

The phase-equilibrium calorimeter, the petrogenetic grid, and a tyranny of numbers¹

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Abstract

Reversed phase-equilibrium experiments implicitly measure the relative energy contents of two-phase assemblages and are thus calorimetric measurements. The degree and nature of approximations used in different methods of calculations for thermodynamic properties of individual minerals, based on these experiments, can be explicitly specified; most existing methods involve the same approximations.

Because P - T coordinates of experimental brackets are determined in part by arbitrary choice of experimentalists, the mean value of P and T derived from the brackets are not necessarily the best estimates. Thus calculation of thermodynamic data from reversed brackets (point data) is better made on individual brackets. From each bracket, an inequality relation is obtained; the pair of inequalities from the pair of brackets then provides limits to the acceptable values. One advantage of this approach is to permit realistic estimation of the standard error.

Calculations based on the breakdown of $2M_1$ muscovite illustrate the procedure. The data of Day (1973) and of Chatterjee and Johannes (1974) led to results showing a high degree of consistency and a standard error commensurate with the recently revised calorimetric data of Robie *et al.* (1976) and Hemingway and Robie (1977). However, the calculated and calorimetric data can be reconciled only by adding to the $2M_1$ muscovite a configurational entropy contributed by disorder of the tetrahedral Al and Si based on crystal chemical data. The corrected $G_f^\circ(298,1)$ for $2M_1$ muscovite varies between -5597.5 ± 4.6 kJ and -5600.3 ± 5.9 kJ, depending on the reaction, based on phase equilibrium calorimetry, and -5600.23 ± 5 kJ, based on Robie *et al.* (1976) and Hemingway and Robie (1977). The corresponding entropy value is 302.8 J/mol-K.

Phase-equilibrium calorimetry complements conventional calorimetry, and more laboratories are equipped to carry it out. Phase-equilibrium calorimetry can be applied to especial advantage on material resistant to dissolution or material having elements in variable valence states. It can be used to calculate entropy of minerals when large samples are not available, when solid-solution effects are significant, or for phases having zero-point entropy contributions not accessible to detection by low-temperature heat-capacity measurements.

The standard error for the Gibbs free energy value of many rock-forming silicates is on the order of 400–800 J/mol oxygen. This value is too large to permit use of the data to calculate meaningful phase diagrams, or to retrieve detailed information such as mixing properties of solid solutions or intrinsic kinetic effects expressed in the widths of the reversed brackets. The standard error might be significantly reduced by multiple determination of the same equilibria by different laboratories on the basis of a standard set of documented samples, using specified procedures, so that the results can be subjected to statistical analysis. Such a program of coordinated effort on pivotal equilibria should be initiated. The effort would be analogous to the establishment of a national land-survey grid; ours would result in a petrogenetic grid that could have immediate petrologic as well as calorimetric applications.

Introduction

In recent years much work has been done by mineralogists, petrologists, and geochemists to extract

thermochemical data for individual minerals from reversed phase-equilibrium studies. These efforts have considerably added to our fund of data, supplementing, verifying, or correcting the information obtained by direct calorimetry and by electrochemical measurements. These data, however, are of variable quality; the quality depends on the quality of the

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phase-equilibrium studies themselves as well as on the method used for extraction of the data (see discussion in Anderson, 1970; Zen, 1972; Gordon, 1973). The problem of estimation of errors of the calculated results and comparison of these errors with those from conventional calorimetry is conceptually difficult and has not been completely studied. My purpose will not be to review the literature, as the reader can do that by consulting references; rather, it is to review some of the problems, promises, and successes, and to suggest some possibly fruitful lines for future studies. My discussions will be concerned mainly with those experimental methods usually referred to as "high-temperature, high-pressure devolatilization reactions"; however, some of the comments probably are applicable also to alternative methods such as aqueous solubility and EMF measurements of minerals and mineral assemblages.

Symbols

$G_f^{\circ}(T, P)$	Standard Gibbs free energy of formation of a phase from the elements at temperature T , in kelvins, and pressure P , in bars. The chosen standard state for solids is 298.15K and 1 bar.
$S_f^{\circ}(T, P)$	Standard entropy of formation of a phase from the elements at T and P .
$S^{\circ}(T, P)$	Standard entropy of a phase at T and P .
S^m	Configurational entropy of mixing for specified atoms and sites.
$\Delta V_s(T, P)$	Volume change of solids for a given reaction, as function of T and P .
$\Delta V_s^{\circ}(298, 1)$	Volume change of solids for a given reaction at 298K, 1 bar.
$\Delta S(T, P)$	Entropy change of solids for a given reaction, as a function of T and P .
$\Delta S_s^{\circ}(298, 1)$	Entropy change of solids for a given reaction at 298K, 1 bar.
ΔS_{total}	Total entropy change for a given reaction.
Te, Pe	Equilibrium values of temperature and pressure
$G_{\text{H}_2\text{O}}^{\#}$	Gibbs free energy of H_2O defined by
	$G_{\text{H}_2\text{O}}^{\#}(Te, Pe) \equiv G_{f, \text{H}_2\text{O}}^{\circ}(Te, 1) +$
	$G_{\text{H}_2\text{O}}(Te, Pe) - G_{\text{H}_2\text{O}}(Te, 1)$
f_i	Fugacity of component i .
$\Delta Cp, s$	Change of heat capacity of solids for a given reaction.
$\Delta\beta, s$	Change of compressibility of solids for a given reaction.

J, kJ	joule; kilojoule
N_i	Mole fraction of component i .
cal, kcal	calories; kilocalories
R	Gas constant
K	kelvins

Conversion factor: 1 calorie = 4.1840 joules

Computational procedures

Many procedures used to calculate thermochemical data of individual minerals from "high P - T " type of phase-equilibrium studies are in the literature, and workers have obtained results whose standard errors are commensurate with those obtained by modern calorimetry. Such methods involve the use of reversed experimental data, so that over the P, T range of the experimental brackets, the Gibbs free energy of the reaction is known to have passed through zero. If the thermochemical data are known for all but a specific mineral or group of minerals, these unknown quantities can be expressed as some algebraic function of the known quantities, and if a sufficient number of relations exist involving the same unknowns (which may themselves bear functional relations to the thermodynamic quantities sought), then the set of simultaneous equations may be solved. This process is well known and, in fact, is not very different from methods of conventional calorimetry. Thus, I propose to refer to computational processes that lead to thermodynamic data from phase equilibrium studies as "phase-equilibrium calorimetry."

The various methods of calculation ultimately depend on the same types of approximations. Table 1 lists the various degrees of approximation that have been used; these approximations need little comment. Given these approximation procedures, there are two general approaches to the methods of calculation. First are the methods that depend on a knowledge of the location and slope of a fitted curve, preferably a straight line; data are calculated on the basis of the line. To this category belong the methods that involve use of $\log f$ vs. $1/T$ plots (for example, Greenwood, 1963; Orville and Greenwood, 1965) and the method of G' vs. T plots advocated by Weisbrod (1968) or as modified by Chatterjee (1970). The second category of methods does not depend on the use of curves but uses the brackets directly. Robie's study (1965) is a pioneer in this approach; other examples that emphasize methodology are Fisher and Zen (1971), Helgeson (1969), Ulbrich and Merino (1974), and Zen (1973). The calculations by Fonarev (1967), Mel'nik and Onopriyenko (1969), and Fed'kin (1970), to cite a few of many examples in the Soviet geochemical

TABLE I. Approximations in thermochemical calculations.

