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FREE ENERGY OF FORMATION OF PYROPHYLLITE FROM HYDROTHERMAL DATA: VALUES, DISCREPANCIES, AND IMPLICATIONS[1]

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ABSTRACT

The standard free energy of formation of pyrophyllite, ΔG°_f(Pr), is calculated from reversed hydrothermal data. The value falls into two distinct groups: about −1251 kcal from breakdown of kaolinite+quartz, and about −1258 kcal from pyrophyllite breakdown into andalusite+quartz, or pyrophyllite+corundum into kyanite. The second value agrees with a direct determination of ΔG_f°(Pr) by solubility measurements. The discrepancy cannot be fully explained by uncertainties in the calculations, in the location of experimental points, or by uncertainties in the entropy and volume data used in the calculations. Instead, large systematic errors appear to exist in the values of free energy of formation for kaolinite and/or the polymorphs of Al_2SiO_5. Petrographic data, namely the apparent stability of kaolinite +quartz relative to pyrophyllite in many rocks, and the common occurrence of muscovite +quartz and rarity of microcline+pyrophyllite, suggest that the error is in the data for the Al_2SiO_5 polymorphs.

INTRODUCTION

Although pyrophyllite is a rare rock-forming mineral, deposits of pyrophyllite form important economic resources. Many of these deposits apparently formed during hydrothermal and regional metamorphism. Knowledge of the stability of pyrophyllite is important in helping to define the conditions of metamorphism of these rocks, as well as stability limits of other, more common, sedimentary and metamorphic aluminum silicate minerals, such as kaolinite, kyanite and its polymorphs. Recent experimental studies of phase equilibria involving pyrophyllite now permit calculation of some of the thermodynamic constants for this mineral. This note presents the results of these calculations, points out certain inconsistencies, compares the data with petrographic experience, and discusses some of their possible implications.

BASIC CALCULATIONS

The standard Gibbs free energy of formation of pyrophyllite, ΔG_f°(Pr), from the elements, is calculated at 25°C and 1 bar pressure from reversed hydrothermal experimental work involving pyrophyllite as one of the phases. Except as otherwise discussed, all basic data for solid phases are taken from the recent compilation of Robie and Waldbaum (1968). For "steam" (H_2O), the free energy of formation values are calculated from the fugacity coefficients, ν, of Holser (1954) and of Anderson (1964), referring to the polythermal values of Robie and Waldbaum (1968) for 1-bar pressure, graphically interpolated where necessary. The

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calculations of Anderson are based on more precise data than those of Holser. However, where the two sets of calculations overlap, the difference between them is, for our purposes, negligible; Holser's data were also used because they extend to lower pressures. The recent measurements of Burnham *et al.* (1968) came to my attention after the calculations were completed; these new data do not significantly affect the results. The relations used in this calculation are simply

$$\mu_w(T, p) = \mu_w(T, 1 \text{ bar}) + RT\, ln\, p\nu(T, p) \tag{1}$$

Corrections being made for the value of ν at 1 bar pressure.

The experimental hydrothermal data used for calculating $\Delta G_f°$ (Pr; 25°C, 1 bar) are the following:

(I) The breakdown reaction for kaolinite:

$$\text{Kaolinite} + 2 \text{ quartz} = \text{pyrophyllite} + \text{steam} \tag{2}$$

For this reaction,

$$\Delta G = \Delta G_f°(\text{Pr}; T, \text{p}) + \mu_w(T, \text{p}) - \Delta G_f°(K; T, \text{p}) - 2\Delta G_f°(Q; T, \text{p}) \quad (3);$$

ΔG is equal to zero at the T, p of equilibrium. We can rewrite (3) as follows:

$$\Delta G(T, p) = 0 = \Delta G_{f,s}°(T, p) + \mu_w(T, p) \tag{3a}$$

where the subscript "s" stands for solid phases. Therefore, approximately

$$\begin{aligned} 0 = \Delta G_f°(\text{Pr}; 25°\text{C}, 1 \text{ bar}) - \Delta G_f°(K; 25, 1) - 2\Delta G_f°(Q; 25, 1) \\ + \Delta V_s \Delta \text{p} - \Delta S_s' \Delta T + \mu_w(T, \text{p}) \end{aligned} \tag{3b}$$

where S′ refers to the entropy of formation of a phase from the elements. Use of S′ values is necessary in (3b) because all Gibbs free energy of formation values of Robie and Waldbaum (1968) are based on them. Justification for assuming V_s and S'_s as constants will be given later.

