GIBBS FREE ENERGY, ENTHALPY, AND ENTROPY OF TEN ROCK-FORMING MINERALS: CALCULATIONS, DISCREPANCIES, IMPLICATIONS[1]

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Abstract

The standard 298°K, 1 bar Gibbs free energy of formation and enthalpy of formation of the following minerals were calculated from reversed hydrothermal equilibrium data: Diaspore, tremolite, zoisite, prehnite, laumontite, wairakite, clinochlore, muscovite, paragonite, pyrophyllite. Calculation was by a procedure previously described by the author, and uncertainties, due to uncertainties in the hydrothermal data and in the thermochemical data input, are included. Where entropy data did not exist, they were calculated from pairs of hydrothermal p-T brackets. The zeolites have anomalously high entropy values, reflecting the highly mobile state of molecular H_2O in the structure. The calculated Gibbs free energy of muscovite is about 10 kcal more negative than calorimetric measurements; however, much of this discrepancy could be caused by a gross error in the basic thermochemical parameters for the aluminum silicates (corundum, kyanite, andalusite, sillimanite, kaolinite) suggesting error in the thermochemistry of corundum. The inconsistency of about 3-4 kcal/gram atom of Al is implicit in the available thermochemical values of aluminum-bearing minerals, but there is at present no *a priori* means to decide which sets of data are wrong. Until this point is resolved, the validity of all thermochemical calculations for mineralogical phase reactions involving aluminum is suspect.

Introduction

Thermodynamic parameters of minerals can be computed from experimental phase equilibrium data when the data define one or more reliably reversed p-T brackets. Various methods of calculation have been proposed in the past (see, for instance, Orville and Greenwood, 1965; Robie, 1965; Weisbrod, 1968; Anderson, 1970); all those cited except Robie used rectilinear graphical fitting of several experimental points. The writer (1969, 1971) previously pointed out that graphical fitting of data has disadvantages, and advocated a method that uses the reversed p-T brackets as such without any assumption as to how these brackets might be related to one another. The major drawback of the method is the need to know most of the thermodynamic parameters of individual phases (including the volatiles when these are involved in the reaction) before the calculations can be made. However, with the steady accumulation of thermodynamic data for rock-forming phases, this method is becoming more widely applicable. One major

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advantage of the method is that it allows direct estimation of thermochemical uncertainties; another is that any mutual inconsistency of the data points is quickly revealed.

Efforts to derive thermodynamic parameters from equilibrium hydrothermal data received a major boost with the recent publication of precise p-T-V measurements of H_2O over wide p-T ranges (Burnham *et al.*, 1969). The data of Burnham *et al.* were converted by Fisher and Zen (1971) to the same reference state used by Robie and Waldbaum (1968) for H_2O and for other minerals, so they can be used directly to derive further thermochemical parameters. A test of the reliability of the method was made by Fisher and Zen (1971) who calculated the standard Gibbs free energy of formation of brucite, for which high-precision calorimetric data are also available. The calculations used a single hydrothermal p-T bracket, and took into account the uncertainties involved in each step. The resulting Gibbs free energy is in excellent agreement with the calorimetric value and shows a comparable determinative uncertainty. This comparison is deemed justification of extension of the method of calculation.

Units, Symbols, and Abbreviations

$G_f{}^0$	Standard (298 K, 1 bar) Gibbs free energy of formation of a phase from the elements
$H_f{}^0$	Standard (298 K, 1 bar) enthalpy of formation of a phase from the elements
S^0	Standard (298 K, 1 bar) entropy ("Third Law") of a phase
$S_f{}^0$	Standard (298 K, 1 bar) entropy of formation of a phase from the elements
$\Delta S_{f,s}$	Sum of entropy of formation of product solids minus the sum of entropy of formation of reactant solids at T and p
$\Delta S_{f,s}{}^0$	The corresponding sums referring to the standard state (298 K, 1 bar)
ΔV_s	Sum of total volumes of product solids minus the sum of total volumes of reactant solids
gibbs/gf	Unit of entropy, 1 Gibbs = 1 calorie per degree, abbreviated Gb (The Gibbs/gf is commonly denoted by the unitless unit e.u.) For original definition, see Giauque et al., 1960
cal/bar	Unit of volume, 1 cal/bar = 41.842 cc
T	Temperature in Kelvins (K)
p	Pressure in bars (b) or kilobars (kbar)
T_e	Temperature at which an univariant reaction is at equilibrium
P_e	The corresponding pressure
gf	Unit gram-formula weight

Thermochemical Calculations

Details of the procedure of thermochemical calculations from hydrothermal data are given in Zen, 1971 and Fisher and Zen, 1971. The sources of information in each set of calculations are given here under each appropriate section and also in Tables 1 and 2, or the data are taken from Robie and Waldbaum (1968). The data of Robie *et al.* (1967) for volumes were used insofar as possible to insure internal consistency.