Function sought	Approximation	Situation	Examples
$G_f^\circ(298, 1)$ or $\Delta[G_{f,A}^\circ(298, 1) - G_{f,B}^\circ(298, 1)]$	I. None (i.e. $\Delta V_s = f(p, T)$ and $\Delta S_s = f(p, T)$)	Ideal world, not yet attainable.	Wish I had one.
	II. $\Delta V_s(298, p)$ and $\Delta S_s(T, 1)$	Pressure and temperature effects decoupled; no cross term.	This study, for reaction "COR".
	III. ΔV_s constant at 298, 1; $\Delta S_s(T, 1)$	Compressibility difference $\Delta\beta_s = 0$	Zen (1972), "Summation method" for entropy; Ulbrich and Merino (1974); Helgeson (1969).
	IV. ΔV_s constant at 298, 1; ΔS_s constant at 298, 1.	$\Delta\beta_s = 0$; $\Delta C_p = 0$	Chatterjee (1970); Zen (1972), "constant entropy" method.
	V. ΔV_s constant at 298, 1; ΔS_{total} constant	$\Delta\beta_s = 0$; $\Delta C_p(\text{total}) = 0$	Orville and Greenwood (1965); Weisbrod (1968).
	VI. $\Delta V_s = 0$; ΔS_{total} constant at 298, 1.		Greenwood (1963).
$G_f^\circ(298, 1)$ and $S_f^\circ(298, 1)$	Data generally do not permit or justify any but the crude approximation IV above, as any polynomial fit of high pressure and temperature data for ΔS_s (and ΔC_p) will lead to highly unstable functions that cannot be extrapolated. Examples of use of approximations are in Weisbrod, 1968; Chatterjee, 1970; Zen, 1972.		

literature, must be put in the same category. Surveys of the then-existing methods and their problems, particularly the problem of internal consistency of the results, were presented by Weisbrod (1968), Anderson (1970), Zen (1971, 1972), Bird and Anderson (1973), and most recently by Kerrick and Slaughter (1976).

One advantage of using fitted curves is that both the slope and intercept generally contain useful information. Moreover, the process of curve-fitting guarantees that the data derived are smoothed values. A major problem of the method is how to fit a curve. The least-squares method is commonly used (e.g., Orville and Greenwood, 1965; Chatterjee and Johannes, 1974). As pointed out by Chayes (1968), the method is irrelevant and inapplicable, because we want to find the curve that best discriminates two subsets of data (the upper and lower brackets). These brackets are not estimates of the equilibrium position of the curve and do not necessarily show any central tendency about the equilibrium position. Even within each subset of data, the scatter of points represents more than just random errors. This nonrandomness must stem from many sources, though a study of the problem has not been made. Possible causes include different reaction rates at different temperatures (for instance, the limiting brackets are commonly farther apart at lower temperatures, reflecting greater overstep necessary to achieve observable reaction in given time), the sensitivity of criteria used to detect small

amounts of reaction, and the partly arbitrary nature of time allotted to each experimental run. These problems make highly suspect any curve-fitting procedure that depends on the assumption of random distribution of points, such as separate least-squares fitting of lower and upper brackets, or even the use of discriminant functions (Chayes, 1968).

Use of curve-fitting methods, including discriminant functions, on P - T projections of experimental data should be avoided, because such curves do not insure thermochemical consistency along the points on the curve. It is better to fit curves on log fugacity *vs.* $1/T$ plots (e.g., Orville and Greenwood, 1965) or G'' *vs.* T plots (Weisbrod, 1968; Chatterjee, 1970), because, consistent with the degree of approximation used, the curve automatically insures thermochemical consistency. The results can then be calculated back to P - T projections; presumably, consistent data can be extracted from this constructed curve. If the ΔC_p term is nonzero, the slope of the fitted curve varies as given functions of T , and computer-fitting is probably necessary.

Use of point data does not, per se, say anything about internal consistency. If we calculate only the Gibbs free energy of formation of a phase, using existing values for the entropy, consistency is not an issue unless the actual values derived from different brackets do not overlap. In that case, it is probably justified to presume that one or more brackets simply are wrong, or else that one of the entropy functions is

incorrect. If, however, we must obtain the entropy as well as Gibbs free energy for a phase from the experimental data (Table 1, second part), then the derived entropy for different combinations of brackets must be not only reasonable but must be mutually consistent. This puts a more severe limit on the derived Gibbs free energy, as well as providing the means to derive a consistent set of P - T coordinates for the reaction (see discussion in Zen, 1972; Bird and Anderson, 1973).

Nonetheless, even if we succeed in achieving internal consistency, we are still faced with the nagging question: is the result right? This question points to a basic problem intrinsic to experimental phase-equilibrium studies, namely, there is no way to tell where within a given pair of reliable brackets the true equilibrium lies: a pair of brackets defines a step function rather than a probability curve. Inasmuch as the limits of the brackets commonly include contributions from systematic errors, including both the worker's idiosyncracies and more objective factors previously discussed, the limits of the step function is "soft," subject to shifts with additional experimental work, and cannot be readily related to thermodynamic or even kinetic factors. Any really meaningful data that might be buried there, such as the overstep necessary to initiate a given reaction, generally cannot be extracted. The median point of a pair of brackets can be used to represent the true equilibrium value (e.g., Zen 1972), but there is no justification other than perhaps a sense of symmetry; it is not an intrinsically "best estimate" (Bird and Anderson, 1973).

To get around this conceptual difficulty, and at least to be more honest, thermochemical data should be calculated not for the presumed equilibrium P , T values but for the actually reported upper and lower brackets. An example of this procedure is the study by Bird and Anderson (1973; see also Gordon, 1973).² We can then calculate for each bracket a thermochemical value, say the Gibbs free energy of formation, and state with assurance that the true value of the Gibbs free energy of formation must be greater (or less) than this given value. The pair of brackets corresponding to the reversal of a reaction then pins the true value to within the limits of the inequalities. If the bracket limits are close together, then the pair of inequalities may define a sharp and thus more precise value; otherwise, the values may be

widespread, expressing our poor experimental control. H. C. Helgeson (1975, oral communication) suggested that data derived from tight brackets can be used to refine the equilibrium curve for the part having only poor control. This is certainly an attractive option, although it does imply heavy weighting of the tight brackets, and we must be conscious of the possibility that tightness is not rightness. This problem of proper weighting of data has been discussed (Zen, 1972; Bird and Anderson, 1973; Zen and Haas, unpublished data) but not yet resolved.

If we treat upper and lower brackets as separate entities, then we can associate with each bracket a set of experimental standard errors in temperature and pressure measurements, in gas fugacity measurements, etc., because the observations at each bracket represent physical events and thus real experimental data (see Bird and Anderson, 1973, for a good discussion). We can then combine these experimental standard errors with those of input data, that is, those errors associated with other thermochemical data used in the calculations, and come out with a 2σ standard error that is more meaningful than would otherwise be possible. For example, we might report the standard Gibbs free energy of formation of a phase as

$$-4508.4 \pm 5.6 \text{ kJ} \leq G^\circ(298, 1) \leq -4503.5 \pm 6.5 \text{ kJ}.$$

Such reporting may make comparison of data sets from different sources more realistic, especially as uncertainties contributed by the input data and fluctuations in physical measurements are now clearly distinguished from those contributed by sluggish reaction or inadequate criteria for reaction (uncertainties associated with the limiting values *vs.* gap between limiting values, respectively, corresponding to lengths of boxes *vs.* gap between pairs of boxes of Fig. 1).³

An example: thermochemical data for $2M_1$ muscovite again

As an example of the procedure I have just advocated, and to bring out some other features that illustrate the power and foibles of phase-equilibrium calorimetry, I present some new computations on the

² Note that the P , T values of the brackets used by Bird and Anderson are not equilibrium values for the reaction, as might be misconstrued from their table headings.