All the required values for "third law" entropy, volume, and Gibbs free energy of formation (from elements) are listed in Robie and Waldbaum (1968) or calculable from this compilation and the data of Anderson (1964) or Holser (1954). The exceptions are the third-law entropy of pyrophyllite and $\Delta G_f°$ (Pr; 25, 1). For this entropy, the proposed value of 63.3 cal/mol-deg (e.u.) (Fonarev, 1967) is used; the effect of the uncertainty of this entropy value will be examined later. Therefore, $\Delta G_f°$(Pr; 25, 1) can be directly computed from equilibrium data.

The reversed equilibrium data used are given in Table 1. The data point of Hemley, 1959, however, is indirect and requires comment. Hemley reported reversible equilibrium for two reactions: kaolinite

TABLE 1. $\Delta G_f°(\text{Pr})$ (25° C, 1 BAR) FROM EXPERIMENTAL DATA

T, ° C	$P_{\text{total}}=P_{H_2O}$	$\Delta G_f°$(Pr), kcal	Reference
(I) Kaolinite+2 Quartz=Pyrophyllite+H_2O			
290°	10,000 psi	−1251.8	R. O. Fournier, 1969, oral communication
350°	1,000 atm	−1250.8	Hemley, 1959 (see text for explanation)
390°	2 kbar	−1250.3	Althaus, 1966
405°	7 kbar	−1250.3	Althaus, 1966
(II) Pyrophyllite=Andalusite+3 Quartz+H_2O			
400°	1 kbar	−1257.7	Hemley, 1967
410°	1.8	−1257.4	Kerrick, 1968
430°	3.9	−1257.2	Kerrick, 1968
490°	2	−1258.1	Althaus, 1967
525°	7	−1256.8	Althaus, 1967
(III) Pyrophyllite+3 Corundum=4 Kyanite+H_2O			
520°	7 kbar	−1259.7	Matsushima *et al.*, 1967
(IV) Direct solubility determination			
25°	1 bar	−1258.7	Reesman and Keller, 1968

$+K^+$=muscovite$+H^++H_2O$ and also pyrophyllite$+K^+$=muscovite$+H^+$+quartz; the two curves intersect at the temperature and pressure given in Table 1. The intersection defines an invariant point from which reaction (2) must emanate; therefore the T, p values are valid for our calculations. In the calculations, the effect of dissolved matter on the fugacity of H_2O is ignored; this will be examined in the next section. These group (I) results cluster around −1251 kcal for the Gibbs free energy of formation of pyrophyllite from the elements with a spread of 1.5 kcal.

(II) The breakdown reaction for pyrophyllite:

$$\text{Pyrophyllite}=\text{andalusite}+3\ \text{quartz}+H_2O \qquad (4)$$

From this reaction we may write, analogous to (3b),

$$0 = \Delta G_f°(A;25,1) + 3\Delta G_f°(Q;25,1) - \Delta G_f°(\text{Pr};25,1) + \Delta V_s\Delta p - \Delta S_s'\Delta T + \mu_w(T,p) \qquad (4a).$$

The reversed equilibrium data used in the calculations are given in Table 1, as are the results of these calculations. The group (II) results cluster about −1258 kcal; the spread is 1.3 kcal. The minimum gap between the data of this group and those of group (I) is about 5 kcal, and the difference between the "average" values is about 7 kcal.

(III) The reaction of pyrophyllite and corundum to form kyanite:

$$\text{Pyrophyllite} + 3\ \text{corundum} = 4\ \text{kyanite} + H_2O \tag{5}$$

For this reaction we can write, analogous to equation (3b),

$$4\Delta G_f^\circ(K_y; 25, 1) - \Delta G_f^\circ(\text{Pr}; 25, 1) - 3\Delta G_f^\circ(\text{Cor}; 25, 1) - \Delta S_s'\Delta T + \Delta V_s\Delta \text{p} + \mu_w(T, p) = 0 \tag{5a}$$

Only one reversed equilibrium reaction point has been used for calculation; this is the point of Matsushima *et al.* (1967). The result (Table 1) is −1259.7 kcal.