Where sufficient numbers of reversed p-T brackets exist for a given reaction, it becomes possible to make several estimates of the thermochemical parameters. For instance, if there are n separate brackets, $(n-1)$ independent evaluations of the entropy of a phase are possible, using the relations in Zen, 1971, eq. 12. In practice, all n points are used in the $(n-1)$ calculations, but pairs of points are selected so that they are remote from each other in order to minimize errors caused by small differences. If the discrepancies between separate estimates are not excessive, they can commonly be resolved. The method of resolution is described in the section on "Errors".

What constitutes an acceptable value of the entropy for a phase is of course a matter of judgment where no independent measurements are available. Occasionally, despite any permissible adjustment the calculated entropy may turn out to be near zero or even negative; such results are prima facie evidence of poor experimental data and the calculations are abandoned. In practice, entropy values somewhere near the value estimated by the "oxide sum" method (Fyfe *et al.*, 1958, p. 25), using a value of 10 Gb/gf for H_2O, are considered reasonable (*ibid.*, p. 117). For phases of high density, values less than this sum may be expected; for zeolites having molecular H_2O, values considerably greater than this sum are reasonable.

When the entropy values of all phases of a given reaction are obtained, it is a simple matter to calculate the standard Gibbs free energy of formation of the phases from the elements, the standard state being at 298 K and 1 bar, using the relationship (Fisher and Zen, 1971, eq. 8):

$$\Delta G(T_E, P_E) = 0 = \Delta G_{f,s}{}^0(298, 1)$$

$$- \int_{298}^{T_E} \Delta S_{f,s}\, dT + \int_{1}^{P_E} \Delta V_s\, dp + G_{H_2O}{}^*(T_E, p_E)$$

The standard enthalpy of formation is obtained from the definition for Gibbs free energy,

$$G \equiv H - TS.$$

Table 1 Entropy of formation of minerals from the elements at 1 bar, in gibbs/g⁴

.K	MERWINITE	GROSSULAR	GEHLENITE	LARNITE	3-2 MULLITE	SILLIMANITE	ANDALUSITE
298.15	-182.144	-293.166	-162.026	-91.892	-303.664	-117.560	-118.250
400	-181.932	-292.816	-161.999	-91.716	-303.484	-117.616	-118.336
500	-181.046	-292.584	-162.089	-91.198	-304.571	-117.935	-118.565
600	-180.180	-291.220	-161.525	-90.620	-303.465	-117.505	-118.065
700	-179.436	-290.056	-161.024	-90.088	-302.215	-117.055	-117.535
800	-178.932	-289.104	-160.692	-89.736	-301.023	-116.659	-117.059
900	-178.458	-288.242	-160.422	-89.404	-300.068	-116.340	-116.670
1000	-180.556	-294.392	-165.762	-88.748	-315.610	-121.508	-121.798
1100	-180.462	-292.582	-165.645	-88.596	-314.572	-121.112	-121.392
1200	-185.164	-296.890	-168.718	-91.642	-313.539	-120.687	-120.987

.K	KYANITE	MAGNESIOFERRITE	SPINEL	PSEUDOBROOKITE	TITANOMAGNETITE	ILMENITE	ANATASE
298.15	-120.510	-89.242	-100.082	-105.450	-77.992	-62.034	-44.386
400	-120.656	-87.766	-100.004	-103.678	-76.836	-61.335	-43.853
500	-120.925	-86.538	-100.288	-102.375	-75.948	-60.621	-43.434
600	-120.355	-85.160	-99.910	-101.375	-75.230	-59.995	-43.040
700	-119.765	-83.448	-99.540	-100.603	-74.628	-59.564	-42.679
800	-119.229	-82.796	-99.222	-100.043	-74.196	-59.230	-42.393
900	-118.790	-82.574	-99.004	-99.750	-73.984	-59.048	-42.152
1000	-123.868	-85.108	-106.596	-99.800	-74.058	-59.026	-41.934
1100	-123.422	-85.766	-106.330	-100.258	-74.466	-59.225	-41.753
1200	-122.967	-85.982	-106.016	-101.143	-75.172	-60.062	-42.451