³ In this connection, see Anderson (1976). Note that this interesting application of the Monte Carlo method still requires an independent selection of the "best estimate" of the equilibrium P , T value; what the method does is to furnish a rational way to estimate the error from the assumed functional nature of uncertainties in the sources.

Gibbs free energy of formation of $2M_1$ muscovite. This mineral is chosen not only because of its petrologic importance and because of the presence of polytypes, which are of thermochemical consequence, but also because some excellent and well-documented experimental phase-equilibrium data now exist, which allow good calculations to be made and which

allow discovery and discussion of several complicating factors.

For primary data, I used the data of Day (1973) for the reaction

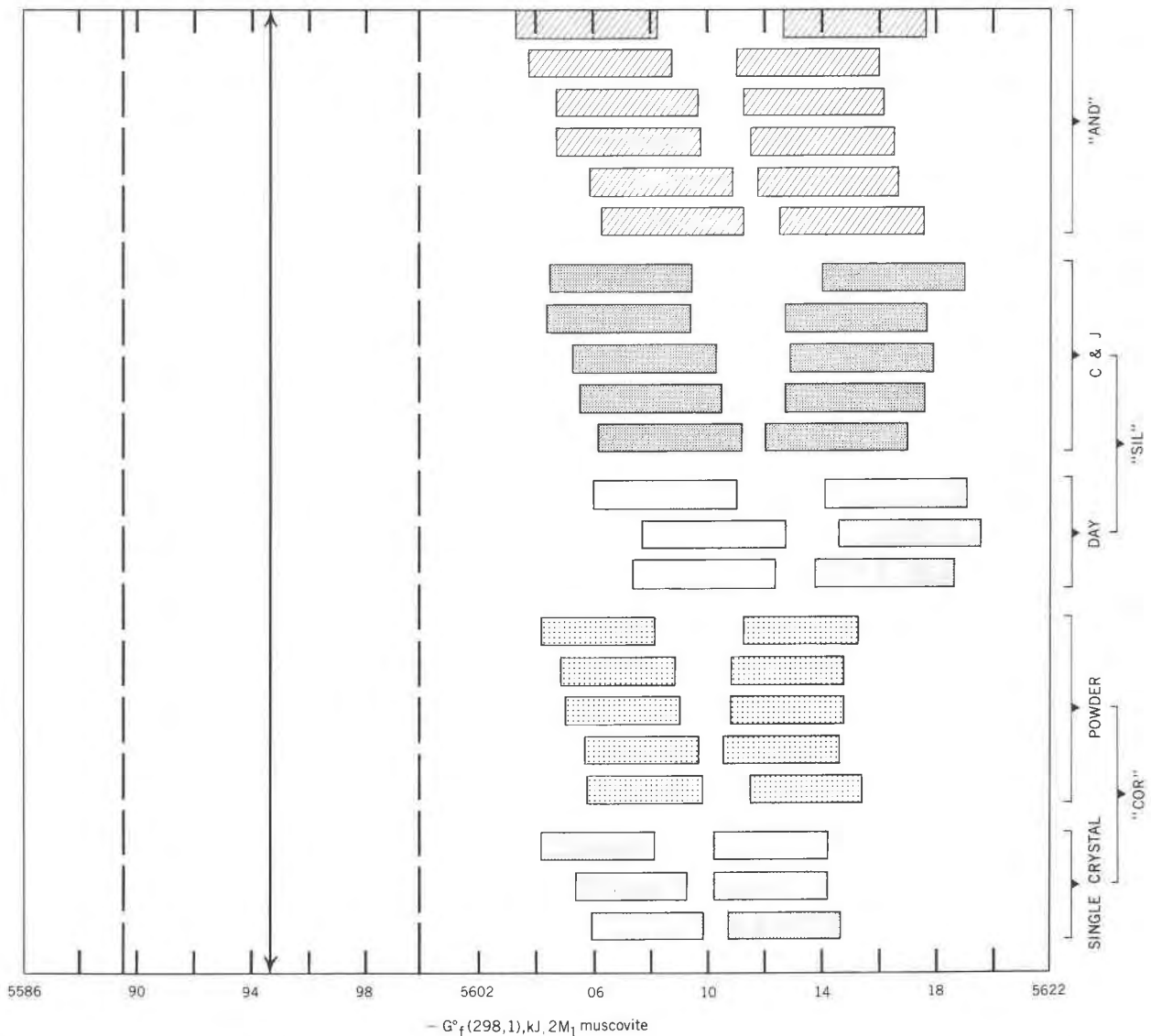
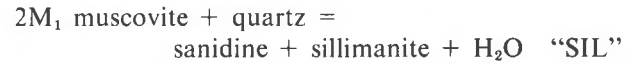
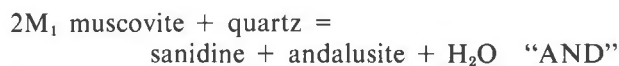


FIG. 1. Comparison of Gibbs free energy of formation of $2M_1$ muscovite at 298 K and 1 bar from calorimetric values and from phase-equilibrium studies. Vertical line on left hand side with arrows, calorimetric data based on Hemingway and Robie (1977) and Robie *et al.* (1976); 2σ uncertainties given by long dashed lines. Values calculated from phase-equilibrium data are shown on right hand side, assuming configurational entropy of mixing $S^M = 0$. Inner edges of each pair of blocks give values from lower limit of reversed bracket (left-hand edge) and from upper limit of bracket (right-hand edge); outer ranges of blocks give 2σ uncertainties from input data alone associated with the pair of values. Data are grouped according to the phase equilibria; their identity and source of data are indicated by braces on right-hand side of figure. Within each group of data, the progressively lower-pressure and lower-temperature brackets are toward the top of the stack.

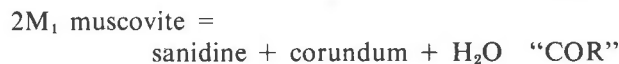
TABLE 2. Experimental data on muscovite stability and calculated standard Gibbs free energy of formation, $G_f^\circ(298,1)$ of $2M_1$ muscovite, $H_2KA_1Si_3O_{12}$ in kilojoules/mol.