Table 1 includes, in addition, the result of a recent direct solubility determination of the Gibbs free energy of formation of pyrophyllite by Reesman and Keller (1968), −1258.7 kcal, which is the average of four determinations having a spread of 2 kcal, and which agrees well with the data of groups (II) and (III) but not with the results of group (I). Reesman and Keller (1968, Table 3) measured a second pyrophyllite sample that gave eight results ranging from −1243.0 kcal to −1255.9 kcal, averaging −1251.3 kcal. Six of the data points range from −1249.7 to −1252.9 kcal, averaging −1251.9 kcal; of these five points range from −1251.8 to −1252.9 kcal, averaging −1252.3 kcal and a spread of just over 1 kcal. Although Reesman and Keller (1968) attribute the more positive values of this group of data to effect of mechanical disorder during grinding, grinding certainly cannot lead to a discrepancy of some 7 kcal, and there seems no intrinsic reason why the more positive values are not as accurate as that accepted by Reesman and Keller. The more positive value agrees well with the result of group (I).

Reesman and Keller used the same experimental procedure to determine the Gibbs free energy of formation of kaolinite. The results show considerable spread and have been briefly discussed by the authors. Their recommended value closely agrees with those that exist in the literature (see below). One might thus place confidence in their recommended pyrophyllite value as well. This value, and those of groups (II) and (III), however, are so grossly out of line with the results of group (I), that attempts at resolution are needed. This need is the more pressing when it is remembered that group (I) data are based on kaolinite breakdown, using the consistent kaolinite data cited above.

Yet another value for the Gibbs free energy of formation of pyrophyllite is in the literature. This value, due to Fonarev (1967), is −1262.14 kcal. The value is derived from calculations based on early, nonreversed experimental work, having poorly characterized phases. Therefore, I recommend that it be disregarded.

ESTIMATION OF ERRORS AND UNCERTAINTIES

The calculations outlined in the previous section inevitably introduced errors and approximations; uncertainties in the original data were possibly magnified.

The free energy values of "steam," H_2O, were from two different sources: Holser (1954), from the measurements of Kennedy (1950); and Anderson (1964), from the data of Pistorius and Sharp (1960). However, using the 1-bar polythermal free-energy of formation values compiled by Robie and Waldbaum (1968), the maximum difference between the high-pressure values computed by the two sets of fugacity coefficients is about 100 cal and commonly much less in the region where the data overlap.

The free energy data for "steam" were interpolated along both temperature and pressure coordinates to fit the p, T conditions for the hydrothermal equilibria used in the calculations. These interpolations were made graphically, and errors were thereby introduced. However, I estimate that the cumulative error from this source is less than 100 cal. Error due to assuming the steam phase to be pure H_2O is more difficult to ascertain, but, even for $T = 700°K$ and activity of H_2O lowered to 0.9, the change of free energy is only about 150 cal.

Extrapolation of the experimental data from elevated temperatures and pressures to 25°C and 1 bar introduces two sorts of errors. First, for the solid phases, the entropies of formation and the volumes may not be constant over the entire range of T, p; second, these assumed constant values of S' and V may themselves be in error. Errors due to the volume term is not significant. For example, for equation (4a), the contribution from the $\Delta V_s \Delta p$ term is only −1172 cal even with an extrapolation over 7 kbar, and as much as 10 percent error in ΔV_s would lead to an error only of about 100 cal. The effects of high temperature and pressure are unlikely to lead to a deviation of ΔV_s of this magnitude.

Entropies of individual phases change rapidly with temperature (see, for example, Robie and Waldbaum, 1968), even though ΔS is more nearly constant for balanced reactions. Because the $\Delta S_s' \Delta T$ term involves only the solid phases, one might at first suspect this term to cause significant error. This in fact is not so, because the entropies of formation from elements, S', for solids are nearly independent of temperature. For instance, for andalusite S' at 298°K is −118 e.u., and at 800°K it is −117 e.u. For muscovite, the corresponding values are −305 e.u. and −304 e.u. The quantities, $\Delta S_s'$, for reactions involving these phases are of a comparable degree of constancy. For instance, for the reaction: muscovite+quartz=kyanite+microcline+vapor, $\Delta S_s'$ at 298°K is +49 e.u. whereas it is +48 e.u. at 700 K°.

