where needed, heat capacity equations and additional data have been taken from Helgeson (1969) and Robie and Waldbaum (1968).

$\text{Al(OH)}_3^-$—Wagman and others (1968) presented a set of values for the enthalpy, Gibbs energy, and entropy of $\text{Al(OH)}_3^-$, Apps (ms) gave a thorough experimental and theoretical examination in which results are derived from solubility measurements of gibbsite (partly taken from the literature) at high pH:

$$\text{Al(OH)}_3 + \text{H}_2\text{O} = \text{Al(OH)}_3^- + \text{H}^+$$  \hspace{1cm} (3)

and depend on the standard enthalpy, Gibbs energy, and entropy of gibbsite (Robie and Waldbaum, 1968). Helgeson (1969, table 4) computed $\log K = -32.73$ at 25°C for:

$$\text{Al(OH)}_3^- = \text{Al}^{3+} + 4\text{OH}^-$$  \hspace{1cm} (4)

from which $G_r^0(\text{Al(OH)}_3^-) = -311036$ cal mole$^{-1}$; the corresponding enthalpy is $-357180$ cal mole$^{-1}$. Parks (1972) derived $G_r^0(\text{Al(OH)}_3^-) = -311.0 \pm 0.100$ kcal mole$^{-1}$, based on reversed solubility measurements of crystalline gibbsite (Kittrick, 1966a). The standard enthalpy of formation and Gibbs energy of $\text{Al(OH)}_3^-$ adopted here (table 2) are those of Wagman and others (1968). These values may be subject to an uncertainty as large as $\pm 1$ kcal mole$^{-1}$ (Parks, 1972) and are consistent with the values adopted here for $G_r^0(\text{Al}^{3+})$ and $G_r^0(\text{gibbsite})$—see p. 519, discussion on gibbsite.

$\text{Al}^{3+}$—The standard thermodynamic properties for $\text{Al}^{3+}$ are based on the early experimental work of Richards, Rowe, and Burgess (1910) and Latimer and Greensfelder (1928), although some indirect confirmation has been obtained from other publications (especially for $H_r^0(\text{Al}^{3+})$, V. B. Parker, 1972, written commun.). The thermodynamic figures are especially biased by the highly uncertain value given for $S^0(\text{Al}^{3+})$, which ranges from $-76.0$ ($\pm 10$) cal K$^{-1}$ mole$^{-1}$ (Latimer, Pitzer, and Smith, 1958) to $-91.5$ cal K$^{-1}$ mole$^{-1}$ (Coble, 1972, written commun.). This large uncertainty in $S^0(\text{Al}^{3+})$ is caused mainly by uncertainties in $S^0(\text{Cs}^{+})$ and especially $S^0(\text{Cs-alum})$ (compare experimental procedure in Latimer and Greensfelder, 1928), for which no newer measurements are available. As a result of the large uncertainty in $S^0(\text{Al}^{3+})$, estimates for $G_r^0(\text{Al}^{3+})$ range from $-116$ kcal mole$^{-1}$ (Wagman and others, 1968) to $-114.8$ kcal mole$^{-1}$ (Coble, 1972, written commun.)

A choice has to be made, though, for the purposes of the present work. As far as $H_r^0(\text{Al}^{3+})$ is concerned, a test can be attempted in the following way. Gayer, Thompson, and Zajicek (1958) measured the solubility of bayerite at 25°C under acid conditions:

$$\text{Al(OH)}_3 = \text{Al}^{3+} + 3(\text{OH})^-$$  \hspace{1cm} (5)

for which $\log K = -32.96$; if $G_r^0(\text{Al}^{3+}) = -116$ kcal mole$^{-1}$, then $G_r^0(\text{bayer}) = -273.7$ kcal mole$^{-1}$, whereas when $G_r^0(\text{Al}^{3+}) = -114.8$
kcal mole\(^{-1}\) (Cobble's figure), \(G_f^o\) (bayer) = \(-272.5\) kcal mole\(^{-1}\). Russell, Edwards, and Taylor (1955) (compare Apps, ms) studied the dissolution of bayerite at higher pH, for which reaction (3) holds. They obtained log \(K = -14.71\) at 25°C, which gives \(G_f^o\) (bayer) = \(-273.6\) kcal mole\(^{-1}\); this figure is comparable to the one obtained by using \(G_f^o\) (Al\(^{3+}\)) = \(-116.0\) kcal mole\(^{-1}\) in reaction (5). In order to bring the Gibbs energy of bayerite computed from reaction (5) (using \(G_f^o\) (Al\(^{3+}\)) = \(-114.8\)) to coincide with the one derived from reaction (3), \(G_f^o\)

### Table 2

<table>
<thead>
<tr>
<th>Substance*</th>
<th>(S_f^*) cal K (^{-1}) mole(^{-1})</th>
<th>(H_f^*) cal mole(^{-1})</th>
<th>(G_f^*) cal mole(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>9.88</td>
<td>-217650 ± 400</td>
<td>-204646 ± 410</td>
</tr>
<tr>
<td>Amorphous silica**</td>
<td>13.90</td>
<td>-214600 ± 580</td>
<td>-202800 ± 650</td>
</tr>
<tr>
<td>Microcline</td>
<td>52.47</td>
<td>-946265 ± 990</td>
<td>-892817 ± 970</td>
</tr>
<tr>
<td>High sanidine</td>
<td>56.94</td>
<td>-944378 ± 930</td>
<td>-892623 ± 980</td>
</tr>
<tr>
<td>Low albite***</td>
<td>50.20</td>
<td>-937146 ± 740</td>
<td>-883988 ± 760</td>
</tr>
<tr>
<td>High albite</td>
<td>54.67</td>
<td>-934513 ± 770</td>
<td>-882687 ± 790</td>
</tr>
<tr>
<td>Adularia</td>
<td>55.99</td>
<td>-945000 ± 1200</td>
<td>-892602 ± 1240</td>
</tr>
<tr>
<td>Kaolinite†</td>
<td>48.53</td>
<td>-980020 ± 950</td>
<td>-903430 ± 960</td>
</tr>
<tr>
<td>Gibbsite†</td>
<td>16.75</td>
<td>-307050 ± 325</td>
<td>-274160 ± 320</td>
</tr>
<tr>
<td>Bayerite†</td>
<td>19.9††</td>
<td>-305890 ± 450</td>
<td>-273670 ± 335</td>
</tr>
<tr>
<td>Biahpore†</td>
<td>8.45†††</td>
<td>-237820 ± 335</td>
<td>-219050 ± 330</td>
</tr>
<tr>
<td>Boehmite†</td>
<td>11.58†††</td>
<td>-234660 ± 390</td>
<td>-216850 ± 320</td>
</tr>
<tr>
<td>Na-montmorillonite§</td>
<td>62.8</td>
<td>-1366840</td>
<td>-1277760</td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>-76.9 ± 10§§§</td>
<td>-127000§§§</td>
<td>-11600 ± 300§§§§</td>
</tr>
<tr>
<td>Al(OH)(_2^{\text{+}})</td>
<td>28.</td>
<td>-356200</td>
<td>-310200 ± 300§§§</td>
</tr>
<tr>
<td>Al(OH)(_3^{\text{+}})</td>
<td>165930 ± 320†</td>
<td>-165930 ± 320†</td>
<td></td>
</tr>
<tr>
<td>H(_2)SiO(_4)</td>
<td>45.84†††</td>
<td>-348060 ± 400‡‡</td>
<td>-312560 ± 410‡‡‡‡</td>
</tr>
</tbody>
</table>

All entropies, except those of amorphous silica, bayerite, and Na–montmorillonite, are from Robie and Waldbbaum (1968); enthalpies and free energies of quartz and alkali feldspars are also from Robie and Waldbbaum (1968). For the rest, see text.

* Formulae of minerals as in text.

** All values are for a "conventional" amorphous silica in Kitahara's experiments (1960); the uncertainty in \(S_f^*\) is as high as \(1\) cal K \(^{-1}\) mole\(^{-1}\).

*** Slightly different values of \(H_f^\text{m}^\text{r}(\text{microcline})\) and \(H_f^\text{m}^\text{r}(\text{low albite})\) are given in Helgeson (1969).

† See text.

†† Entropies may be in error (compare Apps, ms).

§ From Helgeson (1969, table 12).

§§§ From Helgeson (1969); values are close to uncertainty limits in Apps (ms).


### For a reaction:

\(n_A + n_B + \ldots = n_C + n_D + n_X\ldots\)

the uncertainty for phase X is computed as
\[u_x = \sqrt{\sum (u_i)^2}\]

where \(u_i\) is the uncertainty of phase \(i\) with coefficient \(n_i\) and \(u_x\) is the uncertainty in the chemical reaction itself (compare Rossini and Deming, 1939). Uncertainties in free energy from enthalpies—or vice versa—were computed according to Robie and Waldbbaum (1968, p. 10).
(Al(OH)$_4^-$) has to be increased to $-309.0$ kcal mole$^{-1}$—a figure not validated by any author. Therefore, the value $G_f^o(Al^{+++}) = -116.0$ kcal mole$^{-1}$, although rather uncertain, is here chosen.

$H_4SiO_4$—The neutral species $H_4SiO_4$ is dominant at low temperatures in neutral and moderately alkaline solution (for example, Apps, ms). Apps (ms) examines solubility data for the reaction

$$SiO_2(s) + 2 H_2O = Si(OH)_4(aq)$$  

where s = quartz, amorphous silica, or cristobalite. Helgeson (1969) bases his computations on quartz solubility measurements by Morey and others and Kennedy (both papers are referenced in Helgeson, 1969); his figures agree closely, except for the entropy, with those of Apps and are adopted in this paper (table 2). Values by Wagman and others (1968) are apparently too negative.