.K	RUTILE	COESITE	QUARTZ	BRUCITE	PERICLASE	ANTHOPHYLLITE	CRISTOBALITE
298.15	-44.276	-43.846	-43.616	-72.924	-25.868	-576.210	-43.116
400	-43.743	-43.993	-43.733	-73.400	-25.882	-578.803	-43.203
500	-43.324	-43.924	-43.554	-73.550	-25.767	-577.504	-43.054
600	-42.930	-43.770	-43.280	-73.432	-25.645	-575.722	-42.270
700	-42.579	-43.579	-42.939		-25.545	-573.843	-42.009
800	-42.293	-43.393	-42.553		-25.467	-571.923	-41.733
900	-42.072	-43.172	-41.912		-25.426	-570.490	-41.502
1000	-41.904	-42.934	-41.744		-27.712	-585.100	-41.314
1100	-41.763	-42.693	-41.583		-27.682	-583.670	-41.143
1200	-42.491	-42.451	-41.421		-27.641		-40.971

°K	CORUNDUM	HEMATITE	MAGNETITE	WATER	STEAM	MUSCOVITE	TALC
298.15	-74.854	-65.644	-81.522	-38.996	-10.606	-305.474	-304.274
400	-74.803	-64.525	-79.706		-11.309	-307.907	-305.525
500	-75.181	-63.261	-77.858	-11.833	-11.833	-308.068	-304.980
600	-74.885	-62.085	-75.970	-12.237	-12.237	-306.635	-303.842
700	-74.566	-60.994	-73.868	-12.560	-12.560	-305.134	-302.419
800	-74.286	-60.010	-71.586	-12.824	-12.824	-303.701	-300.845
900	-74.088	-59.178	-69.574	-13.032	-13.032	-302.344	-299.188
1000	-79.404	-58.716	-69.918	-13.204	-13.204	-309.168	
1100	-79.189	-59.235	-70.906	-13.346	-13.346	-325.758	
1200	-78.976	-59.432	-71.232	-13.454	-13.454	-323.958	-303.482

°K	NEPHELINE	ALBITE GLASS	HIGH ALBITE	LOW ALBITE	K-SPAR GLASS	ADULARIA	HIGH SANIDINE
298.15	-91.782	-165.544	-173.824	-178.294	-168.454	-175.744	-174.794
400	-93.813	-167.899	-175.999	-180.809	-170.686	-178.086	-177.136
500	-93.316	-167.994	-175.934	-181.004	-170.394	-178.124	-177.174
600	-93.063	-166.953	-175.003	-180.283	-169.523	-177.613	-176.663
700	-92.774	-165.902	-174.132	-179.482	-168.349	-176.749	-175.799
800	-92.458	-164.864	-173.124	-178.714	-167.092	-175.732	-174.782
900	-92.136	-163.860	-172.280	-178.000	-165.934	-174.784	-173.834
1000	-94.546	-165.574	-174.194	-180.034	-167.700	-176.700	-175.750
1100	-94.019	-164.515	-173.365	-179.305	-184.834	-194.014	-193.064
1200	-113.002	-183.174	-192.294	-198.324	-183.599	-193.039	-192.089

°K	MICROCLINE	ANORTHITE	TREMOLITE	JADEITE	CLINOENSTATITE	DIOPSIDE	Ca-Al PYROXENE
298.15	-179.264	-180.024	-582.920	-143.098	-69.584	-139.548	-140.378
400	-181.606	-180.170	-584.601	-145.396	-69.825	-140.029	-140.227
500	-181.644	-180.246	-583.024	-145.540	-69.701	-140.012	-140.402
600	-181.133	-179.340	-580.492	-145.023	-69.475	-139.420	-139.750
700	-180.269	-178.526	-577.643	-144.393	-69.224	-138.667	-139.149
800	-179.252	-177.868	-574.863	-143.751	-68.990	-137.689	-138.645
900	-178.304	-177.308	-572.150	-143.168	-68.758	-136.936	-138.226
1000	-180.220	-182.274	-581.090	-145.350	-70.836	-138.712	-143.820
1100	-197.534	-181.706	-578.400	-144.752	-70.595	-138.299	-143.073
1200	-196.559	-182.728		-163.843	-70.332	-139.533	-144.367

°K	PSEUDOWOLLASTONITE	WOLLASTONITE	CORDIERITE	FORSTERITE	FAYALITE	SPHENE	AKERMANITE
298.15	-67.044	-68.344	-408.834	-95.362	-73.562	-113.380	-158.166
400	-66.945	-68.225	-409.993	-95.686	-71.146	-112.988	-157.991
500	-66.741	-67.881	-410.436	-95.288	-68.738	-112.455	-157.539
600	-66.385	-67.555	-408.830	-94.950	-66.610	-111.865	-156.905
700	-66.104	-67.214	-407.005	-94.498	-64.768	-111.293	-156.292
800	-65.880	-66.910	-405.289	-94.086	-63.206	-110.783	-155.886
900	-65.658	-66.658	-403.878	-93.754	-61.914	-110.310	-155.482
1000	-65.506	-66.506	-418.172	-98.078	-60.888	-109.970	-157.554
1100	-65.405	-66.405	-416.795	-97.776	-60.096	-109.728	-157.361
1200	-66.912	-67.882	-415.357	-97.422	-59.082	-111.963	-160.334