Unfortunately, high-temperature entropy data do not yet exist for kaolinite or pyrophyllite. The constancy of $\Delta S_s'$ for the above example as well as for several other examples involving hydrous silicate phases, calculable from the tables of Robie and Waldbaum, however, makes it appear certain that for kaolinite and pyrophyllite also the approximate constancy will hold.

An error in $\Delta S_s'$ of 1 e.u. over 500° will lead to an error of 500 cal in the free energy data. The actual error introduced by the $\Delta S_s'$ term should be much less than this indicated amount. This is so because we are comparing the data of different groups in Table 1, all of which involve extrapolation from high temperature; as reactions (2), (4) and (5) share several phases in common, contributions to errors by these phases tend to cancel over the range of temperature overlap.

The entropy value of pyrophyllite used in the calculations, 63.3 e.u., is obtained by Fonarev (1967) essentially by the "oxide summation" procedure. The oxide-summation procedure is empirical and fallible, but does seem to work for many silicate phases. Straight summation of oxides, using a value of 10 e.u. for H_2O (approximately that of ice; see Fyfe, Turner and Verhoogen, 1958, p. 117) leads to about 62 e.u.; summation of the entropies of 2 boehmite +4 quartz leads to 62.7 e.u. On the other hand, the entropy of talc, structurally analogous to pyrophyllite, is about 6.5 e.u. less than that to be obtained by the oxide-summation procedure (Robie and Waldbaum, 1968); one might suspect then that the pyrophyllite entropy should be lower by a similar amount (interestingly, summation of 2 diaspore+4 quartz leads to 56.4 e.u., or 6.3 e.u. less than the value derived from the boehmite+quartz summation!). An error in the entropy of pyrophyllite of 6 e.u. would lead to a change of several kilocalories in Gibbs free energy of formation, but the change affects results of calculations of reactions (2), (4), and (5) in the same algebraic sense. Moreover, because pyrophyllite appears in reactions (2), (4), and (5) always with unit stoichiometric coefficient, and because this error enters only through the difference in equilibration temperatures of these reactions (100–200°; Table 1), and not through the difference between any given equilibration temperature and room temperature, the error introduced by using a wrong value for the pyrophyllite entropy is probably less than 1 kcal.

Uncertainties in the location of the hydrothermal equilibrium will introduce errors. For an isobaric shift of equilibrium temperature of as much as 30°, the shift in $\Delta G_f{}^\circ(\mathrm{Pr})$ is typically about 1.5 kcal, which is about the right order for the within-group spreads of free energy values given in Table 1. This source of error is unlikely to be responsible for the much larger between-group discrepancies.

Pyrophyllite has the highest Si:Al ratio of all known aluminum silicates; reactions leading to the formation of this phase will require addition of SiO_2. This fact would seem to rule out silica nonstoichiometry as a possible major cause for the discrepancy in group (I) and group (II) values, though the situation is less certain for group (III) data. Conceivably, polytypism exists in pyrophyllite that depends on the nature of the reaction leading to its formation. Although we do not yet know enough about the crystallography of pyrophyllite to rule out this possibility, polymorphs, including stacking polymorphs, characteristically show free energy differences no more than a few hundred calories instead of several kilocalories. One might surmise the same to be true of possible effects of variable crystallinity of the hydrothermal reaction products.

It seems necessary to conclude, therefore, that the sources of error above considered do not explain the discrepancy of data. It remains to explore the possibility that systematic errors exist in the thermodynamic constants of phases such as kaolinite or andalusite; this possibility seems particularly pertinent because the free energy values appear to depend strictly on the reactions (Table 1).