$Al(OH)^{2+}$—The dominant aluminum species in solution at moderately acid pH is $Al(OH)^{2+}$ (for example, Helgeson, 1969). Equilibrium constants for the reaction

$$Al^{3+} + H_2O = Al(OH)^{2+} + H^+$$

have been measured by several authors (compare, Sillén and Martell, 1964). The extrapolations to infinite dilution most in agreement are as follows: Schofield and Taylor (1954), log $K = -4.98$; Kenttämäa (1955), log $K = -4.98$; Nischide and Tsuchiya (1965), log $K = -4.9$. An average figure is log $K = -4.95$. The free energy of $Al(OH)^{2+}$ at 25$^\circ$C is then taken to be $-165930 \pm 320$ cal mole$^{-1}$.

$OH^-$, $Na^+$, $K^+$—Thermodynamic quantities for the species $OH^-$, $Na^+$, $K^+$ have been taken from Latimer (1952) and are practically equivalent to figures in Wagman and others (1968, p. 263).

CRITICAL SURVEY OF THERMODYNAMIC PROPERTIES OF MINERALS IN THE SYSTEM $SiO_2-Al_2O_3-K_2O-Na_2O-H_2O$

Widely differing values have been proposed for standard thermodynamic properties of the crystalline phases in this system. With few exceptions, the entropies are apparently accurate, but the standard enthalpies of formation of many minerals appear to be highly uncertain. The standard enthalpies and third law entropies adopted for the calculations carried out later in this paper are listed in table 2, and the reasons for their selection are given in the following discussion. The heat capacity coefficients used in our analysis of equilibrium data are from Kelley (1960) and Helgeson (1969) or have been estimated as discussed above.

Quartz, $\alpha-SiO_2$—The standard thermodynamic properties for quartz seem well established, since the work of Wise and others (1962) and Good (1962). The values adopted are those of Robie and Waldbaum (1968).

Amorphous silica, $SiO_2\cdot nH_2O$—Thermodynamic data on amorphous silica (as contrasted to silica glass) are important because natural waters have concentrations of aqueous $H_4SiO_4$ determined largely by the
solubilities of quartz and amorphous silica (for example, Siever, 1957; Garrels and Christ, 1965, p. 361). Amorphous silica is not a well-defined species on account of varying degrees of water content, and so a convention has to be set up. Thermodynamic data have been extracted from a set of careful solubility experiments by Kitahara (1960). His solubility measurements coincide on the whole with those of other authors (for example, Siever, 1962). From his data, \( \Delta H^\circ \) (amorphous silica) = \(-214600 \pm 580\) cal mole\(^{-1}\). Kitahara's high-temperature data fit the function \( C_p = 21.0 + 4.4 \times 10^{-3} \ T - 3.45 \times 10^6 \ T^{-2} \) up to 100°C.

Gibbsite, \( \text{Al(OH)}_3 \).—Enthalpies and Gibbs energies determined calorimetrically are respectively \(-306380 \pm 300\) cal mole\(^{-1}\) and \(-273486 \pm 310\) cal mole\(^{-1}\) (Barany and Kelley, 1961, as slightly modified by Robie and Waldbbaum, 1968). Solubility measurements on well-crystallized gibbsite were performed by several authors. Kittrick (1966a) reversed the hydrolysis reaction (3) and computed \( \Delta G^\circ \) (gibbsite) = \(-274.2 \pm 0.06\) kcal mole\(^{-1}\), whereas Reesman and Keller (1968) derived \( \Delta G^\circ \) (gibbsite) = \(-275.15\) kcal mole\(^{-1}\). Helgeson (1969) and Parks (1972) obtained around \(-275\) kcal mole\(^{-1}\) for the Gibbs free energy, using Kittrick's experimental data and \( \Delta G^\circ \) (Al(OH)$_3$) = \(-311\) kcal mole\(^{-1}\). A set of free energies consistent with the thermodynamic properties adopted here for aqueous aluminous species (table 2) is derived from several solubility measurements in the literature. Kittrick (1966a) determined log K = \(-15.30 \pm 0.05\) for the hydrolysis reaction (3), so that \( \Delta G^\circ \) (gibbsite) = \(-274390 \pm 300\) cal mole\(^{-1}\). Frink (1960, cited in Sillén and Martell, 1964) obtained log K = \(-33.51\) for reaction (5), so that \( \Delta G^\circ \) (gibbsite) = \(-274500\) cal mole\(^{-1}\). Ikkatai and Okada (1962, cited by Apps, ms) reversed the solubility reaction (3) and obtained log K = \(-14.86\), from which \( \Delta G^\circ \) (gibbsite) = \(273800\) cal mole\(^{-1}\). Apps (ms, p. 149 and following) on the basis of his own experiments, obtained log K = \(-14.99 \pm 0.04\) for reaction (3), from which \( \Delta G^\circ \) (gibbsite) = \(-273966 \pm 300\) cal mole\(^{-1}\). From these 4 results, the average Gibbs energy for gibbsite is \(-274160 \pm 320\) cal mole\(^{-1}\), and \( \Delta H^\circ \) (gibbsite) = \(-307050 \pm 325\) cal mole\(^{-1}\). These are the values tentatively adopted here. (Reesman and Keller's value becomes \( \Delta G^\circ \) (gibbsite) = \(-274100\) when made consistent with data in table 2 and compares well with our average.)

It is here assumed that the uncertainties in \( \Delta G^\circ \) (Al\(^{3+}\)) and \( \Delta H^\circ \) [Al(OH)$_3$] are \pm 300 cal mole\(^{-1}\) (Robie and Waldbbaum, 1968) and \pm 300 cal mole\(^{-1}\) (Apps, ms — see table 2). However, true uncertainties for aqueous species may be much larger than this (as suggested, for instance, by the large discrepancy between Cobble's and Wagman's estimates for \( \Delta G^\circ \) (Al\(^{3+}\))) in spite of the fact that experimental errors in dissociation constants and other figures may be very small.

Differences between values obtained from solubility experiments, on the one hand, and the figure based on calorimetry, on the other, may arise from variation in crystallinity and grain sizes of the starting

\(^2\)See note 1, table 2.
materials, as discussed by Parks (1972). Gibbsite varieties crystallize both in the monoclinic and triclinic systems (Saalfeld, 1960), and this may presumably affect their Gibbs energies of formation as well.

*Bayerite, Al(OH)₃.—* Gayer, Thompson, and Zajicek (1958) dehydrated an aluminum hydroxide precipitate, which, after annealing, crystallized as bayerite; solubility measurements on their sample yield log K = −32.96 for reaction (5) at 25°C, and G°ₜ(bayer) = −273756 cal mole⁻¹. Russell, Edwards and Taylor (1955) dissolved bayerite according to reaction (3), for which log K = −14.71 (see Apps, ms). With it, G°ₜ(bayer) = −273584 cal mole⁻¹. The average value is G°ₜ(bayer) = −273670 ± 335 cal mole⁻¹ and is the one adopted here as compared to G°ₜ = −274.6 in Parks (1972). Bayerite is rare in nature and known to be less stable than its polymorph gibbsite (for example, Deer, Howie, and Zussman, 1963). The Gibbs energies adopted here are consistent with this observation. The entropy of bayerite is here estimated to be 19 ± 1.0 cal K⁻¹ mole⁻¹ by using a volume-corrected summation of entropies of oxides (and taking S°ₜox = 9.4 cal K⁻¹ mole⁻¹; see discussion on entropy estimation above); this entropy would yield a tentative H°ₜ(bayerite) = −305890 ± 450.

**Diaspore, α-AlO(OH).—** Of the two polymorphs diaspore and boehmite, the first is considered the stable phase in nature under surface conditions by Kennedy (1959) and Apps (ms). The following solubility measurements are available. Apps (ms) measured log K = −16.29 ± 0.09 for the hydrolysis reaction

\[
\text{AlO(OH)} + 2\text{H}_2\text{O} = \text{Al(OH)}₄⁻ + \text{H}^+ \tag{8}
\]

so that our adopted value is G°ₜ(diaspore) = −219050 ± 330 cal mole⁻¹ and H°ₜ = −237820 ± 335 cal mole⁻¹. By comparison, Reesman and Keller (1968) obtained G°ₜ(diaspore) = −218.6 ± 0.4 kcal mole⁻¹. Apps (ms) pointed out for the first time that entropies of diaspore and/or boehmite may be in error by several units (see, however, preceding footnote).

**Boehmite, γ-AlO(OH).—** Russell, Edwards, and Taylor (1955) and Apps (ms) investigated the hydrolysis of boehmite according to reaction (8); the first authors obtained log K = −14.50 ± 0.08, and Apps derived log K = −14.85 ± 0.10. From these, G°ₜ(boehmite) is −216609 ± 320 and −217087 ± 330 cal mole⁻¹, respectively. The average, −216850 ± 330 cal mole⁻¹, is the value adopted in table 7. Correspondingly, H°ₜ(boehmite) = −284660 ± 330 cal mole⁻¹. The third-law entropy of boehmite may be in error (see discussion in Apps, ms, and preceding footnote).