Table 2. Calculated thermodynamic parameters of phases

Phase	Composition	$S°(298,1)$, gibbs/gf	$S_f(298,1)$, gibbs/gf	$G_f°(298,1)$, kcal	$H_f°(298,1)$, kcal	V/gf, cal/bar	Reference
Clinochlore	$Mg_5Al_2Si_3O_{10}(OH)_8$	109	-523	-1974	-2130	(4.970)[a]	3,7
Diaspore	$HAlO_2$	(8.43),	-62.94	-219.93 ± .38	-238.69 ± .38	(0.4245)	1,3
Laumontite	$CaAl_2Si_4O_{12}\cdot 4H_2O$	119.3 ± 4.6	-439.0 ± 4.6	-1598 ± 4	-1729 ± 5	(4.858)	8
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	(69.0)	-305.5	-1339.9[b] ± 1.5	-1431.0[b] ± 1.5	(3.363)	1,3
	same	same		-1337.4[c] ± 1.4	-1428.5[c] ± 1.5	same	1,3
Paragonite	$NaAl_3Si_3O_{10}(OH)_2$	66.9[d] ± 4.1	-304.3[d] ± 3.7	-1327.9[d] ± 2.4	-1418.6[d] ± 2.6	(3.167)	5
Prehnite	$Ca_2Al_2Si_3O_{10}(OH)_2$	69.7 ± 3.0	-302.4 ± 2.4	-1389.8 ± 1.7	-1480.0 ± 1.9	(3.369)	6
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	(56.6)	-300.1	-1253.2[e] ± 1.3	-1342.7[e] ± 1.3	(3.009)	2,3
	same	same		-1260.2[f] ± 1.5	-1349.7[f] ± 1.5	same	2,3
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	(131.19)	-582.92	-2775.2 ± 2.6	-2949.0 ± 2.6	(6.523)	1,3
Wairakite	$CaAl_2Si_4O_{12}\cdot 2H_2O$	110.8 ± 1.0	-335.8 ± 1.0	-1477.3 ± 1.5	-1577.4 ± 1.6	(4.558)	4
Zoisite	$Ca_2Al_3Si_3O_{12}OH$	67.9 ± 3.9	-319.5 ± 3.4	-1552.7 ± 1.4	-1647.9 ± 1.8	(3.262)	3

Notes. a, Values in parentheses are taken from the stated references. b, Calculation using high sanidine. c, Calculation using microcline. d, Calculation using high albite. e, According to the kaolinite reaction. See also table 2. f, According to the andalusite reaction. See also table 2.

References. 1-Robie and Walbaum, 1968. 2-King and Weller, 1970. 3-Robie et al., 1967. 4-Liou, 1970. 5-Chatterjee, 1970. 6-Liou, 1971a. 7-Deer, et al., 1962, v. 3, p. 131. 8-Liou, 1971b.

The differences between the sum of entropies of formation of the product solid phases and that of the reactant solid phases, $\Delta S_{f,s}$, is a very slowly varying function of temperature and also of pressure (Fisher and Zen, 1971, p. 299). Therefore, good estimates of $G_f{}^0$ for a phase can be obtained by approximating the integral $\int \Delta S_{f,s}\, dT$ by the quantity $\Delta S_{f,s}{}^0\, \Delta T$. The difference between the two, where data allow estimation, is not more than about 1 kcal even in the worst case. The approximation will be called the "constant-entropy" method. Where high-temperature heat capacity data do exist, for instance from the tabulation of Robie and Waldbaum (1968), a more accurate calculation is possible. Then the integral $\int \Delta S_{f,s}\, dT$ can be replaced by a sum, $\sum_{\Delta T} \overline{\Delta S_{f,s}}\, \Delta T$ in which the mean value, $\overline{\Delta S_{f,s}}$ is obtained from entropy-of-formation values for successive even-hundred degree entries. This will be called the "summation" method.

To facilitate calculation, the Third Law entropy values for common rock-forming minerals, as listed in Robie and Waldbaum (1968) for even hundred degrees K, are converted into entropy-of-formation values. The results are given in Table 1, in units of Gibbs/gf. The anthophyllite data are from Mel'nik and Onopriyenko (1969). The mineral formulae are those of Robie and Waldbaum; for anthophyllite the formula is based on 24 oxygens.