The free energy of formation of kaolinite used in calculations of equation (3b) was the value recommended by Robie and Waldbaum, −902, 868 cal. This value is in close accord with that of Barany and Kelley (1961), 903.0 kcal, determined by calorimetric measurements, and with the values of −904.0 kcal recommended by Reesman and Keller (1968) and with a range from −902.5 to −903.8 kcal (depends on the sample) given by Kittrick (1966). Kittrick, and also Reesman and Keller, used a method of solubility measurements, but used different methods to analyse for dissolved Al. The agreement of all the results thus would seem to lend credence to the value. Somewhat different values would result, of course, if different values for the standard free energy of formation of dissolved species were used. For instance, if the values for $Al(OH)_4^-$ and for H_4SiO_4 were respectively −310.2 and −314.7 kcal, as listed by Wagman and others (1968) instead of −311.3 and −312.65 kcal as given by Reesman and Keller, the free energy of formation for kaolinite would be about 2 kcal more negative. By equation (3b), the pyrophyllite value would be similarly affected, reducing the discrepancy between the data of groups (I) and (II). If Wagman *et al.*'s value for H_4SiO_4 were used while retaining Reesman and Keller's value for $Al(OH)_4^-$, the free energy of formation of kaolinite (and by (3b) also of pyrophyllite) would be more negative by 4.1 kcal. The discrepancy between groups (I) and (II) would then be reduced to less than 3 kcal, somewhat on the order of hydrothermal experimental, calorimetric and computational uncertainties. Such changes would help in bringing about conformity of data, but as we shall see in the next section, they do not obviate several major petrographic objections to the data.

The free energy data for andalusite and kyanite used in the calculations were taken from Robie and Waldbaum (1968), based primarily on the measurements of Holm and Kleppa (1966). These data are presumably of high precision. The thermodynamic data as such do not afford a criterion for choosing between the results of group (I) and of group (II). Petrologic reasonableness of the data should help in our choice.

Petrographic Tests of Thermodynamic Data

An important test of the reasonableness of the data is the stability of the assemblage quartz+kaolinite relative to pyrophyllite at near-surface conditions. If we accept the free energy of formation of kaolinite as given by Robie and Waldbaum, and assuming reaction (2) to involve formation of liquid water (pure H_2O), then for equilibrium at 25°C and 1 bar pressure, we require

$$
\begin{aligned}
\Delta G_f^\circ(\mathrm{Pr}; 25, 1) &= \Delta G_f^\circ(K; 25, 1) + 2\Delta G_f^\circ(Q; 25, 1) - \mu_{\mathrm{w}}(25, 1) \\
&= -\ 1255.5 \text{ kcal.}
\end{aligned}
$$

Thus group (I) data indicate that kaolinite and quartz are relatively more stable than pyrophyllite+water at surface conditions, whereas groups (II) and (III) values imply the converse. We might note that replacement of quartz by some other polymorph of silica having higher activity, or replacement of pure water by aqueous solutions or by undersaturated water vapor (except the improbable metastable steam phase!) having of necessity lower values of activity, would both further restrict the stability of kaolinite+quartz relative to pyrophyllite. We might also note that any shift of the free energy of formation of kaolinite, as discussed in the preceding section, changes the free energy of formation of pyrophyllite by exactly the same amount and so the problem would not be reduced.

Kaolinite and quartz or some silica polymorph commonly are found together in sediments and sedimentary rocks which had formed near surface conditions. In rare instances, cogent arguments for their equilibrium has been presented (Altschuler *et al.*, 1963). In general, however, evidence for equilibrium between associated kaolinite and quartz is absent and to my knowledge none exists that the equilibrium might not be metastable relative to pyrophyllite.

On the other hand, kaolinite and quartz are common products of hydrothermal wall-rock alteration, under conditions of presumably much greater possibility of equilibrium. Kaolinite, quartz and pyrophyllite are found together in apparently unmetamorphosed shales in Utah (Ehlmann, 1958) and in many pyrophyllite deposits of metamorphic origin, for instance in North Carolina, where their mutual relations might be explained as equilibrium coexistence (Zen, 1961a) or, alternatively, the kaolinite could represent retrograde alteration product of pyrophyllite in the presence of quartz. For these deposits, the problem of metastable equilibrium involving these coexisting phases do not arise, and the observations indicate that under proper geologic conditions kaolinite+quartz is in equilibrium with or is more stable than pyrophyllite. To see whether the thermodynamic data are compatible with this conclusion, we use the method of Schreinemakers' bundles.