**Corundum, α-Al₂O₃.—** The currently accepted value for the enthalpy of formation of corundum is −400.400 ± 0.300 kcal mole⁻¹ which has

---

*S* Since in calculations we are mainly interested in stability fields, a correct set of free energies or equilibrium constants is all that is needed: errors in entropies, as long as they are transmitted into enthalpies, do not affect the calculated boundaries of stability fields (compare eq. 1, above).
been obtained consistently in the three most recent combustion calorimetric studies on aluminum (see Mah, 1957). Helgeson (1969) and especially Zen (1972) proposed that large discrepancies in the Al$_2$SiO$_5$ data relative to other minerals may reflect an error as large as +7 kcal mole$^{-1}$ in the corundum value. Waldbaum (ms) calculated a value of $-396$ kcal mole$^{-1}$ for corundum from a reaction scheme that included some of the same auxiliary solution calorimetric data used to derive values of the enthalpies of formation of muscovite, kaolinite, and the alkali feldspars. Waldbaum believes that the combustion calorimetric data are probably correct and that the discrepancies between the enthalpies of formation of corundum, mica, feldspar, kaolinite, and pyrophyllite are due mainly to errors in the solution calorimetric data for AlCl$_3$$cdot$6H$_2$O or Al(OH)$_3$, gibbsite. In the discussion that follows, however, we shall attribute the discrepancies between the phase equilibrium and calorimetric data to errors in the calorimetric enthalpies of formation of corundum and muscovite, recognizing that new calorimetric measurements on these minerals and on related substances may lead to a different interpretation.

**Aluminum silicate polymorphs Al$_2$SiO$_5$ and mullite Al$_6$Si$_2$O$_{12}$**—The earliest standard enthalpies of the polymorphs were measured calorimetrically by Neumann (1925), but they have been questioned repeatedly (for example, Flood and Knapp, 1957; Pankratz and Kelley, 1964b; Waldbaum, 1965) and finally redetermined calorimetrically by Holm and Kleppa (1966). The standard enthalpies of formation from the elements at 25$^\circ$C were calculated from those from the oxides, obtained in turn from reactions like corundum $+$ quartz $=$ Al$_2$SiO$_5$, or 3 corundum $+ 2$ quartz $=$ 3:2 mullite.

Mullite poses a special problem because of its compositional variability (for example, Kennedy, 1955; Waldbaum, 1965; Zen, 1969b). For this reason mullite enthalpies and entropies derived from calorimetric measurements or calculated from hydrothermal experiments may represent only approximations to the true values for a hypothetical end-member 3:2 mullite and have to be used with caution.

**Alkali feldspars, NaAlSi$_3$O$_8$–KAlSi$_3$O$_8$**—Values for potassium feldspars (microcline, orthoclase, sanidine, adularia) and sodium feldspars (low albite, high albite) are listed by Robie and Waldbaum (1968). Reaction schemes in the calorimetric determinations of the heats of solution involved only quartz, feldspars, and chlorides in hydrofluoric acid (Waldbaum, 1968; Waldbaum and Robie, 1971; Hovis, Waldbaum, and Thompson, 1970). More recent heat of solution measurements showed the need to correct the enthalpy of formation by +1.7 kcal mole$^{-1}$, but this is still a provisional figure (Waldbaum, 1971, personal commun.). Until definitive enthalpy figures are available, the set of data in Robie and Waldbaum is adopted.

4 Whatever the possible corrections for albite and potash feldspar are, they have to be of the same magnitude and sign for both phases (Helgeson, 1972, personal commun.) as also suggested by an analysis of activity diagrams (compare our chapter on implications for diagenetic assemblages).
Muscovite, $\text{KA}_{2}\text{Si}_4\text{AlO}_{10}(\text{OH})_2$.—The standard enthalpy for muscovite has been determined calorimetrically by Barany (1964) as $1421.2 \pm 1.25$ kcal mole$^{-1}$. The sample used in the experiment is a pegmatitic, coarse-grained variety but is not an end-member muscovite, since the analysis shows 3.3 percent $\text{Fe}_2\text{O}_3$, 1 percent $\text{Na}_2\text{O}$, and 0.8 percent $\text{MgO}$; no crystallographic data are given. Corrections to end-member composition amounted to $+1066$ cal per mole of muscovite (Barany, 1964). The calorimetric reaction scheme is based on known calorimetric quantities: the heats of solution of quartz, gibbsite, $\text{HCl(H}_2\text{O)}_{12.731}$, $\text{KCl}$, and muscovite in hydrofluoric acid. One possible error in the measurement of the heat of solution of muscovite may be related to grain size of the ground sample (for a discussion of the influence of grain size on heats of solution, see Giauque, 1949; MacDonald, 1955; and Parks, 1972). Barany used for gibbsite ($2\text{Al(OH)}_3$) a heat of solution of $-71.48$ kcal in hydrofluoric acid (Barany and Kelley, 1961). This value represents probably the heat of solution of a metastable cryptocrystalline variety (Parks, 1972), since the standard values of gibbsite derived from it show a considerable difference from the ones obtained by solubility measurements at $25^\circ\text{C}$. However, in order to obtain the standard enthalpy of formation from the elements, Barany set up a second reaction scheme—with gibbsite in it—so that the possible error in the first reaction scheme is algebraically cancelled (see details in Barany, 1964). Reesman and Keller (1968) report a $G^\circ_i(\text{muscov})$ of $-1327$ cal mole$^{-1}$ from a solubility measurement of only one sample. Although there is nothing in Barany's experiments that can be questioned a priori, it has been indicated that the calorimetric enthalpy is probably in error (Helgeson, Brown, and Leeper, 1969; Helgeson, 1970, p. 185; see also discussion in Zen, 1972), but the magnitude of the adjustment is not known. New calorimetric determinations will settle the question, especially when an end-member muscovite of known structural state is used as starting material.

Paragonite, $\text{NaAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$.—No experimentally determined enthalpy or entropy values are available for paragonite. Chatterjee (1972) computed $G^\circ_i(\text{parag}) = -1320.9 \pm 4.0$ kcal mole$^{-1}$, $H^\circ_i = -1411.4 \pm 2.7$ kcal mole$^{-1}$, and $S^\circ = 67.61 \pm 3.9$ cal K$^{-1}$ mole$^{-1}$ from hydrothermal equilibrium data for the reaction:

\[
\text{paragonite} + \text{quartz} = \text{low albite} + \text{andalusite} + \text{H}_2\text{O}
\]

based on $G^\circ_i(\text{corindum}) = -371.0$ kcal mole$^{-1}$. Alternatively, Zen (1972) calculated $G^\circ_i(\text{paragonite}) = -1318$ kcal mole$^{-1}$. There is no independent confirmation for the validity of these figures.

Pyrophyllite, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$.—The only measured value of standard Gibbs energy is the one given in Reesman and Keller (1968) of approximately $-1256.14$ kcal mole$^{-1}$ (consistent with values in our table 2), based on solubility measurements. On grounds discussed in detail by Zen (1969a, 1972), this figure may be in error by several kilocalories.
No data are known as to the effect of crystallinity or polymorphism on the Gibbs energy values.

**Kaolinite, Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}(OH)\textsubscript{4}.—** Thermodynamic quantities for kaolinite were obtained by Barany and Kelley (1961), Kittrick (1966a, 1967), and Reesman and Keller (1968). The calorimetric reaction scheme developed by Barany and Kelley involves dissolution of kaolinite, quartz, and AlCl\textsubscript{3}·6H\textsubscript{2}O in hydrofluoric acid; the results are $H^\circ_r$(kaolinite) = $-979465 \pm 950$ cal mole$^{-1}$, corresponding to $G^\circ_r$(kaolinite) = $-902868 \pm 960$ cal mole$^{-1}$ (consistent with new data for quartz, Robie and Waldbaum, 1968).

Clays and most hydroxides appear in nature as generally fine-grained, often poorly crystalline material. Variations in Gibbs energies of more than 2 or 3 kcal can be ascribed to the different physical state of the starting material used in experiments. With this in mind, it can be shown that results from solubility studies agree, within the expected uncertainties, with the values obtained by Barany and Kelley. The results cited by several authors have been adjusted to our values for solution species (table 2). A range of values from $-903.37$ to $-904.67$ kcal mole$^{-1}$ for the kaolinite Gibbs energy was derived by Kittrick (1966a, 1967), who also showed a good correlation between free energy and crystallinity, the more negative values being those of the more stable kaolinites with higher crystallinities. When adjusted to the values adopted here for aqueous species (table 2), Reesman and Keller’s value becomes $G^\circ_r$(kaolinite) = $-902$ kcal mole$^{-1}$. Helgeson (1969, table 7) adjusted the calorimetric values to $H^\circ_r$(kaolinite) = $-980020$ cal mole$^{-1}$ and $G^\circ_r = -903430$ cal mole$^{-1}$, well within the limits of uncertainty of the calorimetric measurements. Helgeson’s set of values is adopted as representative of the “average” natural kaolinite.

**Sodium montmorillonite, Na\textsubscript{33}Al\textsubscript{2.52}Si\textsubscript{6.67}O\textsubscript{10}(OH)\textsubscript{2}.—** Sodium montmorillonite is a possible end-member of the smectite group (Warshaw and Roy, 1961) and the only one that can be represented in our limited chemical system. Data on Na-montmorillonite have been given by Helgeson (1969, table 12) and are reproduced in table 2. The $C_P$ function has been estimated as $84.9 + 34.3 \times (10^{-3}) \times T - 19.7 \times (10^5) \times T^{-2}$ (Helgeson, 1969).