I. $2M_1$ muscovite + quartz = andalusite + high sanidine + H_2O						
P, Kbar	Temperature, °C		$S^M = 0$	$S^M = 18.71$ J/mol-K		Notes
	Lower bracket	Upper bracket	Sum. Meth.	C.E. Meth.	Sum. Meth.	
0.5	520		-5608.213	-5599.389	-5598.953	Source: Chatterjee and Johannes, 1974.
		560	-5612.631	-5603.309	-5602.627	
1.0	550		-5608.803	-5599.602	-5598.983	Muscovite is $2M_1$ polytype.
2.0	590	570	-5611.003	-5601.334	-5600.811	S^M = entropy of mixing of tetrahedral Al and Si per mole muscovite.
		605	-5609.748	-5599.836	-5599.179	
3.0	620		-5609.740	-5599.694	-5598.610	Sum. Meth. = summation method to calculate $f\Delta s dT$; C.E. Meth. = constant entropy method to calculate $f\Delta s dT$.
		640	-5611.489	-5601.234	-5599.987	
4.0	660		-5610.903	-5600.451	-5599.029	
5.0	690	670	-5611.769	-5601.401	-5599.895	
		705	-5611.317	-5600.564	-5598.878	
			-5612.572	-5601.669	-5599.853	
Mean value ($S^M = 18.71$ J/mol-K), Sum. meth.: Lower bracket, -5598.939 ± 5.008 kJ/mol; upper bracket, -5600.591 ± 5.422 kJ/mol; all brackets, -5599.765 ± 5.482 kJ/mol.						
II. $2M_1$ muscovite + quartz = sillimanite + high sanidine + H_2O						
0.5	540		-5609.510	-5600.665	-5599.878	Source: Chatterjee and Johannes, 1974.
2.0	595	580	-5614.020	-5604.744	-5603.640	
		630	-5609.409	-5599.974	-5598.748	Muscovite is $2M_1$ polytype.
3.0	630		-5612.690	-5602.886	-5601.376	
		660	-5610.271	-5600.468	-5598.958	
5.0	680		-5612.915	-5602.866	-5601.041	
		705	-5610.526	-5600.309	-5598.276	
6.0	710		-5612.644	-5602.217	-5599.924	
		720	-5611.196	-5600.732	-5598.384	
1.0	580		-5612.041	-5601.493	-5599.041	
		610	-5611.049	-5601.774	-5600.669	Source: Day, 1973.
2.0	630		-5614.120	-5604.527	-5603.179	Muscovite is mixture of $2M$ and $1M$ polytypes.
		650	-5612.748	-5602.949	-5601.435	
3.0	656		-5614.589	-5604.623	-5602.899	
		668	-5612.376	-5602.359	-5600.573	
			-5613.727	-5603.610	-5601.702	
Mean value ($S^M = 18.71$ J/mol-K), Sum. meth.: Lower bracket, -5598.849 ± 5.158 kJ/mol (C + J); -5600.892 ± 5.109 kJ/mol (Day); -5599.615 ± 5.532 kJ/mol (all points). Upper bracket, -5601.004 ± 6.091 kJ/mol (C + J); -5602.593 ± 5.260 kJ/mol (Day); -5601.600 ± 5.940 kJ/mol (all points). All brackets: -5599.927 ± 6.017 kJ/mol (C + J); -5601.743 ± 5.479 kJ/mol (Day); -5600.608 ± 5.000 kJ/mol (all points).						
III. $2M_1$ muscovite = corundum + high sanidine + H_2O						
1.0	600		-5608.179	-5597.895	-5597.426	Source: Chatterjee and Johannes, 1974.
		630	-5611.271	-5600.548	-5599.958	
2.0	640		-5608.907	-5598.046	-5597.405	Muscovite is $2M_1$ polytype.
		660	-5610.782	-5599.652	-5598.906	
4.0	690		-5609.058	-5597.518	-5596.619	
6.0	740	710	-5610.832	-5599.020	-5598.020	
		750	-5609.765	-5597.373	-5596.393	
8.0	780		-5610.593	-5598.284	-5597.033	
		800	-5609.807	-5597.146	-5595.686	
			-5611.434	-5598.539	-5596.941	
1.0	600		-5608.179	-5597.895	-5597.426	Source: Chatterjee and Johannes, 1974.
		620	-5610.233	-5599.654	-5599.106	
3.0	670		-5609.322	-5598.053	-5597.258	Muscovite is $2M_1$ polytype.
		680	-5610.238	-5598.833	-5597.988	
5.0	720		-5609.825	-5597.880	-5596.825	Single-crystal, weight-change method.
		730	-5610.687	-5598.615	-5597.502	
Mean value ($S^M = 18.71$ J/mol-K), Sum. method: Lower bracket, -5596.880 ± 4.188 kJ/mol; upper bracket, -5598.182 ± 4.529 kJ/mol; all brackets, -5597.531 ± 4.546 kJ/mol.						

and the data of Chatterjee and Johannes (1974) for the same reaction as well as for these two other reactions:



and



The experimental data are given in Table 2. Table 3 gives the thermochemical values of related phases used in the calculations; for the Gibbs free energy of H₂O the tabulation of Fisher and Zen (1971) was used. Some of the thermochemical values of Table 3 differ from those in Robie and Waldbaum (1968), and represent a new set of data compiled by Hemingway and Robie (1977) and by Robie *et al.* (1976); in these revised values, the earlier erroneous ΔH_f° for the aluminum silicates (Zen, 1972; Thompson, 1974) has been resolved, and the values are compatible with that of corundum. The values are also compatible with the latest correction for the heat of solution of quartz (Hemingway and Robie, 1977).

The method of calculation used is as described previously (Fisher and Zen, 1971), based on the equation

$$\Delta G(Te, Pe) = 0 = \Delta G_{f,s}^\circ(298, 1) - \int_{298}^{Te} \Delta S_{f,s} dT + \int_1^{Pe} \Delta V_s dP + G_{H_2O}^*(Te, Pe),$$

and using the "summation method" which takes into account the fact that ΔS_s is temperature dependent (Table 1). Because Robie *et al.*'s (1976) C_p values for muscovite only extend to about room temperature, I used, for higher temperatures, the C_p data of Pankratze (1964), assuming that the two sets of heat-capacity data are compatible. Because the use of high-temperature heat-capacity data to calculate the Gibbs free energy is itself a second-order correction term, having a magnitude of only a few hundred calories (at most less than 3 kJ; see later section), however, a correction of even 10 percent on this value would hardly affect the results and needs no further attention.

Results of the calculations for all the data points are in Table 2 and are shown in Figure 1, together with the 2σ standard error calculated for each point. Each level of each stack, identified by marginal braces in Fig. 1, represents a given isobaric reversed bracket. Figure 1 also gives the $G_f^\circ(298, 1)$ value of $2M_1$ muscovite and the 2σ standard error derived from direct calorimetry, according to the corrected ΔH_f° value for the aluminum silicates and newly-determined heat capacity and ΔH_f° of muscovite (Hemingway and Robie, 1977; Robie *et al.* 1976). In this figure, I have deliberately used only the entropy corresponding to the directly measured value (*i.e.*, $S_T - S_0$), which corresponds to an apparent entropy of muscovite of 287.80 J/mol-K (68.78 cal/mol-K), or -1278.86 J/mol-K (-305.64 cal/mol-K) for the standard entropy of formation of $2M_1$ muscovite from the elements. The tremendous discrepancy be-

TABLE 3. Thermodynamic constants used in calculations.

Mineral	Formula	Volume	Standard entropy (298, 1) joule/K	Standard entropy of formation from the elements, (298, 1), joule/K	Standard Gibbs free energy of formation from the elements (298, 1) kJ
Muscovite	H ₂ KAl ₃ Si ₃ O ₁₂	140.808 ± .029 ^a	285.10 ± 1.59 ^{b,e}	-1281.701	---
High sanidine	KAlSi ₃ O ₈	108.91 ± .057 ^a 108.61 ± .13 ^f	233.05 ± 0.42 ^b	-736.526	-3739.994 ± 3.35 ^b
Corundum	Al ₂ O ₃	25.575 ± .007 ^d	50.96 ± 0.13 ^c	-313.189	-1581.895 ± 1.300 ^c
Andalusite	Al ₂ SiO ₅	51.472 ± .038 ^a	93.22 ± 0.42 ^c	-494.758	-2444.017 ± 3.00 ^c
Sillimanite	Al ₂ SiO ₅	49.836 ± .063 ^a	96.11 ± 0.42 ^c	-491.871	-2441.782 ± 3.00 ^c
Quartz	SiO ₂	22.688 ± .001 ^d	41.34 ± 0.08	-182.489	-856.239 ± 1.72 ^c
Steam	H ₂ O ^g	---	---	---	---

a) Chatterjee and Johannes, 1974; b) Robie, Hemingway and Wilson, 1976; Hemingway and Robie, 1977; c) Robie and Waldbaum, 1968; d) Robie *et al.*, 1967; e) See text for discussion; value does not include configurational entropy of mixing of tetrahedral Al and Si; f) Day, 1973; g) Burnham *et al.*, 1969; Fisher and Zen, 1971.

tween the two sets of values of comparable precision for G_f^0 is apparent; there is no overlap of the refined calorimetric data and the best experimental phase-equilibrium data, calculated on a basis consistent with the calorimetric values.