Because of the nature of reactions (2) and (4), we choose for our system the five phases quartz, Q, andalusite, A, pyrophyllite, Pr, kaolinite, K, and "steam," W, of composition H_2O. These five phases belong to the ternary System Al_2O_3-SiO_2-H_2O for which an invariant point, metastable or otherwise, may be constructed. The chemography of the phases is given in Fig. 1a; from this, it follows that the progression of univariant lines about the invariant point is (A), (Q), (K), (Pr) and (W) (see Zen, 1966). Curve (W) is readily computed because it involves only solid phases. Using the value of -1258 kcal for $\Delta G_f{}^\circ(\mathrm{Pr})$ and using other data given by Robie and Waldbaum, we get an equation for curve (W):

$$\Delta T = -902.7 - .04225\, \Delta p$$

for p in bars and $\Delta T = T - 25°\mathrm{C}$. Obviously, if either curve (A) (which is equation (2), or (K), which is equation (4)) is stable within the five phase system, then Schreinemakers' bundle must be oriented as in Fig. 1b, in which the chemography of divariant fields are also shown. The invariant point itself is not at geologically accessible T and p (because the curve (W) itself is not). Curve (K) of course is located at geologically realistic conditions, corresponding to the experimental condition listed in Table 1 for group (II) values. Curve (Q) is located at approximately 2.2 kbar at 25°C and has a positive slope. From this we conclude that within geologically accessible T and p region, kaolinite and quartz have no field of coexistence. Moreover, kaolinite has no intrinsic field of stability to andalusite and pyrophyllite except at very low temperatures and simultaneous high pressures. This conclusion would seem to contradict a large body of petrographic evidence.

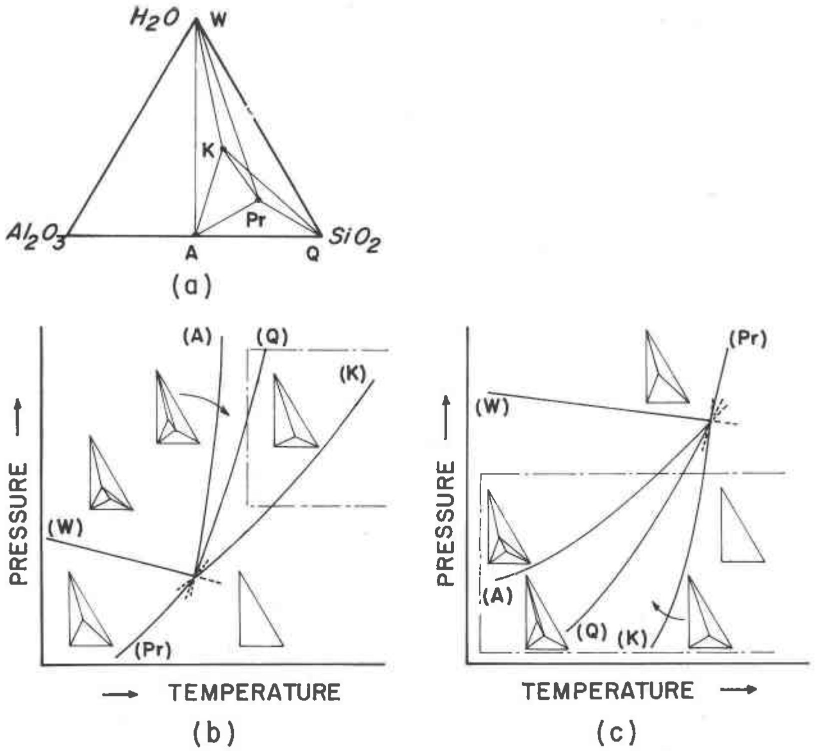

FIG. 1. Schreinemakers' bundle for the five phases andalusite, A, quartz, Q, pyrophyllite, Pr, kaolinite, K, and "steam", W in the ternary system Al_2O_3-SiO_2-H_2O. (a), chemography of the phases. (b), proper orientation of the bundle using a value of −1258 kcal for the free energy of formation of pyrophyllite, assuming that the experimental curve (K) is stable. See text for numerical values. (c), alternative orientation of the bundle using a value of −1251 kcal for the free energy of formation of pyrophyllite, assuming that the experimental curves (K) and (A) are stable. See text for numerical values. Rectangle defined by dash-dot lines qualitatively indicates geologically reasonable p, T conditions, at $T \geq 25°C$ and $p \geq 1$ bar.