*Results obtained from buffered hydrothermal equilibrium curves in pure water; some comments*

The equilibrium points reported by different authors for several geologically important reactions (table 3A) are listed in table 4. The thermodynamic data in table 2 are accepted and taken as a base for further calculations; the reasons for it are given in the section on revision of published data. Possible errors in some of the values accepted (for example, in the feldspars) will of course affect the values here derived; but for the purposes of our investigation, there is no other choice than to accept temporarily the figures in table 1. $C_P$ functions are taken from Kelley (1960) and Helgeson (1969), with the exceptions of those for the
Al₂SiO₅ polymorphs (from Pankratz and Kelley, 1964b) and mullite (from Pankratz, Weller, and Kelley, 1963), or have been estimated whenever necessary. An example shows the computing procedure. For reaction 3 (table 3A), equation 1 can be solved for the difference between the standard enthalpies of muscovite and corundum, which are in this example the minerals with suspect enthalpies of formation. This yields 1081000 cal for the quantity H°ᵢ(corundum)−H°ᵢ(muscovite). Similar calculations with equation 1 have been performed for every T-P equilibrium bracket for all the reactions of table 3A, and the calculated differences between enthalpies of formation are listed in table 4.

There are several minor points to be stressed as far as data for certain minerals are concerned. Comments follow.

Paragonite.—The entropy and Cᵣ function of paragonite are not known; they have been estimated with the methods described previously and are as follows: third law entropy, 65.03 cal K⁻¹ mole⁻¹—compare with 65.7 and 67.61 in Chatterjee (1970, 1972), an average 67.0 in Ivanov and Gusynin (1970), and 67.0 in Zen (1972). Cᵣ function: 91.74 +

<table>
<thead>
<tr>
<th>Table 3</th>
</tr>
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<tbody>
<tr>
<td>A. Buffered hydrothermal reactions (for references, see table 4)</td>
</tr>
<tr>
<td>1. 1 musc = 1 cor + 1 sanid + 1 w</td>
</tr>
<tr>
<td>2. 1 musc + 1 qtz = 1 and + 1 sanid + 1 w</td>
</tr>
<tr>
<td>3. 1 musc + 1 qtz = 1 sill + 1 sanid + 1 w</td>
</tr>
<tr>
<td>4. 1 musc + 1 qtz = 1 kyan + 1 sanid + 1 w</td>
</tr>
<tr>
<td>5. 3 musc + 2 qtz = 1 mull + 3 sanid + 3 w</td>
</tr>
<tr>
<td>6. 1 par = 1 cor + 1 alb + 1 w</td>
</tr>
<tr>
<td>7. 1 par + 1 qtz = 1 and + 1 alb + 1 w</td>
</tr>
<tr>
<td>8. 3 pyro = 1 mull + 10 qtz + 3 w</td>
</tr>
<tr>
<td>9. 1 pyro = 1 and + 3 qtz + 1 w</td>
</tr>
<tr>
<td>10. 1 kaol + 2 qtz = 1 pyro + 1 w</td>
</tr>
<tr>
<td>11. 2 dias = 1 cor + 1 w</td>
</tr>
</tbody>
</table>

B. Hydrothermal reactions in salt solutions and under non-buffered conditions (for references, see table 6)

| 1. 1 pyro + 5 H₂O = 1 kaol + 2 H₄SiO₄(aq) |
| 2. 2 boehm + 2 H₄SiO₄(aq) = 3 H₂O + 1 kaol |
| 3. 1 and + 1 H₄SiO₄(aq) = 1 kaol |
| 4. 1 par + 6 H₄SiO₄(aq) + 2 Na⁺ = 3 alb + 2 H⁺ + 12 H₂O |
| 5. 1 musc + 6 H₄SiO₄(aq) + 2 K⁺ = 3 K-feld + 2 H⁺ + 12 H₂O |
| 6. 1 musc + 6 quartz + 2 K⁺ = 3 K-feld + 2 H⁺ |

Reaction (5), table 3B, is buffered with quartz.

All chemical reactions are written conserving aluminum among the solid phases.

and: andalusite   alb: albite
boehm: boehmite   cor: corundum
dias: diasore      kao: kaolinite
K-feld: potash feldspar   kyan: kyanite
musc: muscovite   mull: 3:2 mullite
par: paragonite   pyro: pyrophyllite
qtz: quartz       sanid: sanidine
sill: sillimanite  w: steam
standard enthalpies of formation of selected minerals 525

31.53(10^-3) T - 20.67(10^3) T^-2 (compare with 90.57 + 26.82(10^-3) T - 20.63(10^3) T^-2 in Ivanov and Gusynin, 1970). In Chatterjee's experiment, the feldspar formed as product is practically high albite (Chatterjee, 1972, p. 293; Zen, 1971, personal commun.); no structural data are reported in the results by Ivanov and Gusynin (reaction 7, table 3). Ivanov and Gusynin equilibrated X-andalusite in their experiments (reaction 7, table 4), but the difference in enthalpies between the stable andalusite and the metastable variety is presumably only very small and should not affect the value of H°_f(andal)-H°_f(parag). Calculations have also been performed with low albite as reaction product, and a summary is given in table 5 (reactions 6 and 7).

From comments in Chatterjee's paper, it may be assumed that both 1M and 2M₄ paragonites were crystallized; the effect of paragonite polytypism and structural state on its stability has not been investigated, but it seems reasonable to expect more negative free energies for the stable 2M₄ phase.

Pyrophyllite.—For pyrophyllite (reactions 8 and 9, tables 3A and 4), a third-law entropy of 56.6 cal K⁻¹ mole⁻¹ was taken from King and Weller (1970); its G_P function (81.37 + 35.62 (10^-3) T - 19.18 (10^3) T^-2) was estimated. In reaction 9 (table 4) powdered samples as reacting materials (two points by Kerrick; Althaus' points) yield values close to the one derived from Aramaki and Roy's point (who used a mixture of gels and natural crystals as starting powders). Polymorphs of andalusite were obtained as reaction products by some authors ("AS-II" andalusite by Aramaki and Roy, X-andalusite by Althaus) but do not seem significantly to affect the results. Reaction-rate methods (two points by Kerrick) and Hemley's solubility point give slightly more positive enthalpy figures. As with paragonite, the effect of the structural state of pyrophyllite on its stability field is unknown.

Test for internal consistency in thermodynamic data within the system SiO₂-Al₂O₃-K₂O-Na₂O-H₂O

Internal consistency in the standard enthalpies and free energies of minerals in the system SiO₂-Al₂O₃-K₂O-Na₂O-H₂O was tested by steps, as shown in the following paragraphs:

A. Internal consistency in the data of the Al₄SiO₇ polymorphs.—A calculation of the univariant curves for the pairs andalusite–kyanite, andalusite–sillimanite, and sillimanite–kyanite provides a sensitive check on the internal consistency of their enthalpies and free energies, because the three phase boundaries should meet at a triple point. A triple point at 6670 bars, 480°C is calculated with Robie and Waldbaum's data (see also Holm and Kleppa, 1966, who calculated a triple point at 5.9 ± 1 kb, 432°C ± 65°C). It can therefore be safely assumed that the enthalpies and free energies are internally consistent. Once this is accepted, it is clear that whatever errors exist in the enthalpies or free energies are bound to have the same sign and absolute value for all three polymorphs.
Table 4
Set of constraint equations derived from hydrothermally

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>Equilibrium points</th>
<th>Equation (values in cal)</th>
<th>Remarks</th>
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<td>Author</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Evans, 1965</td>
<td>$H^<em>_{cor} - H^</em>_{musc} = 1081221$</td>
<td>RRM; natural crystals</td>
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<td></td>
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<td>680 2000</td>
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<td></td>
<td></td>
<td>710 9000</td>
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<td></td>
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<td>660 1000</td>
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<td></td>
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<td>688 2000</td>
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<td>$H^<em>_{sill} - H^</em>_{musc} = 811856$</td>
<td>RRH; natural crystals</td>
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<td>605 2000</td>
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<td>525 1050</td>
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<td>675 2000</td>
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<td>662 3000</td>
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<td>4</td>
<td>Evans, 1965</td>
<td>$H^<em>_{mull} - 3H^</em>_{musc} = 2665348$</td>
<td>Calculated Synthetic and natural mixtures. NR</td>
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<td>680 2000</td>
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<td>5</td>
<td>Evans, 1965</td>
<td>$H^<em>_{cor} - H^</em>_{psr} = 1019805$</td>
<td>Ground synthetic crystals</td>
</tr>
<tr>
<td></td>
<td>Segnit and Kennedy, 1961</td>
<td>700 2000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chatterjee, 1970</td>
<td>540 1000</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>565 2000</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>590 3000</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>633 5000</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>635 6000</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>660 7000</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Ivanov-Gusynin, 1970</td>
<td>540 980.66</td>
<td>Ground synthetic crystals</td>
</tr>
</tbody>
</table>

B. Internal consistency in the enthalpies and free energies of muscovite, $Al_2SiO_5$ polymorphs, corundum, and mullite.—The values obtained from equilibrium points for $H_0^\circ$(cor)—$H_0^\circ$(musc) (reaction 1, table 5) show discrepancies with the corresponding values obtained from calorimetric measurements: the difference between $H_0^\circ$(corundum) and $H_0^\circ$(muscovite) is approximately 1,031,000 cal, whereas the value obtained using tabulated calorimetric data from Robie and Waldbaum (1968) is 1,020,780 cal, showing a discrepancy of about 10 kcal. Since the results calculated from equilibrium data should agree closely with the figures derived from calorimetric or solubility data, this discrepancy can only be interpreted as the combined error in the standard enthalpies of formation of corundum and muscovite. Similar deviations are found in other cases and are summarized in table 5.