It does not take long to find the source of this discrepancy. The $S_{298}-S_0$ value of muscovite from heat-capacity measurements does not include possible frozen-in residual entropy. Burnham and Radoslovich (1964) and Güven (1971) determined that samples of $2M_1$ muscovite polytype they studied show no evidence of tetrahedral Al/Si order. As it is very unlikely that Al/Si ordering could take place in the low-temperature calorimeter, a configurational entropy term must be added to the low-temperature calorimetric data (see also Ulbrich and Waldbaum, 1976). If we assume complete and ideal mixing of the tetrahedral Al and Si, then the configurational entropy of mixing, $S^M = (-4R \sum N_i \ln N_i) = 18.70$ J/mol-K must be added, leading to a 298K, 1 bar Third Law entropy of 306.50 J/mol-K (73.25 cal/mol-K), or standard entropy of formation from the elements, $S_f^0(298, 1)$ of -1260.16 J/mol-K (-301.19 cal/mol-K). This correction makes the calorimetric value of G_f^0 more negative (muscovite more stable because of the mixing effect), but makes the phase-equilibrium values more positive because these values are extrapolated from higher temperatures to the standard conditions.

The results of these recalculations are given in Figure 2, where the mode of presentation of the data is same as that for Figure 1. The improvement in agreement is striking; none of the calculated results based on limiting brackets (inner edges of pairs of blocks) lies outside the permissible 2σ range of the calorimetric data. The similarity of the precision of conventional calorimetric and the phase-equilibrium calorimetric calculations, at least for this set of reactions, is also forcefully displayed.

The relations shown in Figure 1 and Figure 2 argue persuasively that the zero-point configurational entropy of tetrahedral Al/Si disorder is an important factor and that this term amounts to approximately that predicted by a model of complete and ideal mixing of these two entities.⁴

⁴ The calculations assumed that the "high sanidine" samples are fully disordered in their Al-Si distribution. The degree of disorder may be described by the Z value (Hovis, 1974) of the sanidine; $Z = 0$ for fully disordered sanidine and $= 1$ for fully ordered potassium feldspar. The sanidine samples in Chatterjee and Johannes (1974) study have Z values between 0.1 and 0.2, and the sanidine of Day's study is calculated to have a Z value of 0.16. The difference in Gibbs free energy amounts to only about 120 joules even at 1000K.

Figure 2 shows that there are systematic differences between groups of data points. Thus, the three pairs of brackets from Day's (1973) work give values more negative (muscovite more stable) than the five pairs of brackets from Chatterjee and Johannes' (1974) work, for the same "SIL" reaction. The eight pairs of brackets for the "COR" reaction all give results that are internally in agreement but that are more positive than those for the other two reactions. The values derived from Chatterjee and Johannes' data for the "AND" and "SIL" reactions are in remarkable mutual agreement. The mutual relations of these groups of data suggest that the thermochemical data for corundum are not quite consistent with those for andalusite and sillimanite, but that those for the latter two minerals are entirely compatible. Detailed examinations of these fine structures are being made (Zen and Haas, unpublished data).

The PHAS20 correlation program (Haas and Fisher, 1976) can be used to calculate the "best fit" value for the entropy of mixing of tetrahedral Al and Si in the $2M_1$ muscovite. If all the data points are used, a value of 17.30 joule/mol-K is obtained for this quantity, which is significantly different from the ideal-mixing value of 18.70 joule/mol-K. However, when only the "AND" and "SIL" reactions are used, a value of 18.5 joule/mol-K is obtained, which is indistinguishable from the ideal-mixing value, whereas when only the "COR" reaction is used, a value of 15.1 joule/mol-K is obtained. Tentatively, it seems better to accept the value derived from "SIL" and "AND" because of its coincidence with the ideal-mixing value, and to attribute the lower value for the "COR" reaction to inconsistent thermochemical data for this phase, as discussed. The difference between the two sets of data amounts to a Gibbs free energy correction of only about 2.7 kJ (even when the values derived from Day's data are included in the "SIL" group) or 650 cal, considerably less than the 2σ uncertainty on muscovite, and is probably not detectable by conventional calorimetric methods. *Note added in proof.* Another source for the discrepancy of the calculated muscovite free energy values from different equilibria may be the slight differences in the compositions of the product sanidine (Chatterjee and Johannes, 1974). One might therefore also question the identity of the compositions of the product muscovite for the different reactions. I am grateful to my colleague Steve Ludington for pointing out to me this possibility. The reader's attention is also called to the following relevant paper: Chatterjee, N.D., 1977, Thermodynamics of dehydration equi-

libria: Proc. NATO Advanced Study Institute, Oxford, England, 1976.

If we accept the 18.70 joule/mol-K value for the entropy of mixing, then from the "AND" and "SIL" reactions, the Gibbs free energy of formation of $2M_1$

muscovite is -5599.33 kJ/mol when the lower brackets alone are used, and the 2σ uncertainty is 5.35 kJ/mol, which is the root-mean-square sum of the standard deviations of individual lower-bracket values and the uncertainties in the input thermochemical