On the other hand, using a value of −1251 kcal for $\Delta G_f°$ of pyrophyllite, curve (W) is described by

$$\Delta T = T - 25°C = 1288 - .04225\,\Delta p$$

and for either experimentally determined (K) or (A) to be stable within the five phase system, the phase diagram must have the appearance of Fig. 1c and the invariant point is located, very roughly, at around 400°C and 17 kban. Curve (A) is located directly by the experimental data, Table 1. Clearly, curve (K), which must be at higher temperature than

(A) and (Q), cannot be located consistently. Nonetheless, Fig. 1c shows that kaolinite does have an extensive field of stability and, kaolinite +quartz are stable together at near-surface conditions. The assemblage excluded at low to moderate pressures is kaolinite+andalusite+quartz, unique to the divariant field between (W) and (Pr), but this probably causes no petrologic contradiction. Fig. 1c seems much more in accord with petrographic data than does Fig. 1b.

We can check the above conclusions by another, independent reaction:

$$\text{Pyrophyllite}+\text{microcline}=\text{muscovite}+4\ \text{quartz}$$

For which we obtain, using the data of Robie and Waldbaum (1968), the relation

$$\Delta T = T - 25°\text{C} = 671.7 + .012691\ \Delta p$$

where $\Delta G_f°(\text{Pr})$ is taken to be -1251 kcal; and

$$\Delta T = .012691\ \Delta p - 293.8$$

where $\Delta G_f°(\text{Pr})$ is taken to be -1258 kcal. In both equations, the slope dp/dT is positive. Therefore, according to the first equation muscovite +quartz is stable relative to microcline+pyrophyllite at all geologically reasonable conditions and the breakdown of muscovite+quartz occurs before the reaction to pyrophyllite+microcline (Yoder and Eugster, 1955 and Evans 1965). According to the second equation, however, microcline+pyrophyllite is relatively more stable at all temperatures and pressures likely to be encountered in geologic conditions. Muscovite and quartz are found together in all kinds of rocks, whereas microcline +pyrophyllite is practically unknown. From this we infer that the free energy of formation of pyrophyllite must be more positive than about -1255 kcal, and probably considerably more so; this conclusion is independent of doubts on the free energy value for kaolinite, discussed in an earlier section. Uncertainty of the entropy of pyrophyllite also is unlikely to alter the major conclusion.

Finally, we can compute the isobaric-isothermal piercing points for some zeolitic reactions, using the chemical potentials of CO_2 and H_2O as independent variables (Zen, 1961b). The thermodynamic parameters for leonhardite, a "dehydrated" form of laumontite, are listed in Robie and Waldbaum (1968). We can write the reactions

$$2\ \text{calcite} + 2\ \text{kaolinite} + 4\ \text{quartz} + 3H_2O = \text{leonhardite} + 2CO_2 \quad (6)$$

$$\text{and } 2\ \text{calcite} + 2\ \text{pyrophyllite} + 5H_2O = \text{leonhardite} + 2CO_2. \quad (7)$$

At 25°C and 1 bar pressure, and using $\Delta G_f°(\text{Pr}) = -1251$ cal, we have for (6)

$$+17188 + 2\mu_{CO_2} - 3\mu_w = 0 \tag{6a}$$

and for (7),

$$-105{,}132 + 2\mu_{CO_2} - 5\mu_w = 0 \tag{7a}$$

for the two univariant reactions. Solving simultaneously, we get for the piercing point

$$\mu_w = -61{,}160 \text{ cal} \qquad f_w = 1.7 \times 10^{-5} \text{ bar}$$

$$\mu_{CO_2} = -100{,}334 \text{ cal} \qquad f_{CO_2} = 3.5 \times 10^{-5} \text{ bar}$$

If $\Delta G_f{}^\circ(\text{Pr}) = -1258$ kcal were used, we get for the corresponding fugacities the values of 2.2 bar and 1.7×10^3 bar. The first set of values may or may not be correct, but the second set constitutes an explosive mixture because the total pressure is 1 bar. The first set of values thus are compatible with a stable piercing point, whereas the second set demands that kaolinite+leonhardite as well as kaolinite+calcite are unstable.