An examination of table 5 leads to the following conclusions: (1) Published enthalpies for minerals in the chemical system under discussion are not internally consistent (compare, also Zen, 1972). (2) The discrepancies for reactions 1 to 5 are near to 10 kcal per mole of mus-
Table 4 (continued)
determined equilibrium points in buffered systems

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>Author</th>
<th>T, °C</th>
<th>P, bars</th>
<th>Equilibrium points</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Ivanov-Gusynin, 1970</td>
<td>500</td>
<td>980.66</td>
<td>H°<em>{and} - H°</em>{par} = 801155</td>
<td>Ground synthetic crystals; X-andalusite n.d.</td>
</tr>
<tr>
<td>8</td>
<td>Kennedy, 1955</td>
<td>500</td>
<td>150</td>
<td>H°<em>{mull} - 3H°</em>{pyro} = 2426640</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>550</td>
<td>450</td>
<td>2426843</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Aramaki and Roy, 1963</td>
<td>565</td>
<td>4000</td>
<td>H°<em>{and} - H°</em>{pyro} = 73298</td>
<td>Gels and natural crystals, AS II-andalusite; NR</td>
</tr>
<tr>
<td></td>
<td>Hemley, 1967</td>
<td>400</td>
<td>1000</td>
<td>730516</td>
<td>SiO₂ solubility</td>
</tr>
<tr>
<td></td>
<td>Kerrick, 1968</td>
<td>410</td>
<td>1800</td>
<td>730570</td>
<td>RRM; natural</td>
</tr>
<tr>
<td></td>
<td></td>
<td>430</td>
<td>3900</td>
<td>729982</td>
<td>crystal idem</td>
</tr>
<tr>
<td></td>
<td></td>
<td>473</td>
<td>3900</td>
<td>731561</td>
<td>Powdered</td>
</tr>
<tr>
<td></td>
<td></td>
<td>447</td>
<td>1750</td>
<td>731085</td>
<td>natural crystals</td>
</tr>
<tr>
<td></td>
<td>Althaus, 1966</td>
<td>490</td>
<td>2000</td>
<td>731798</td>
<td>Powdered</td>
</tr>
<tr>
<td></td>
<td></td>
<td>525</td>
<td>7000</td>
<td>730671</td>
<td>crystals; X-andalusite; NR.</td>
</tr>
<tr>
<td>10</td>
<td>Thompson, 1970</td>
<td>325</td>
<td>1000</td>
<td>H°<em>{pyro} - H°</em>{sol} = -362022</td>
<td>RRM; natural</td>
</tr>
<tr>
<td></td>
<td></td>
<td>345</td>
<td>2000</td>
<td>-362814</td>
<td>crystals</td>
</tr>
<tr>
<td></td>
<td></td>
<td>375</td>
<td>4000</td>
<td>-362685</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Althaus, 1966</td>
<td>390</td>
<td>2000</td>
<td>-362399</td>
<td>Powdered</td>
</tr>
<tr>
<td></td>
<td></td>
<td>405</td>
<td>7000</td>
<td>-362436</td>
<td>crystals; NR?</td>
</tr>
<tr>
<td></td>
<td>Fournier, (in Zen, 1969)</td>
<td>290</td>
<td>689.5</td>
<td>-363372</td>
<td>n.d.</td>
</tr>
<tr>
<td>11</td>
<td>Haas and Holdaway, 1970 (also)</td>
<td>407</td>
<td>2400</td>
<td>H°<em>{cor} - 2H°</em>{diss} = 77328</td>
<td>RRM; natural</td>
</tr>
<tr>
<td></td>
<td></td>
<td>420</td>
<td>3500</td>
<td>77226</td>
<td>and synthetic</td>
</tr>
<tr>
<td></td>
<td>Zen, 1972</td>
<td>398</td>
<td>1750</td>
<td>77318</td>
<td>crystals</td>
</tr>
<tr>
<td></td>
<td></td>
<td>428</td>
<td>4800</td>
<td>77048</td>
<td></td>
</tr>
</tbody>
</table>

Equilibrium points with widely differing results were rejected. Some equilibrium points were not reversed; however, since results calculated from them are in close agreement with those derived from other points, they have been included.

RRM: reaction-rate method (see Fyfe, 1960; Evans, 1965).
NR: not reversed.
n.d.: no data as to the type of experiment performed.
Reactions 6 and 7: quoted results are calculated with analbite as the product feldspar (see also table 5).

Covellite or corundum; that is, the ratios of the discrepancies are the same as the ratios of the coefficients of muscovite in reactions 1 to 5 and also the same as those of the coefficients of corundum in the formation of aluminosilicates from oxides:

\[
1 \text{Al}_2\text{O}_3 + 1 \text{SiO}_2 = 1 \text{Al}_2\text{SiO}_5 \text{(Al–Si polymorph)}
\]

\[
3 \text{Al}_2\text{O}_3 + 2 \text{SiO}_2 = 1 \text{Al}_2\text{Si}_2\text{O}_13 \text{(3:2 mullite)}
\]

Zen (1972) found a discrepancy of around 7 kcal per mole of \text{Al}_2\text{O}_3. (3) From the discussion above, and from the fact that the enthalpies of formation for the \text{Al}_2\text{SiO}_5 polymorphs are internally consistent, the suggestion emerged that, whatever the nature of the errors causing the discrepancies, they must affect either corundum or muscovite or both at the same time and are being transmitted into mullite and other aluminosilicates. Therefore, an average correction term for the enthal-
pies and free energies of corundum and/or muscovite can be computed: it is 9800 ± 350 calories (weighted average, see table 5). If \( \epsilon(\text{corundum}) \) and \( \epsilon(\text{muscovite}) \) are, respectively, the errors in the enthalpies of corundum and muscovite as tabulated (Robie and Waldbaum, 1968), then

\[
\epsilon(\text{corundum}) - \epsilon(\text{muscovite}) = 9800 \pm 350 \text{ cal},
\]

expressed per mole of corundum and muscovite.

How much of this error is in corundum and how much in muscovite cannot be wholly decided on the grounds provided by the set of equations in table 5. Also, errors in some of the figures may be translated disproportionately into other standard enthalpies. For instance, values obtained from reactions with mullite are suspect on account of the problems posed by mullite stoichiometry. But the main use of the set of equations in table 5 is that they provide definite constraints. It is obvious, for instance, that once a certain value is estimated for the standard enthalpy of corundum, the corresponding figures for muscovite and paragonite are also fixed within rather narrow limits.

The next task is then to find other ways to estimate one or several of the suspect enthalpies appearing as variables in the set of equations in table 5. We now turn to an examination of results of experiments in salt solutions and under non-buffered conditions.

**Table 5**

Comparison of enthalpy differences, derived from hydrothermal phase equilibria in buffered reactions (table 3A), and from calorimetric and solubility data

<table>
<thead>
<tr>
<th>Reaction Points</th>
<th>Equation</th>
<th>Calculated from curves (A)</th>
<th>From calorimetric or solubility data (B)</th>
<th>Discrepancy (A - B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 4 H_r^<em>(cor) - H_r^</em>(musc)</td>
<td>1031581 ± 380</td>
<td>1020800</td>
<td>10781</td>
<td></td>
</tr>
<tr>
<td>2 4 H_r^<em>(and) - H_r^</em>(musc)</td>
<td>811117 ± 600</td>
<td>801810</td>
<td>9307</td>
<td></td>
</tr>
<tr>
<td>3 7 H_r^<em>(sill) - H_r^</em>(musc)</td>
<td>811965 ± 380</td>
<td>802550</td>
<td>9415</td>
<td></td>
</tr>
<tr>
<td>4 1 H_r^<em>(kyan) - H_r^</em>(musc)</td>
<td>811109 ± 600*</td>
<td>801270</td>
<td>9839</td>
<td></td>
</tr>
<tr>
<td>5 2 H_r^<em>(mull) - 3H_r^</em>(musc)</td>
<td>2664596 ± 1500</td>
<td>2634057</td>
<td>3x(10179)</td>
<td></td>
</tr>
<tr>
<td>6 7 H_r^<em>(cor) - H_r^</em>(par)</td>
<td>1018746** ± 100</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>7 1 H_r^<em>(and) - H_r^</em>(par)</td>
<td>800340** ± 200*</td>
<td>801155** ± 200*</td>
<td>n.d.</td>
<td></td>
</tr>
</tbody>
</table>

n.d.: No calorimetric or solubility values.

* Estimated uncertainty.