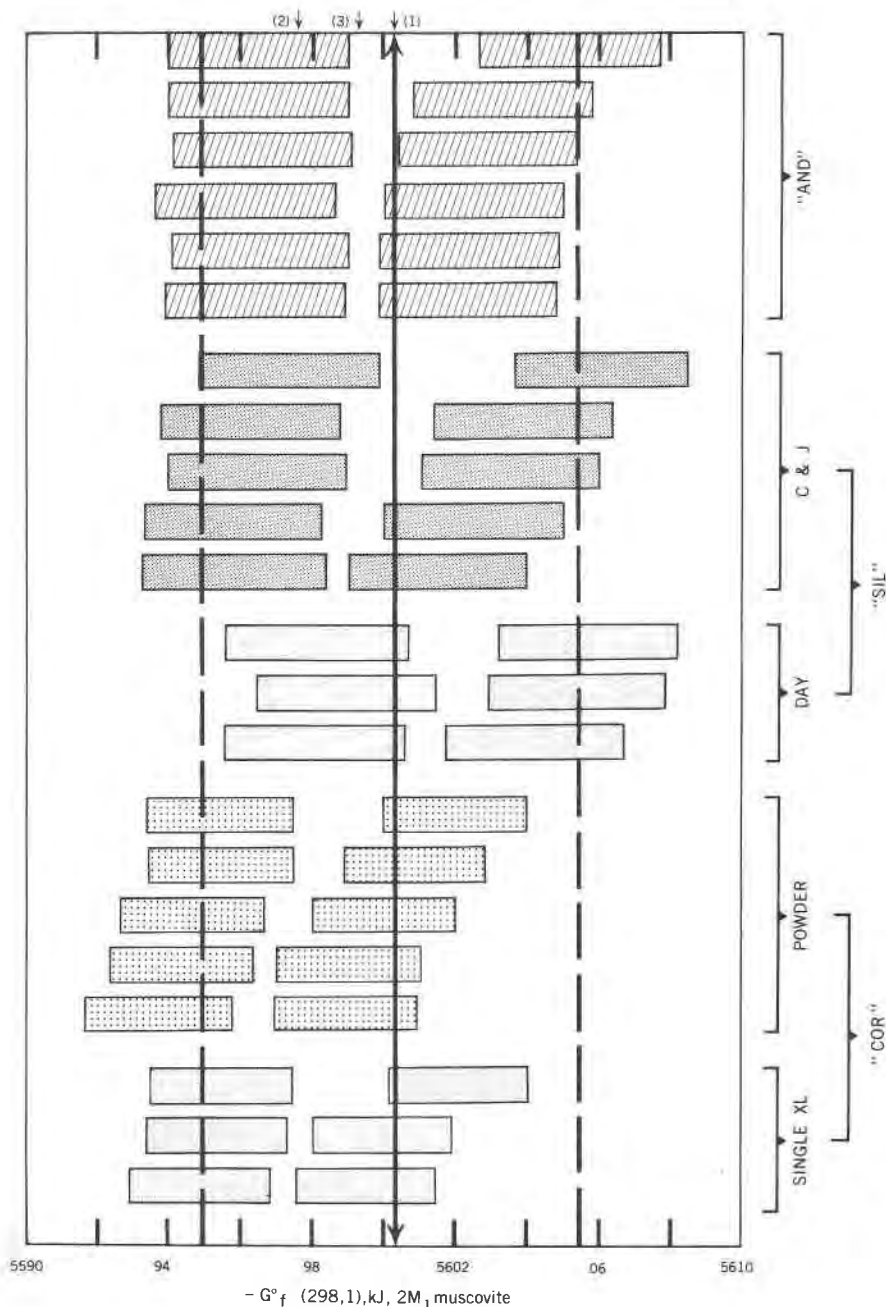


FIG. 2. Comparison of Gibbs free energy of formation of $2M_1$ muscovite at 298 K and 1 bar from calorimetric values and from phase-equilibrium studies, assuming that the configurational entropy of mixing $S^M = 18.70$ joule/mol-K (ideal and complete mixing of tetrahedral Al and Si). Small arrow at upper edge labeled (1) gives unweighted mean of the values calculated from "SIL" and "AND," all brackets; (2) gives the corresponding mean from "COR," and (3) gives the mean of all brackets for all three reactions. For other explanations, see caption for Fig. 1.

data. When the upper brackets alone are used, the corresponding values are -5601.17 ± 5.78 kJ. When both sets of values are used together, the mean value is -5600.25 ± 5.85 kJ/mol (-1338.491 ± 1.40 kcal). This value is indistinguishable from the "corrected" value (including an entropy of mixing of 18.70 joule/mol-K) based on Hemingway and Robie (1977) and Robie *et al.* (1976), of -5600.23 kJ/mol or -1338.488 kcal/mol. For the record, similar cal-

culations using the "COR" reaction alone give -5596.88 ± 4.19 kJ/mol for the lower brackets, -5598.18 ± 4.53 kJ for the upper brackets, and -5597.53 ± 4.55 kJ/mol for all the brackets.

Figure 2 shows a pronounced temperature dependence of values derived from upper brackets. This dependence cannot be due to systematic errors in high-temperature heat-capacity data because it emerged after the configurational entropy correction. The stubbornly wider range of values at lower T and P undoubtedly partly reflects differences in reaction rate. In general, however, even for the same difference in temperature between a higher and a lower limit, the higher temperature brackets lead to a smaller range in the Gibbs free energy because at higher temperatures both the rate of change of Gibbs free energy value of H_2O with temperature and the quantity ΔS_s become smaller. The difference between values from Day's (1973) work and those from Chatterjee and Johannes' (1974) work cannot be readily explained. Day's muscovite was initially of the 1M polytype, which partially inverted to 2M during the experiment (Day, 1973). Inasmuch as under the experimental conditions the 2M₁ polytype is the stable one, its Gibbs free energy must be more negative, so possible 1M interference in Day's work should not lead to more-negative calculated values. Here, I suspect, different experimental starting material, temperature calibration, equipment, and criteria for reactions may have led to the disparate results; the difference between the mean values of the two laboratories corresponds to a systematic difference of temperature reading of about 8° at the site of the experimental charge, well within the authors' stated uncertainties.

A side issue is to test the "constant entropy method" of approximation (Zen, 1972). The high-quality muscovite experiments spur a systematic test. For the data corresponding to Figure 2 ($S^M = 18.70$ J/mol-K), the Gibbs free energy of muscovite calculated by both the constant entropy method and the summation method are shown in Table 2 and Figure 3. For this particular set of phases and reactions, the maximum error introduced by using the constant-entropy method is about 2.5 kJ (600 cal). Ulbrich and Merino (1974) discussed the problem from a somewhat different point of view; they used the method of assigning to each phase a heat-capacity function expressed as polynomials in temperature, and calculating for each phase the maximum error that would be introduced relative to the known values (see Helgeson, 1969). These errors amount to a few hundred

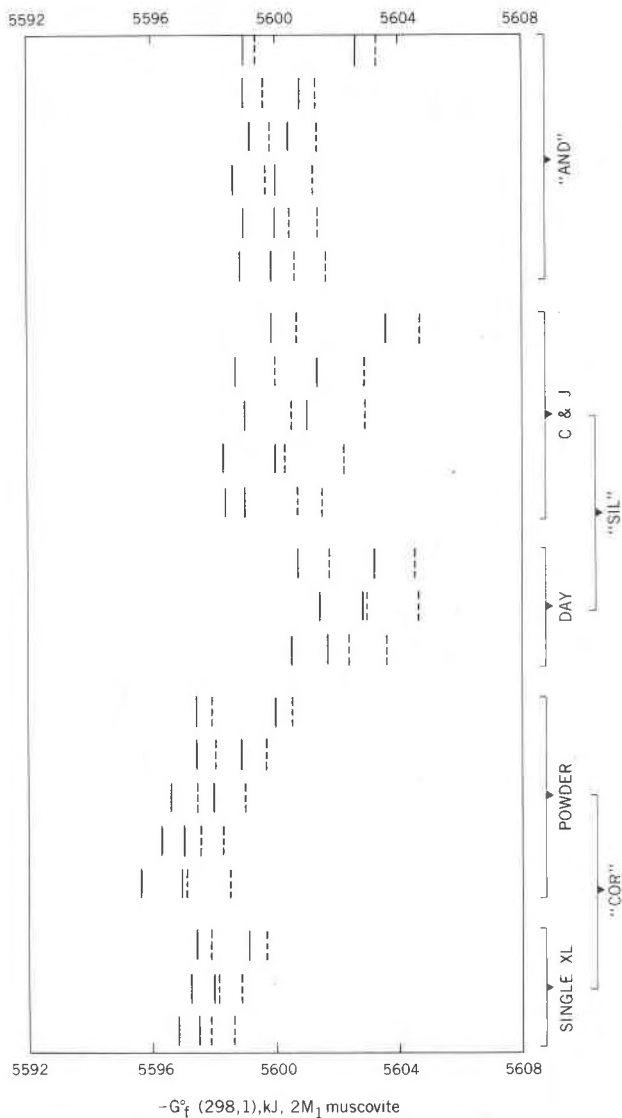


FIG. 3. Comparison of errors introduced by approximation methods. The solid vertical lines are the calculated Gibbs free energy of formation of 2M₁ muscovite shown as inner ranges of pairs of blocks in Fig. 2. The dotted lines are the results of calculations using the "constant-entropy method" of approximation. The maximum difference between the two methods is about 2.4 kilojoules (about 600 calories).

calories for muscovite and about 1 kcal for microcline at 500°C, and about twice that amount at 700°C. The errors for the reactions are smaller because they tend to cancel out; however, it seems likely that the method would not, for this instance, be an improvement over the constant-entropy approximation.