Calculations at pressures and temperatures likely found in zeolite facies, roughly corresponding to the suggestions of Fyfe, Turner and Verhoogen (1958, p. 216) and using, in addition, the CO_2 data computed by Robie (1966), show that the piercing point becomes less stable even when $\Delta G_f{}^\circ$ (Pr) of -1251 kcal is used, but the value of -1258 kcal makes the explosion more violent.

CONCLUSIONS

The free-energy of formation values for pyrophyllite calculated from different reversed hydrothermal experimental data show large and systematic discrepancy that depends on the nature of the reaction used. These errors cannot be accounted for by experimental and computational uncertainties alone, partly because of the within-group consistency of data: If experimental errors are alone responsible, then the location of the univariant curves for at least one of the groups would have to be consistently wrong by several hundred degrees. Instead, it appears that the free energy of formation values, for kaolinite and/or andalusite, used in the calculations, are in error.

While it seems unlikely that several concordant determinations of the free energy of formation of kaolinite, using different procedures, are all in error by the same amount, the possibility cannot be excluded. If the kaolinite value were in error alone, however, the prevalence of muscovite +quartz and rarity of pyrophyllite+microcline in rocks still remains to be explained. On the other hand, this awkward contradiction is avoided, as is the exclusion of the apparently compatible association of kaolinite

+quartz at near-surface conditions, if the free energy of formation of pyrophyllite derived from kaolinite is correct, but the andalusite data are too negative by several kilocalories. A minor consequence of this hypothesis is that calculated zeolitic equilibria then assume reasonable numerical values.

The entropy data for andalusite and its polymorphs, as well as the experimental equilibrium relations of these phases, show that the relative values of the free energy of formation for these polymorphs cannot be changed by more than a very few hundred calories. Therefore, if the free energy of formation of andalusite is wrong by several kilocalories, those of the other polymorphs would have to be off by similar amounts. The free energy of formation of andalusite, kyanite, and sillimanite were recently determined by Holm and Kleppa (1966) through independent measurements of heats of solution of these phases, combined with independent measurements of the entropies. Erroneous values for the heat of solution of one of the product species in the calorimeter could lead to precisely this sort of discrepancy, and would explain the similarity in groups (II) and (III) free energy values for pyrophyllite. Large systematic error in the accepted free energy values for one or more aluminum silicate phases seems definite, and for the present these values must be used with extreme caution.

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APPENDIX: SAMPLE CALCULATIONS

Experimental data:

kaolinite+2 quartz=pyrophyllite+water

$T=663°\text{K}$ (390°C) $p=2$ kbars, p (total) $=p$ (water) (Althaus, 1966)

$\Delta T=T-298°\text{K}=365°$; $\Delta p=2{,}000-1\cong 2{,}000$ bars

Phase	S', cal/mole/deg	V, cal/bar	$\Delta G_f°$(25°C, 1 bar), cal
Kaolinite	−256.91	2.378	−902,868
Quartz	− 43.62	0.5422	−204,646
Pyrophyllite	−293.4	3.026	?

μ_w (663°K, 2 kbar) $=-42{,}500$ cal, which is obtained as follows.

The fugacity coefficient, ν is 0.085 at 300°C and 2 kbar, and 0.215 at 400°C and 2 kbar. Hence by equation (1) and Robie and Waldbaum's data,

$$\mu_w(300°\text{C, 2 kbar}) = -45{,}633 \text{ cal}$$

$$\mu_w(400°\text{C, 2 kbar}) = -42{,}140 \text{ cal.}$$

And interpolation gives the value for 390°C

Therefore, substituting the values into equation (3b), we obtain the value for free energy of formation of pyrophyllite at 25°C and 1 bar of −1250.3 kcal given in Table 1.

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