The pressure-volume contribution to the calculations of the energy and entropy-of-formation is based on the assumption that the integral $\int \Delta V_s dp$ can be replaced by the term $\Delta V_s \Delta P$. The approximation is reasonable because the volume term itself is always a small contribution, and the difference between the volumes of the solid product phases and the solid reactant phases is largely independent of temperature and pressure. For example, an unusually large value of ΔV_s might be 1 cal/bar; for a pressure range of 3 kbar this would lead to a contribution of 3 kcal. Even as much as a 10 percent error in the volume data would lead only to a Gibbs free energy error of 300 cal. If a temperature difference of 50 deg is associated with the 3 kbar pressure difference, the corresponding contribution to the entropy would be 60 gb/gf, and a 10 percent error in volume would lead to 6 gb/gf of error, which is significant but not fatal. The compressibility of solids being on the order of 10^{-6} per bar, it seems improbable that the pressure correction for the differences of volumes of reactants and products could amount to 10 percent of ΔVs; the effect of elevated temperature on ΔVs tends to offset the pressure effect.

To be rigorous, one should carry out the temperature and pressure integrations in sequence, e.g., from 298 K, 1 bar to T_e, 1 bar, then from 1 bar to p_e bar at T_e. Our assumption that the volume integrand

can be replaced by a constant term amounts to stating that the result of the calculation is independent of the sequence of integration.

In all the calculations, the fluid phase is assumed to be pure H_2O so that $G_{H_2O} = \mu_{H_2O}$. The various paths of calculation are summarized in Figure 1.

ERRORS

Estimating the uncertainties associated with each calculated thermochemical value is a complex problem, involving sources of error of different kinds. One property of the p-T brackets is that it is a step function: Within the bracket, there is equal chance that the true equilibrium p, T value lies anywhere, but outside the bracket the chance is, by the definition of limits of the brackets, zero. Thus the data do not represent conventional distribution function, and standard statistical procedures do not apply.

The experimental results are commonly reported in terms of an lower temperature, T_1, which is the lowest observed temperature at some pressure at which the endothermal reaction proceeded. There is a corresponding upper temperature, T_2. To each temperature is associated an uncertainty in measurement, δT_1 and δT_2; the true bracket lies within the range of $T_1 - \delta T_1$ and $T_2 + \delta T_2$.

Thus, to each p-T bracket is associated first a thermochemical uncertainty because the true location of p_e, T_e values is unknown. For Gibbs free energy G_f^0, this uncertainty is readily calculated by comparing the G_f^0 at the limits of the bracket with the calculated value. Second, there is the uncertainty in G_f^0 associated with the input values for the free energy, volume, and entropy of the individual phases. This uncertainty is readily calculated (Fisher and Zen, 1971), but how to combine the two types of uncertainty is not obvious because the first source does not involve normal distribution. I have simply added the two sources together.

In this way, when the Gibbs free energy of formation is calculated for the same phase from different brackets, there results an uncertainty for each calculated value. The "best" value as well as the associated uncertainty are computed as follows. Let the uncertainty associated with a particular value G_i be g_i, and let $w_i = 1/g_i^2$. Then the "best" value of G_i, or $\hat{G}_i$ is $\hat{G}_i = \sum_{i=1}^{K} G_i w_i / \sum_i w_i$ and the "best" estimate of the uncertainty, $\hat{g}_i = (1/\sum_{i=1}^{K} w_i)^{1/2}$ (see Mandel, 1964, p. 132 ff; I am much indebted to G. M. Anderson for suggesting using this approach). I have adopted the two-σ convention in reporting uncertainties (Robie and Waldbaum, 1968). Calculation of the uncertainty associated with the standard enthalpy of formation from the Gibbs