** First value calculated with low albite as reaction product; second value, with high albite as product.

Uncertainties in the enthalpy differences are twice the standard error of the mean: \( 2\sigma = 2[(\bar{x} - \bar{X})^2/n(n - 1)]^{1/2} \), where \( x_i \) are individual values in table 4, \( \bar{x} \) is the average enthalpy difference for a certain reaction, and \( n \) is the number of observations (compare Rossini and Deming, 1939). The weighted average discrepancy for reactions 1 to 5 is 9800 ± 350 cal; the uncertainty is \( 2\sigma = 2[(d_i - 9800)^2/n(n - 1)]^{1/2} \), where \( d_i \) is the individual discrepancy for each points, reactions 1 to 5.
THERMODYNAMIC DATA CALCULATED FROM STUDIES OF MINERAL EQUILIBRIA IN SALT SOLUTIONS AND NON-BUFFERED SYSTEMS

The calculation procedure to be described below has been applied to the non-buffered hydrothermal reactions in Table 3B. The standard enthalpies of formation obtained are shown in Table 6. The calculation consists essentially in computing: first, the log \( K(T, P) \) of the reaction investigated at the T and P of the experiment; then, \( \Delta H^\circ(T, P) = RT \ln K(T, P) + T \Delta S^\circ(T, P) \), the change of enthalpy across the reaction at the T and P of the experiment; next, \( \Delta H^\circ(T_r, P_r) \), the enthalpy of reaction at the temperature and pressure of reference; and, finally, the unknown standard enthalpy of formation of the mineral in question.

Method of calculation.—An example of calculation follows for the experimental results of Hemley (1972, personal commun.) for the equilibrium between albite and paragonite at 300°C and 15,000 psi (1000 bars). This equilibrium can be represented by the reaction

\[
3 \text{ albite} + 2 \text{H}^+ + 12 \text{H}_2\text{O} \rightleftharpoons 1 \text{paragonite} + 6 \text{Na}^+ + 6 \text{H}_4\text{SiO}_4(aq)
\] (9)

for which the mass-action law is written as

\[
\log K(300,1000) = 2 \log a_{\text{Na}^+} - 2 \log a_{\text{H}^+} + 6 \log a_{\text{H}_4\text{SiO}_4} - 12 \log a_{\text{H}_2\text{O}}
\] (10)

The above reaction was reversed at concentrations of \( \log m_{\text{SiO}_2} = -2.4 \) and \( \log m_{\text{HCl}} = -4.95 \); the supporting electrolyte was a 4-molar NaCl solution. The feldspar used was natural low-albite (Hemley, 1972, personal commun.).

A. The true ionic strength \( \bar{I} \) and the activity of water have been extrapolated from data in Helgeson (1969, table 2) and are: \( \bar{I} = 2.6; a_{\text{H}_2\text{O}} = 0.9 \). For neutral species, the activity coefficients are calculated with

\[
\log \gamma^\circ = \sigma \bar{I}
\] (11)

where \( \sigma = 0.14 \) (for 300°C) is a slope constant (Helgeson, 1969).

B. The activity coefficients \( \gamma \) for individual ions are in our example \( \gamma_{\text{H}^+} = 0.58; \gamma_{\text{Na}^+} = 0.36; \gamma_{\text{Cl}^-} = 0.292 \) and provide for high temperature and high pressure (Helgeson, 1972, personal commun.). The activity coefficient \( \gamma^\circ \) for neutral species involved (H\(_4\)SiO\(_4\), NaCl\(^\circ\), HCl\(^\circ\)) is: \( \log \gamma^\circ = 0.14 \times 2.6 = 0.364 \) and \( \gamma^\circ = 2.312 \).

C. Molalities of Na\(^+\), Cl\(^-\), and NaCl\(^\circ\) are obtained by solving the system

\[
\begin{align*}
\text{m}_{\text{Na}^+} + \text{m}_{\text{NaCl}^\circ} &= 4 \\
\text{m}_{\text{Na}^+} &\approx \text{m}_{\text{Cl}^-} \\
\frac{\text{m}_{\text{Na}^+} \gamma_{\text{Na}^+} \text{m}_{\text{Cl}^-} \gamma_{\text{Cl}^-}}{\text{m}_{\text{NaCl}^\circ} \gamma_{\text{NaCl}^\circ}} &= K(300^\circ,1000;\text{NaCl}^\circ) 
\end{align*}
\] (12)

where all the activity coefficients are known. The equilibrium constant at 300°C and 1000 bars can be approximated by that at 250°C and 1 bar
Table 6
Enthalpies derived from experiments in salt solutions and non-buffered conditions (table 3B)

<table>
<thead>
<tr>
<th>Reaction†††</th>
<th>T (°C)</th>
<th>P (bars)</th>
<th>log K(T,P)</th>
<th>Mineral and its standard enthalpy (in cal mole⁻¹)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>1000</td>
<td>4.160 ± 0.10</td>
<td>pyrophyllite</td>
<td>-1342182 ± 1400†††</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>1000</td>
<td>5.060 ± 0.08</td>
<td>boehmite</td>
<td>-235000 ± 660</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>1000</td>
<td>2.000 ± 0.08*</td>
<td>andalusite</td>
<td>-614789 ± 1090</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>1000</td>
<td>1.901 ± 0.20*</td>
<td>paragonite</td>
<td>-1414599 ± 3020</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>1000</td>
<td>1.059 ± 0.25*</td>
<td>paragonite</td>
<td>-1414219 ± 3050</td>
</tr>
<tr>
<td>6</td>
<td>400</td>
<td>1000</td>
<td>1.918 ± 0.10</td>
<td>muscovite</td>
<td>-1425756 ± 4340</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>2000</td>
<td>2.234 ± 0.10</td>
<td>muscovite</td>
<td>-1423803 ± 4340</td>
</tr>
<tr>
<td>7</td>
<td>300</td>
<td>85</td>
<td>-8.44 ± 0.12</td>
<td>muscovite</td>
<td>-1427010 ± 4344</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1</td>
<td>-11.72 ± 0.06</td>
<td>muscovite</td>
<td>-1428006 ± 4332</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1</td>
<td>-12.02 ± 0.06</td>
<td>muscovite</td>
<td>-1422868 ± 4332</td>
</tr>
</tbody>
</table>

Volume changes of all reactions are considered constant. Average C_p of ions and water from Helgeson (1969). C_p functions and volumes of minerals as cited in text. Partial molar volumes of ions from Millero (1969). Other data from table 1. Data for reaction 1 to 4, from Hemley (1972, personal commun.); for reaction 5, from Barnes (1972, personal commun.); for reaction 6, from Usdowski and Barnes (1972).

† Estimated.
** For calculation of uncertainties, see footnote, table 1.
*** Equilibrium conditions of reaction as implicit in data by Hemley (1972, personal commun.).
†† Hemley (1972, written commun.).
††† Barnes (1972, written commun.); Usdowski and Barnes (1972).
†††† Reaction numbers are those of table 3B.
because dissociation constants of aqueous complexes are essentially controlled by the dielectric constant of water (Helgeson, 1969, fig. 4); the points (300°, 1 kb; and 250°, 1 bar) are on the same isodielectric line on the P-T diagram for water. From Helgeson (1969, table 4) log K (250°, 1; NaCl°) = −0.15. The solutions to the system are m_{Na^+} = m_{Cl^-} = 3.3; m_{NaCl^*} = 0.7.

D. The molalities m_{H^+} and m_{HCl^*} are calculated from the following system of equations

\[
\frac{m_{H^+} \gamma_{H^+} m_{Cl^-} \gamma_{Cl^-}}{m_{HCl^*} \gamma_{HCl^*}} = K(300°, 1000; HCl°) \quad (13)
\]

\[
m_{H^+} = 10^{-4.95} = m_{H^+} + m_{HCl^*} \quad (13')
\]

where, as in (C), log K(300,1000; HCl°) is approximately equal to log K(250,1; HCl°), which in turn is equal to −0.67 (Helgeson, 1969, table 4). The solutions to the system are

\[
m_{H^+} = 1.017 \times 10^{-5}, \quad \log m_{H^+} = −4.993
\]

and

\[
m_{HCl^*} = 1.049 \times 10^{-6}, \quad \log m_{HCl^*} = −5.979
\]

E. With the values obtained in (A), (B), (C), and (D), equation (10) gives log K(300,1000) = −1.059, from which

\[
\Delta G°(300,1000) = −RT \ln K(300,1000) = 2776 \text{ cal}
\]

F. The equation

\[
\Delta H°(T,P) = \Delta G°(T,P) + T \Delta S°(T,P) \quad (14)
\]

allows to calculate \(\Delta H°(300,1000)\), because the entropy of reaction \(\Delta S°(300,1000) = 16.216 \text{ cal K}^{-1} \text{ mole}^{-1}\) has been independently calculated from knowledge or estimation of the third-law entropies and \(C_P\) functions. The result is \(\Delta H°(300,1000) = 2776 + (573.15 \times 16.216) = 12070 \text{ cal}\).

G. From

\[
\Delta [\Delta H°(T)]_{25,1}^{300,1000} = \Delta H°(300,1000) - \Delta H°(25,1) \quad (15)
\]

one obtains \(\Delta H°(25,1) = 14080 \text{ cal}\). The change in the enthalpy of reaction from 300° and 1000 bars to 25° and 1 bar can be calculated independently and is −2010 cal; the assumption is that the heat capacities of the solids and water and the average heat capacities of ions do not change significantly with pressure. Average heat capacities of ions have been taken from Helgeson (1969), volumes of ions from Millero (1969).

H. Finally, knowing the enthalpy of reaction at 25°C and 1 bar, the standard enthalpy of formation of paragonite can be calculated to be −1414219 cal mole −1 (using low albite).

For non-buffered reactions of the type

\[
1 \text{ andalusite} + 3 H_4SiO_4(aq) \rightleftharpoons 1 \text{ pyrophyllite} + 5 H_2O \quad (16)
\]

the mass-action law is written as

\[
\log K(T,P) = −3 \log a_{H_4SiO_4} + 5 \log a_{H_2O} \quad (17)
\]
Hemley (1972, personal commun.) reversed reactions like (16) and measured the molalities of $H_2SiO_4(aq)$. Since in this case molalities and activities are essentially equivalent, log $K(T,P)$ can be directly computed, and calculating the standard enthalpies of formation becomes simpler than in the example treated in detail above. Assuming unit activity of water simplifies the calculation further.