A final point is to test the assumption that the ΔV_s term may be taken as constant. Using the compressibility data compiled by Birch (1966) for muscovite, corundum, and "orthoclase," given as functions of pressure, I calculated for the "COR" reaction two higher order terms for ΔV_s for the 8-kbar bracket of Chatterjee and Johannes (1974). The first-order term (ΔV_s constant) required a correction of about +5 kJ or +1.2 kcal. The second-order term added about -220 joules or -55 calories, and the third-order term added only about +25 joules or +6 cal; both terms have large uncertainties due to the uncertain nature of the sample and the uneven quality of the compressibility data. The results, however, fully justify ignoring higher order terms for pressures up to about 10⁴ bars.

The phase-equilibrium calorimeter: a preliminary assessment

The example just discussed permits a few observations on the usefulness of the systematics of calculation that I call phase-equilibrium calorimetry. Needless to say, my overall verdict is favourable; but what are some strong and weak points of the method?

The phase-equilibrium calorimeter permits detection of hidden inconsistencies in the data and of hidden additional contributions to the thermochemical values of phases. A good example of the former ability is the detection of the two sets of reference values for aluminum (Zen, 1972; Thompson, 1974; Chatterjee, 1976). This important discrepancy, though suspected by geochemists, remained undefined for quite a few years; only by phase-equilibrium calculations was this major problem clearly discerned, defined, and quantitatively predicted. It has since been amply verified by careful additional calorimetry (Gross and Hayman, 1970; Hemingway and Robie, 1977), and our consciousness of possibilities for other such problems has been raised. The data on muscovite, derived from the corundum reaction, suggest another discrepancy, which at this time is beyond the resolving power of conventional calorimetry. The configurational contribution to the entropy of 2M₁ muscovite, though long suspected by many and recently suggested by Ulbrich and Waldbaum (1976), is

now verified by direct observation to correspond to ideal mixing. The calculations presented here show the utility of the phase-equilibrium calorimeter as a check and complement to the conventional approach to calorimetry.

The phase-equilibrium calorimeter, true, cannot be used unless there are sufficient ancillary data on the volumes, entropies, heat capacities, and Gibbs free energies of other phases participating in the reactions. To that extent its usefulness is restricted, and data thus derived are built on a foundation of uncertain firmness. But this is true for all the calorimetric methods. To be sure, problems of correlated errors and propagation of errors in sequential calculations can be devastating for the end results, but this is a problem shared by all approaches.

Perhaps more serious is the problem that the calculated uncertainties for each bracket can never be better than the uncertainties in the input data—the old adage about garbage. The hope would seem to lie in the possibility of obtaining tight brackets on several related reactions, then formulating the thermochemical values of several phases as a series of simultaneous equations—what Thompson (1974) called Difference Functions. Such a scheme of calculation should allow not only mutually compatible results but should permit the adoption of smaller standard errors for individual phases. Using this stratagem, Zen and Chernosky (1976) obtained an estimate of the Gibbs free energy of orthoenstatite which is probably an improvement over the data on clinoenstatite (Robie and Waldbaum, 1968) commonly used in calculations.

Phase-equilibrium calorimetry provides an additional way to get thermochemical data; there are many more practitioners of phase equilibrium studies than of calorimetry. Moreover, it may not be possible to get a sufficient amount of material for direct calorimetry, especially for low-temperature heat-capacity measurements; phase-equilibrium studies require only small quantities of material. With sophistication in planning experiments, one could hope to get materials of different composition and/or structural state and measure their thermochemical values, thus obtaining insights on properties of different structural states or polytypes, of solid solutions, and so forth. As an example, Bailey (1975) showed that there can be no tetrahedral Al/Si order-disorder process for certain polytypes of muscovite because of space-group restrictions. These polytypes should have Gibbs free energy values on the order of several kilojoules different from those that show order-disorder,

and the difference ought to show up in the stability boundaries of the equilibrium curves. Examples of the use of phase-equilibrium data to derive thermochemical parameters of solid solutions are the studies on the alkali feldspar systems (Thompson and Waldbaum, 1968, 1969a), on the alkali halides (Thompson and Waldbaum, 1969b), and on the muscovite-paragonite micas (Chatterjee and Froese, 1975).

Another circumstance where phase-equilibrium calorimetry could be used to advantage is to measure the free energy and heat of formation of resistant phases that do not dissolve readily in solution calorimeters. Schuiling *et al.* (1976) gave examples of application of the method to zircon, thorite, and phenacite; other applications of this approach to the thermochemistry of zircon have been given by Matwejew *et al.* (1969), Naumov *et al.* (1971) and Karpov *et al.* (1971), based on the phase-equilibrium work of Rosén and Muan (1965). The phase-equilibrium method is also potentially useful in obtaining thermochemical data on phases having elements in variable and possibly even mixed valence states (*e.g.*, ferric and ferrous iron in riebeckite); however, this subject has not been much explored.

Unfortunately, one thing we cannot yet do, despite various valiant efforts, is to reverse the procedure and use thermochemical data to calculate the locations and slopes of univariant curves that are not experimentally determined. We cannot do that for a rather simple reason. We can get reasonable thermochemical data for minerals from phase-equilibrium studies because, by good luck, the thermochemical values, especially of dehydration reactions, are not very sensitive to the accurate locations of the curves. By the same token, however, a small error in the thermochemical value leads generally to large uncertainties in the location of the calculated curve, so much so that the curve may be useless, even geologically. The source of this problem is not hard to find. In phase-equilibrium calorimetry for a reaction involving a hydrous phase, the procedure involves, in the final analysis, matching the Gibbs free energy contents of the solid phases with that of H₂O. In the procedure of calculating univariant curves from thermochemical data, we seek combinations of values of temperature and pressure such that null points are obtained in the Gibbs free energy change for the reaction; the loci of these null points define the univariant curve. For H₂O, a volatile whose *P-V-T* data are probably better known than for any other volatile component of geologic interest, a typical

change of Gibbs free energy value is about 120 joules or 30 calories per degree, regardless of the pressure (Burnham *et al.*, 1969; see Fisher and Zen, 1971). Now a characteristic magnitude for the combined uncertainties of thermochemical data for univariant reactions, taking into account the fact that errors on the same calorimetric process that appears on both sides of a reaction tend to cancel out (G. M. Anderson, 1976, written communication), is on the order of 500 joules per mole of oxygen. This means that if the reaction releases 9 percent of its oxygen in the form of H₂O—such as dehydration reaction for the micas—then we cannot hope to locate the calculated univariant curve to better than about 45°, let us say $\pm 25^\circ\text{C}$.

An uncertainty of $\pm 25^\circ\text{C}$ is perhaps larger than could be achieved by modern experimental techniques, but for many geologic problems it is still useful. For some other reactions, however, the effect of a given value of uncertainty could be considerably larger. Take the extreme example of the location of the triple point of the aluminum silicate polymorphs, a problem that was examined by Richardson *et al.* (1969). These workers showed that an uncertainty as small as 100 calories would give the location of the triple point an uncertainty of about $\pm 50^\circ\text{C}$ and ± 1 kbar, because of the small volume and entropy differences among the polymorphs. Therefore, I urge that all who would calculate *P-T* diagrams for mineral reactions fully consider the effect of taking the uncertainties into account. This may seem an obvious and even trivial suggestion, but how often it is forgotten, and what delusions one is led to!