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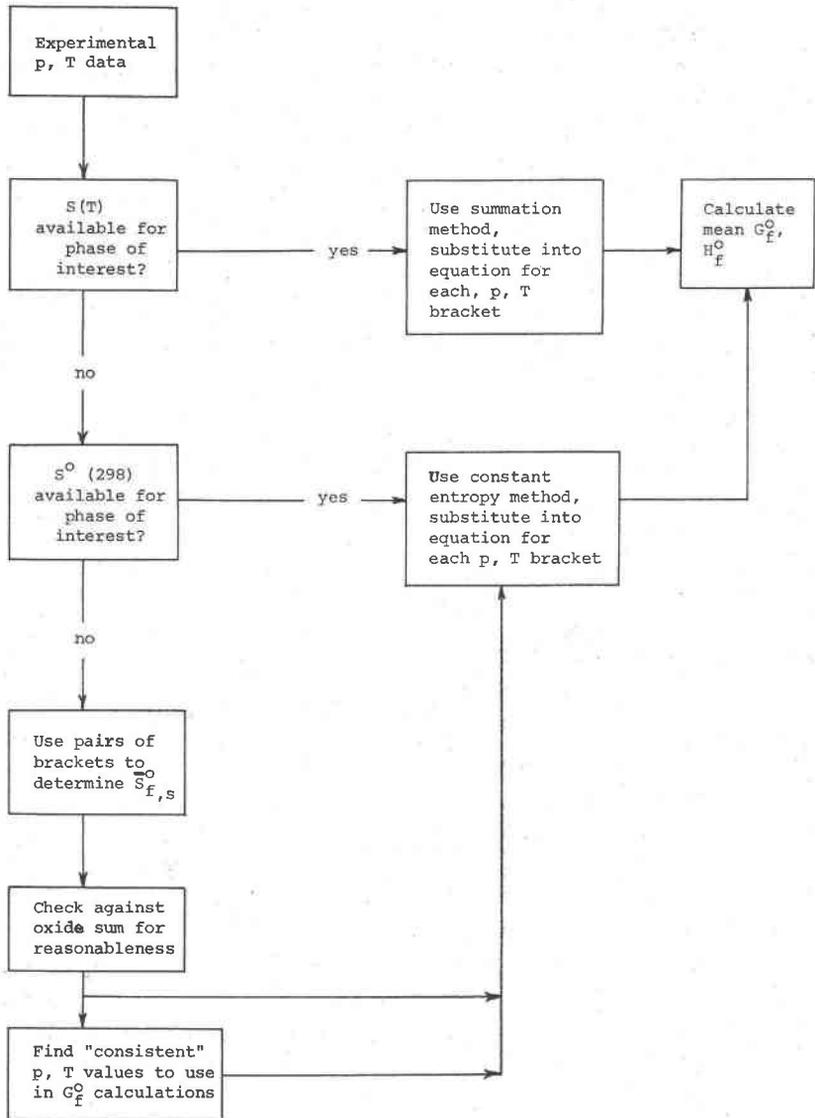
Fig. 1. Scheme of calculation of thermodynamic parameters for minerals from hydrothermal equilibrium data.

free energy and entropy data simply follows the conventional procedure for combining sums; see Fisher and Zen, 1971.

Estimating the uncertainty in entropy calculations is more difficult because each calculation involves pairs of p-T brackets. Use of brackets that are not adjacent to each other is preferred, as such pairs tend to reduce the uncertainty. For each pair, a maximum value and a minimum value of the entropy of formation of a phase can be computed, and to each extremal value can be attached an error due to uncertainties in the data input. In practice, for each pair of p-T brackets, one gets a mean value of the entropy directly, and the spread of values gives an estimate of the uncertainty. From the various pairs of p-T values, then, the "best" entropy-of-formation value and the "best" uncertainty can be calculated by the formulae given above. From the value of entropy of formation thus derived, the "Third Law" entropy value, S^o, is obtained. The uncertainty due to the uncertainties of the entropy data input is obtained from the root-mean-square of the uncertainties of the *Third-Law* entropies of the solid phases plus those of hydrogen and oxygen gas, taking into account the stoichiometric coefficients of the reaction.

The determination of a "best" value of the entropy of formation of a solid phase allows estimation of an internally consistent set of p and T values for the univariant equilibrium. This is done by plotting, for each pair of brackets, the entropy values against p and T, and reading off the plot the values of p and T corresponding to the "best" entropy value. Any remaining discrepancies arising from the use of different pairs of brackets are resolved by taking the mean values. These adjusted p and T values are automatically within the experimental p-T brackets and are used in the G_f^o calculations.

Entropy values that do not permit such treatment, because the "best" value falls outside the range obtained from one or more pairs of p-T brackets, are handled as individual problems and discussed in the appropriate sections.

RESULTS OF CALCULATIONS

Diaspore

Haas and Holdaway (1970) studied the dehydration of diaspore according to the reaction

$$\underset{\text{diaspore}}{2HAlO_2} = \underset{\text{corundum}}{Al_2O_3} + \underset{\text{vapor}}{H_2O}$$

The p-T brackets are: (1) $398 \pm 5°C$, 1.75 kbar; (2) $409 \pm 5°C$,

2.4 kbar; (3) 420 ± 5°C, 3.5 kbar; (4) 428 ± 8°C, 4.8 kbar (the first and last points as well as the uncertainties were given by Haas during oral presentation of his paper). Using the mean temperatures, the data of Tables 1 and 2, those in Robie and Waldbaum (1968) and those in Fisher and Zen (1971), G_f^o of diaspore was obtained from each of the brackets; the constant-entropy approximation was used. The mean value is −219.93 ± .38 kcal/gf diaspore; the uncertainty includes about 50 cal for the temperature brackets. The actual values of the four brackets are respectively −219.98, −220.01, −219.91, and −219.81 kcal. The H_f^o of diaspore calculated from the Gibbs free energy value is −238.69 ± 0.38 kcal. The G_f^o value may be compared with the values given by Wagman *et al.* (1968) and by Fyfe and Hollander (1964), −220 kcal.