**FREE ENERGIES AND ENTHALPIES: TWO DIFFERENT SETS OF INTERNALLY CONSISTENT DATA AS DEDUCED FROM CALCULATIONS**

It has been shown previously that the error in $H^\circ$(corundum) minus that in $H^\circ$(muscovite) is about 9800 ± 350 calories—a constraint imposed by hydrothermal experimental data on the true enthalpy values of both minerals. Several conclusions can be drawn from the calculations and literature review:

A. Data by Hemley (1972, personal commun.) yield $H^\circ_f$(boehmite) = $-235000 \pm 660$ cal mole$^{-1}$ (table 6), a value that does not depend on the thermodynamic constants for any of the aluminum complexes in solution (see eq 2, table 3B). It is close to $-234660 \pm 240$ cal mole$^{-1}$, the enthalpy independently calculated from solubility measurements (table 2) and consistent with our set of values for aluminum solution species.

B. From data for non-buffered reactions, $H^\circ_f$(pyrophyllite) = $-1342180 \pm 1400$ cal mole$^{-1}$ (table 6). Independently, from the constraint for reaction 10 in table 5, $H^\circ_f$(pyrophyllite) = $-1342655 \pm 985$ cal mole$^{-1}$. Since these values were calculated from data obtained by several authors with different techniques and starting materials, the thermodynamic values for pyrophyllite to be adopted are: $H^\circ_f = -1342420 \pm 630$ cal mole$^{-1}$ (avg value); $G^\circ_f = -1252930 \pm 640$ cal mole$^{-1}$, where the uncertainties are now twice the standard error of the mean; the Gibbs energy is based on the third-law entropy measured by King and Weller (1970).

C. From the $H^\circ_f$(diaspore) of table 1 and using the constraint 11 of table 5, $H^\circ_f$(corundum) = $-398410$ cal mole$^{-1}$. This value is considered tentative because it is affected by a possible error in the entropy of diaspore.

D. From the results obtained by Hemley (1972, personal commun.) for the equilibrium andalusite + $H_2SiO_4(aq) \rightleftharpoons$ kaolinite (see tables 3B and 6, reaction 3), we have calculated $H^\circ_f$(andal) = $-614800 \pm 1090$ cal mole$^{-1}$. Robie and Waldbaurn (1968) give $H^\circ_f$(andal) = $-619300 \pm 710$ cal mole$^{-1}$. The difference, about 4600 cal mole$^{-1}$, is also the error that affects the heats of formation of corundum, sillimanite, and kyanite given by Robie and Waldbaurn (1968). $H^\circ_f$(corundum) as implied by our $H^\circ_f$(andal) is therefore $-400400 + 4600 = -395800$ cal, which is very close to the $-396$ kcal tentatively calculated by Waldbaurn (1971, unpub. rept., Princeton Univ.).

Similarly, the implied error in the $H^\circ_f$(musc) becomes 4600 − 9800 = $-5200$ cal, and $H^\circ_f$(musc) is then $-1426380 \pm 1350$ cal mole$^{-1}$. 
With all these values, based, as we have shown, on the $H_f^\circ$ (andalusite) calculated from the results of Hemley and coworkers, a set of internally consistent standard enthalpies of formation has been computed—set I, table 7. The value for $H_f^\circ$(paragonite) listed in set I, which has been calculated by means of constraint 7 of table 5 and the $H_f^\circ$(andalusite) given in (D), is fairly close to the $H_f^\circ$(paragonite) calculated directly from the experimental data of Hemley (1972, personal commun.), for example, $H_f^\circ$(paragonite) = $-1414409$ cal mole$^{-1}$ (avg value, table 6). Unfortunately, the uncertainty in the calculations precludes any definite conclusion.

E. As an alternative to the $H_f^\circ$(andalusite) used in building set I (see part (D) above), we have calculated another value for the standard enthalpy of formation of andalusite from the $H_f^\circ$(pyroph) accepted in part (A) and using the constraint for reaction 9, table 5. This gives $H_f^\circ$(andalusite) = $-611370$ cal mole$^{-1}$. Now the error in Robie and Waldbaum’s heats for the Al$_2$SiO$_5$ polymorphs and corundum becomes $619390 - 611370 = 8020$ cal mole$^{-1}$; for muscovite, the error is $-9800 + 8020 = -1780$ cal mole$^{-1}$ and $H_f^\circ$(musc) = $-1422960$ cal mole$^{-1}$.

Independently from these considerations, the average enthalpy of muscovite as calculated from data by Shade (ms). Barnes (written commun., 1972) and Usdowski and Barnes (1972) turns out to be $-1424649$ cal mole$^{-1}$ (table 6), only about 1.6 kcal more negative than the previous value. However, the uncertainties are large, and so this fair coincidence may be merely apparent.

The $H_f^\circ$(muscovite) = $-1422960$ cal mole$^{-1}$ calculated above is 1780 cal more negative than the value determined by Barany (1964),

### Table 7

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$H_f^\circ$ (cal mole$^{-1}$)</th>
<th>$G_f^\circ$ (cal mole$^{-1}$)</th>
<th>$H_f^\circ$ (cal mole$^{-1}$)</th>
<th>$G_f^\circ$ (cal mole$^{-1}$)</th>
<th>$S_f^\circ$ (cal K$^{-1}$ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corundum</td>
<td>$-395800 \pm 460$</td>
<td>$-373482 \pm 470$</td>
<td>$-391900$</td>
<td>$-369582$</td>
<td>12.18</td>
</tr>
<tr>
<td>Andalusite</td>
<td>$-614790 \pm 790$</td>
<td>$-579534 \pm 800$</td>
<td>$-610890$</td>
<td>$-575634$</td>
<td>22.28</td>
</tr>
<tr>
<td>Sillimanite</td>
<td>$-614050 \pm 790$</td>
<td>$-579000 \pm 800$</td>
<td>$-610150$</td>
<td>$-575100$</td>
<td>22.97</td>
</tr>
<tr>
<td>Kyanite</td>
<td>$-615330 \pm 640$</td>
<td>$-579400 \pm 650$</td>
<td>$-611430$</td>
<td>$-575500$</td>
<td>20.02</td>
</tr>
<tr>
<td>3:2 Mullite</td>
<td>$-1615743 \pm 1740$</td>
<td>$-1525202 \pm 1770$</td>
<td>$-1604043$</td>
<td>$-1513502$</td>
<td>64.43</td>
</tr>
<tr>
<td>Muscovite</td>
<td>$-1426380 \pm 1350$</td>
<td>$-1335803 \pm 1370$</td>
<td>$-1422480$</td>
<td>$-1331403$</td>
<td>69.0</td>
</tr>
<tr>
<td>Paragonite</td>
<td>$-1415850 \pm 540$</td>
<td>$-1324355 \pm 620$</td>
<td>$-1412050$</td>
<td>$-1320755$</td>
<td>65.03</td>
</tr>
</tbody>
</table>

Both sets are also consistent with values in table 1. Figures for pyrophyllite are the same for both sets. Paragonite values were calculated assuming high-albite as reaction products in equations setting up constraints (table 5).

Set I: error in $H_f^\circ$(corundum) is $+4600$ cal mole$^{-1}$, in muscovite $-5200$ cal mole$^{-1}$.

Set II: error in $H_f^\circ$(corundum) is $+8500$ cal mole$^{-1}$, in muscovite $-1300$ cal mole$^{-1}$.

Uncertainty in $H_f^\circ$(pyrophyllite) is twice the standard error of the mean. Uncertainty in $H_f^\circ$(paragonite) was computed from the average uncertainty as implied in equations 6 and 7, table 5. For uncertainties in $G_f^\circ$, the method described in Robie and Waldbaum (1968) has been followed. Uncertainties in the rest of the minerals include the uncertainties quoted in Robie and Waldbaum (1968) and the uncertainty ($\pm 550$ cal) associated with the discrepancy $\epsilon$(cor)–$\epsilon$(musc) ($= 9800$ cal) (see text and table 5). Values for mullite are tentative. Entropies from Robie and Waldbaum (1968), King and Weller (1970) are estimated.
H$_f^o$(muscovite) = $-1421180 \pm 1300$ cal mole$^{-1}$, but it is only 480 cal more negative than the most stable muscovite as allowed by Barany's uncertainty ($-1421180 - 1300 = 1422480$). Therefore, rather than reject Barany's H$_f^o$(muscovite), we adopt as our second set of self-consistent enthalpies of formation one in which the H$_f^o$(muscovite) determined by Barany and listed by Robie and Waldbaum (1968) is corrected by $-1300$ cal. Consequently, the H$_f^o$'s for corundum and the aluminosilicate polymorphs are corrected by $9800 - 1300 = 8500$ cal mole$^{-1}$. The results are presented as set II in table 7.