Toward a carefully surveyed petrogenetic grid

As the preceding discussions show, one basic problem is to reduce the uncertainties of the calculated thermochemical data in order to make them more useful. We would like to be able to calculate meaningful *P-T* grids. We would like to study the detailed variations of thermochemical properties of solid solutions and polytypes; we are frustrated because the magnitude of the variations is probably no larger than the uncertainties in the values. In the example for muscovite, we found tantalizing trends in the data that might be real but that cannot be brought into focus against the large uncertainties. We suspect that there may be certain irreducible widths to the *P-T* brackets for a given reaction that are dictated by reaction kinetics, activation energy barrier, and the like, independent of the particular experimentalist's technique. These are important things to study, but

again the possibilities cannot be investigated because of the large uncertainties associated with the phase-equilibrium as well as thermochemical data. These large uncertainties also preclude attempts to make inter-laboratory comparisons, because the situation would be like trying to calibrate two precision ball-bearings with cheap plastic school rulers.

If we can reduce the uncertainties of dehydration reactions by an order of magnitude, say to a typical value of 50–75 joules (10–15 calories) per mole of oxygen, then the thermal effects of many of the phenomena mentioned above may begin to emerge. How can we achieve this improvement? This is one task to which calorimetrists, experimental petrologists, geochemists, and mineralogists can address themselves. I can only make a few tentative, perhaps obvious, suggestions here.

First, we must insist on thorough characterization of experimental material and procedures, whether used in conventional calorimetry or in phase-equilibrium studies. The samples must have full documentation; their chemical compositions and homogeneity must be determined, their site-occupancy data collected, the oxidation states of elements of variable valence ascertained, the grain size and impurities recorded, and, needless to say, the crystallographic data fully gathered. It is surprising how often this sort of documentation is not prepared for calorimetric and phase-equilibrium material.

Second, documented and measured material should be equally carefully curated and be made available to other laboratories and future workers. Recently I had occasion to try to get a particular sample of muscovite, the thermochemical data of which were measured by a major national laboratory, in order to determine whether the tetrahedral Al and Si atoms are disordered. I wrote to the attributed source of the sample, who replied that the sample was from an unknown locality and presumably from a pegmatite. This situation is quite typical; we all recognize it to be unfortunate, and we should improve it. Last year, my colleague Bruce S. Hemingway and I introduced the idea of an effort for workers in thermochemistry to be encouraged to send portions of their studied samples as well as the documentation to a central repository, with the idea that such precious samples would then become available to future workers for other studies, for calibration of their own experiments, and for redetermination. The Department of Mineral Sciences at the Smithsonian Institution already has such a system, and that Department encourages mineralogists, petrologists, and

calorimetrists to do just that. I urge you to participate if you work in this field. The Smithsonian is a neutral, readily accessible, prestigious, and we hope, permanent repository for samples of scientific value; deposition of samples there would relieve individual workers the chore of having to answer requests.

But I would go further. I suggest that the time has come for research workers to get together and make a cooperative, coordinated effort to establish selected phase-equilibrium curves to high precision. Let me draw an analogy. We have in the United States a system of national land grids established by the former Coast and Geodetic Survey. To a primary grid of very high precision are tied grids of lesser precision. Why don't we establish an analogous grid of the P - T space of geologic interest, that is, a petrogenetic grid, in similar fashion? We can select important mineral systems for our primary grid, then tie to them other equilibria until eventually we obtain a system of general usefulness, whose component curves, based on precisely studied material, bear known and reproducible relations to one another, and whose uncertainties can be specified and are of such sizes that they do not mask useful information.

Obviously, for this to be done a good deal of drudgery must be assumed by different laboratories. Interlaboratory comparison of techniques must be undertaken (an example of a noteworthy effort along this line is the interlaboratory comparison of piston-cylinder equipment; Johannes *et al.*, 1971). Temperature scales and methods of measurement and reporting must be standardized, because the uncertainty in the Gibbs free energy of a hydrous mineral contributed by ± 1 K is on the order of 100–200 joules. The criteria of reaction and equilibrium must be made uniform, and of course, the same set of samples must be used in all studies. These samples could be the mineralogical equivalent of rock samples G-1 and W-1, which have contributed much to the calibration, correlation, and interlaboratory standardization of methods of chemical analyses of rocks and rock-forming oxides. I suggest that good candidates of mineralogical samples are those that have had calorimetric measurements made on them. A low-temperature heat-capacity measurement requires something like 50 grams of a sample. Think how many phase-equilibrium experiments can be made on so much sample! A set of these can be made into primary standards useful for many purposes.

The primary equilibria to be studied do not have to be immediately useful in petrology or mineralogy but should be relatable to other pertinent equilibria. I

would suggest that solid-state hydrogen buffer equilibria, such as hematite-magnetite, quartz-fayalite-magnetite, nickel-bunsenite, and iron-wüstite, which already are reference reactions for most studies of redox equilibria, be part of the primary grid. Also, P - V - T data on volatiles and especially on mixed volatiles obviously are candidates of the primary grid. Just recall how much progress has been made possible by the precise measurement of the P - V - T relations of H_2O by Burnham *et al.* (1969)! And how much ahead we would be if we had somehow found ways and resources to get good data on H_2O - CO_2 , H_2 - H_2O , C-H-O, C-H-O-S, and O-H-Cl/F gas mixtures!

Measurement of the same equilibria by different laboratories, based on the same samples, could probably eliminate many sources of uncertainty in the data, could uncover the idiosyncracies of individual equipment so compensations might be made, could bring out biases of experimental techniques, and perhaps could spur workers to refine their methodology—for example, to establish better criteria than those in use for reversal of reaction, so that the P and T coordinates of brackets might be narrowed and placed rationally. The results of large numbers of experiments, done on the same material, could then be rationally analysed, perhaps through some sort of program of statistical correlation (Gordon, 1973; Haas and Fisher, 1976), to obtain consistent sets of thermochemical values whose limitations are known and whose variations can be related to physical phenomena. In this fashion, I think, we will be able to reduce the uncertainties in our data considerably, perhaps by the order of magnitude that we need to begin to utilize the data in a predictive rather than simply in retrospective fashion, and in order to begin to discern finer structures in mineralogical reactions for which we have at best an inkling today.

By their very nature, thermochemical values are relative quantities having only arbitrary reference points. The whole set of thermodynamic values for substances can be arbitrarily increased by a million kilojoules per mole of hydrogen and still retain its usefulness and lead to the same correct or incorrect physical answers. That is not our problem. We are, rather, victims of numbers that are mutually inconsistent and that cannot be related to one another; it is as if the country had been surveyed by private land companies each using its own datum level. How, then, would we know that a mountain is indeed higher than a mole hill?

Because we do not possess a set of consistent data except for restricted sets of minerals, computer correlation programs, however sophisticated, can help us but little. Such programs may be able to tell us how bad the scatter of data is, or which source is particularly out of line from the others, but it cannot tell us what is relatively the most precise value, or what is signal and what is noise. We must guard against producing arrays of numbers that merely look nice. Phase-equilibrium calorimetry is a tool that could help us produce numbers and test their mutual consistency for a wide range of bulk compositions that are of interest to mineralogists, petrologists, and geologists.

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