Tremolite

The upper thermal stability of magnesian tremolite was studied by Boyd (1959). The reaction is:

$$Ca_2Mg_5Si_8O_{22}(OH)_2 = 2CaMgSi_2O_6 + 3MgSiO_3 + SiO_2 + H_2O$$
$$\text{tremolite} \qquad \text{diopside} \qquad \text{enstatite} \quad \text{quartz} \quad \text{vapor}$$

The univariant curve passes through the following points: (1) 810°C, 0.6 kbar; (2) 835°C, 1 kbar; (3) 855°C, 1.5 kbar; and (4) 870°C, 2 kbar. These values were obtained by interpolation from the p-T diagram of Boyd; I estimate the temperature uncertainty to be 10°C.

Using the data of Tables 1 and 2, of Robie and Waldbaum (1968), and of Fisher and Zen (1971), and using the summation method for the entropy term, the G_f^o of tremolite has a mean value of −2775.20 ± 2.62 kcal; the actual values are respectively −2775.46, −2775.22, −2775.09, and −2775.03 kcal. To the uncertainty associated with the data input has been added a maximum of 0.2 kcal for the temperature bracket. The large uncertainty of data input reflects the large uncertainty in the Gibbs free energy of diopside, 2.2 kcal per gram-formula. The H_f^o of tremolite at 298 K and 1 bar is −2949.00 ± 2.64 kcal.

The Gibbs free energy and enthalpy values are to be compared with the data given by Robie and Waldbaum (1968), resp. −2,779,137 ± 4150 cal and −2,952,935 ± 4140 cal. These values and my results show acceptable overlap. In the present calculations, the Gibbs free energy and entropy values of clinoenstatite have been used, even though in the experimental work enstatite was the phase encountered; the approximation was necessary because no thermochemical data exist for enstatite. One might expect the Gibbs free energy for ensta-

tite to be more negative than for clinoenstatite at low temperature and pressure, so the calculated tremolite values are apt to be too positive; the deviation is in the right direction for the discrepancy between the present calculated value and the direct thermochemical determination given by Robie and Waldbaum.

The Gibbs free energy value for diopside in Robie and Waldbaum (1968) was derived from the arithmetic mean of two independent values for the heat of solution of this phase. One, determined on an iron-bearing natural sample (Robie and Waldbaum, 1968, ref. 116), leads to a $G_f{}^0$ of $-724\ 534$ cal/gf; the other, on an artificial sample of unspecified composition (Robie and Waldbaum, 1968, ref. 95), leads to a $G_f{}^0$ of $-727\ 044$ cal/gf. If the more negative value for diopside is used in the preceding computations, a $G_f{}^0$ for tremolite of -2777.7 kcal/gf would have resulted, in much better accord with the value in Robie and Waldbaum. However, in view of the compositional uncertainties associated with both diopside samples, the agreement is probably illusory. This feeling is reinforced by the fact that the tremolite used by Weeks (1956) in his enthalpy determination showed large compositional departure from the ideal formula. Therefore, I have simply used the rather artificial mean $G_f{}^0$ value for diopside, and also retained the large uncertainty, as given by Robie and Waldbaum.

Zoisite

The stability relations of zoisite were studied by Newton (1966). The reaction I analysed is the upper stability of zoisite in the presence of quartz:

$$4Ca_2Al_3Si_3O_{12}OH + SiO_2 = 5CaAl_2Si_2O_8 + Ca_3Al_2Si_3O_{12} + 2H_2O$$
$$\underset{\text{zoisite}}{} \qquad \underset{\text{quartz}}{} \qquad \underset{\text{anorthite}}{} \qquad \underset{\text{grossularite}}{} \qquad \underset{\text{vapor}}{}$$

Newton used different types of experimental apparatus to achieve equilibrium under different sets of p-T conditions, but applied pressure correction for the results, so I have presumed that his reported p-T values are reduced to the same datum. The experiments were carried out with all solid reactant and product phases present, so the relative growth or diminution of phases is a good measure of the direction of the reversible reaction. The p-T values cited below are taken from Newton, 1966, tables 2 and 3: (1) 610–640°C, 4.6 kbar; (2) 650°C, 5.6–5.9 kbar; (3), 650–700°C, 6 kbar; (4), 720°C, 7.0–7.3 kbar; (5), 750–770°C, 8 kbar. The final p-T values adopted, using the method of deriving the mean entropy values explained in the "Errors" section, are, respectively, 618°C, 4.6 kbar; 650°C, 5.6 kbar; 670°C, 6 kbar; 720°C, 7.2 kbar; 765°C, 8 kbar.