AN EXAMINATION OF SETS OF INTERNALLY CONSISTENT THERMODYNAMIC DATA: PREDICTIONS AND IMPLICATIONS FROM THEORETICAL EQUILIBRIUM DIAGRAMS

Calculation of theoretical equilibrium diagrams are a necessary step to decide on the relative merits of the two sets of proposed values (table 7). Best suited for our purposes are equilibrium diagrams in which the stability fields of minerals are represented as functions of the activities of aqueous species (Garrels and Christ. 1965; Helgeson, Brown, and Lueper, 1969; Brown, ms). The two sets of data are different enough so that significant shifts will appear in the relative stability fields of several minerals, easily depicted in activity diagrams. A great deal is now known not only of alteration assemblages in soils and sedimentary rocks but also about the composition of the coexisting natural waters and brines. These waters can be represented in activity diagrams, and the mineral associations theoretically in equilibrium with them should correspond to the ones found in nature.

Studies recording weathering and diagenetic assemblages in soils and sedimentary rocks are plentiful. Most of them indicate clearly that total conversion to a final equilibrium assemblage has not been reached. But the same alteration minerals occur time and again, suggesting in many cases that it is not so much the nature of the minerals in itself that is going to change given enough time for the reactions to be completed but rather their relative proportions with respect to the unaltered assemblage.

Activity diagrams have been constructed with the two different sets of table 7 (fig. 2). In our case, we are mainly interested in the activities of the aqueous species K$^+$, Na$^+$, H$^+$, and H$_2$SiO$_4$. A few examples show that set II of table 7 leads to stability fields that are consistent with observations in nature, whereas set I does not meet this test.

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5 Information about theory and geometry of activity diagrams is given in the cited bibliography.

6 No additional information is gained from calculation of equilibrium curves in a P-T diagram for such buffered chemical reactions as: muscovite $\Leftrightarrow$ sanidine $+\$ andalusite $+\$ steam. Identical equilibrium curves are calculated with both sets of thermodynamic values.

7 The reader is referred to Merino (ms), where a more detailed compilation is given of alteration mineralogies of soils and diagenetic occurrences in the system SiO$_2$–Al$_2$O$_3$–K$_2$O–Na$_2$O–H$_2$O.

8 Diagrams were constructed with a program written by Brown (ms).
linite has been found by several authors (for example, Feth, Roberson, and Polzer, 1964; Marchand, ms, 1971) in soils deriving from granitic rocks. Waters percolating these soils have been analyzed, and the activities of their aqueous species should plot within the kaolinite field (or at the kaolinite–muscovite boundary). The stability field of muscovite is enlarged in set I at the expense of that of kaolinite (fig. 2A), so that the composition of natural waters (shaded areas, fig. 2A) would favor the mica rather than the clay. By contrast, set II defines a stability area for muscovite that leaves the water compositions within the kaolinite field (fig. 2C), in accordance with the observations of Feth, Roberson, and Polzer (1964) and Marchand (ms, 1971).

Merino (ms) has found the diagenetic association quartz–albite ± K-feldspar ± kaolinite ± muscovite in sandstones from Kettleman North Dome, Calif. These minerals occur at depths of 2400 to 3500 m and have formed at about 100°C; textural evidence suggests that kaolinite is being replaced by muscovite. Compositions of interstitial waters from Kettleman have been taken from Kharaka (ms), converted to activities at 100°C (Merino, ms), and plotted in figures 2B and 2D. The enthalpies of set I produce so wide a stability field for paragonite that the Kettleman waters plot in it, appearing to favor the crystallization of diagenetic paragonite. However, no paragonite is present in the diagenetic association, and it is again set II that defines stability fields consistent with the observed mineralogy and water chemistry. For instance, the waters of the Kettleman area lie mostly within the stability field of albite, which is indeed a widespread diagenetic mineral in the sandstones.

Although set II of table 7 provides calculated stability fields that on the whole are consistent with what is observed in nature, future work—especially better calorimetric data on some of the suspect minerals—may provide room for different results. Nevertheless, certain conclusions from our comparison of stability relations of minerals vis-a-vis natural occurrences are also clear. So the relationship between the enthalpy values for kaolinite and muscovite cannot vary too much from what is proposed here. Muscovite cannot be much more stable vis-a-vis kaolinite, because this would widen the mica field at the expense of kaolinite with the implication that muscovite rather than kaolinite should be the abundant mineral in soils and diagenetic associations. Conversely, destabilizing muscovite enlarges the stability field of kaolinite and would theoretically prevent muscovite from becoming a possible diagenetic mineral. An identical reasoning applies to paragonite. Similar constraints are imposed on the enthalpy values of gibbsite and boehmite as compared to that of kaolinite. It may be quite possible that the true enthalpy figures for these Al-hydroxides are more negative than the ones we propose. But they cannot vary too much; otherwise, Al-hydroxides would impinge at lower temperatures (25° to approx 200°C) on the stability field of kaolinite and might, in an extreme case, even become stable in the presence of quartz. Again, experiments (for example, Hemley, per-
Fig. 2. Phase relations at P = 1 to 500 atm, in the systems SiO₂-Al₂O₃-H₂O-KCl-HCl and SiO₂-Al₂O₃-H₂O-NaCl-HCl in the presence of an aqueous phase with unit activity of water. Diagrams A and B are constructed with data from set I (table 7); C and D are constructed with data from set II. Shaded areas represent interstitial solutions: those at 25°C (A, C) are from Feth, Roberson, and Polzer (1964) and Marchand (ms, 1971), those at 100°C (B, D) are from Kharaka (ms) recalculated by Merino (ms). Ab = albite; A = saturation with amorphous silica; B = boehmite; G = gibbsite; K = kaolinite; M = microlite; Mu = muscovite; Na = Na-montmorillonite; P = pyrophyllite; Pa = paragonite; Q = quartz saturation line.
sonal commun., 1972) and nature (for example, Valeton, 1967) negate such a possibility.

**SUMMARY AND CONCLUSIONS**

1. A consistent set of enthalpy values is adopted from the literature for the following solution species: Al$^{3+}$, Al(OH)$^{2+}$, Al(OH)$_3^-$, H$_4$SiO$_4$, K$^+$, Na$^+$, OH$^-$ (table 2).

2. The following values were adopted for Al-solution species: $H^o_r (Al(OH)_{3^-}) = -310200$ and $H^o_r (Al^{3+}) = -127000$ cal mole$^{-1}$. From these and from solubility results by several authors, $H^o_r (boehmite) = -234660 \pm 325$ cal mole$^{-1}$. This last value is very close to the one calculated from hydrothermal experiments in non-buffered conditions, which is only based on the enthalpies of kaolinite and H$_4$SiO$_4$(aq). From here follows the implication that our values for aqueous Al-complexes are probably accurate.

3. The enthalpy adopted for gibbsite ($H^o_r = -307050 \pm 325$ cal mole$^{-1}$) is based on our enthalpies of formation for Al(OH)$_3^-$ and Al$^{3+}$ and on solubility constants by Apps (ms), Kittrick (1966a), Frink (1960, cited by Sillén and Martell, 1964), and Ikkatai and Okada (1962, cited by Apps, ms).

4. The proposed standard enthalpies for diaspore and bayerite are, respectively, $-237820$ and $-305890$ cal mole$^{-1}$. A tentative standard enthalpy of $-214600$ cal mole$^{-1}$ is proposed for amorphous silica, as computed from the experimental results of Kitahara (1960). Thermodynamic values used in this paper for quartz, alkali feldspars, and water are from Robie and Waldbaum (1968), and those for kaolinite, Na-montmorillonite, and H$_4$SiO$_4$(aq) are from Helgeson (1969).

5. The value $H^o_r (pyrophyllite) = -1342420 \pm 630$ cal mole$^{-1}$, computed from equilibrium curves determined experimentally by several authors, is based only on the corresponding values for water, quartz, kaolinite, and H$_4$SiO$_4$(aq).

6. A constraint, based on hydrothermal equilibrium data, is set up such that:

$$\varepsilon(\text{corundum}) - \varepsilon(\text{muscovite}) = 9800 \pm 350 \text{ cal},$$

where $\varepsilon$ are the errors per mole in the enthalpies of corundum and muscovite.

7. An analysis of the available data—both from buffered hydrothermal experiments and from experiments with salt solutions and in non-buffered systems—shows that there are no more than two sets of internally consistent values for the suspect enthalpies of corundum, the aluminosilicate polymorphs, mullite, muscovite, and paragonite characterized in our nomenclature as set I and set II (table 7).

8. In activity diagrams, where stability fields of minerals are represented as a function of chemical composition of aqueous solutions, the fields of boehmite, gibbsite, and pyrophyllite—calculated with the enthalpies proposed in this paper—portray relationships to other minerals
that are indeed observed in experimental work and in natural occurrences.

9. Activity diagrams have the additional advantage of permitting comparison of the relative merits of the two sets of self-consistent thermodynamic data of table 7. Set II of table 7 defines stability fields for muscovite, paragonite, and kaolinite that are compatible with observed mineralogies in soils and diagenetic occurrences.

10. An internally consistent set of enthalpies (set II) provides reasonable implications for natural assemblages. The enthalpies are: \( H_f^o \) (muscovite) = -1422480 cal mole\(^{-1}\); \( H_f^o \) (corundum) = -391900; \( H_f^o \) (andalusite) = -610890; \( H_f^o \) (sillimanite) = -610150; \( H_f^o \) (kyanite) = -611430; \( H_f^o \) (paragonite) = -1412050.

11. A final answer can only be furnished by the calorimetric determination of the enthalpies of pyrophyllite, paragonite, and at least one of the following minerals: corundum, andalusite, kyanite, and sillimanite. Also needed is a reexamination of the enthalpy of muscovite. Crystallographic studies determining the structural state should complement the calorimetric information.

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