With five p-T brackets, four independent estimates of the entropy of zoisite were made. The pairs of values selected were: 1, 4; 1, 5; 2, 4; and 3, 5 of the above list. The S_f^0 has a mean value of -319.54 Gb/gf, the mean uncertainty is 3.4 Gb/gf. The entropy obtained is 67.9 ± 3.9 Gb/gf, taking into account the uncertainties of the thermochemical data input. The value may be compared with the "oxide-sum" estimate, which is 72.3 Gb without applying any volume correction. The entropy value of H_2O used in the estimate was 10 Gb/gf (Fyfe $et\ al.$, 1958, p. 117). The agreement is good considering that zoisite is a fairly dense phase so its entropy should be less than the oxide sum.

From the S_f^0 of zoisite, the G_f^0 of zoisite is calculated, using the data of Table 2 and assuming that $\Delta S_{f,s}$ of the solids is a constant. The result is -1552.66 ± 1.4 kcal per gram formula of zoisite. The actual values for the five p-T brackets are respectively -1552.72, -1552.57, -1552.62, -1552.62, and -1552.80 kcal. The H_f^0 of zoisite from the elements is -1647.93 ± 1.8 kcal. No uncertainty due to the T or p brackets is attached because this is already taken into account in the range of entropy values.

Prehnite

The thermal stability of prehnite was studied by Liou (1971a). The reaction is:

$$Ca_2Al_2Si_3O_{10}(OH)_2 = CaAl_2Si_2O_8 + CaSiO_3 + H_2O$$
$$\text{prehnite} \quad\quad\quad\quad \text{anorthite} \quad \text{wollastonite} \quad \text{vapor}$$

Liou gave five reversed p-T brackets for this reaction. These are at (1) $440 \pm 5°C$, 1 kbar; (2) $465 \pm 5°C$, 2 kbar; (3) $495 \pm 5°C$, 3 kbar; (4) $520 \pm 5°C$, 4 kbar; and (5) $550 \pm 5°C$, 5 kbar. The consistent values, adopted by the criterion of the mean value of the entropy, are respectively at $439°$, $467°$, 495, $522°$, and $549°C$. The gram formula volume of prehnite calculated from Liou's data is 3.369 ± 0.003 cal/bar.

Four independent estimates of the entropy of prehnite are possible with the five sets of p-T data. I used the combinations of points 1, 4; 1, 5; 2, 5; and 3, 5. The value of S_f^0 of prehnite is -302.43 ± 2.42 Gb/gf. The Third-law entropy of prehnite at 298 K, 1 bar is therefore 69.7 ± 3.0 Gb/gf. This value may be compared with a value of 71.5 Gg/gf obtained by the "oxide sum" method, using for H_2O a value of 10 Gb/gf.

Using the mean entropy of formation value given above, the G_f^0 of prehnite at 298 K, 1 bar from the elements is next calculated to

be -1389.82 ± 1.71 kcal. The actual values are respectively -1389.83, -1389.79, -1389.80, -1389.81, and -1389.88 kcal. The $H_f{}^0$ of prehnite is -1479.99 ± 1.86 kcal. As for zoisite, no uncertainty due to the p-T brackets is given because the uncertainty due to the entropy term is a better estimate of the same phenomenon.

Wairakite

The upper stability limit of the zeolite mineral, wairakite, was recently studied by Liou (1970). The reaction is:

$$CaAl_2Si_4O_{12} \cdot 2H_2O = CaAl_2Si_2O_8 + 2SiO_2 + 2H_2O$$
$$\text{wairakite} \qquad\qquad \text{anorthite} \qquad \text{quartz} \quad \text{vapor}$$

Liou gave the following reversed p-T brackets: (1) $330 \pm 5°C$, 0.5 kbar; (2) $348 \pm 5°C$, 1 kbar; (3) $372 \pm 5°C$, 2 kbar; and (4) $385 \pm 5°C$, 3 kbar. For reasons discussed below, the mean temperatures are used in my calculations and no adjustment for internal consistency has been made.

Liou (1970) also gave numerous unit cell parameters for the wairakite prepared in his experimental work and from natural occurrences; these parameters lead to closely agreeing cell volumes. From these, an average value of 4.558 ± 0.1 cal/bar-gf was obtained (Table 2).

From the data cited above and given in Table 2, three independent estimates of the entropy of wairakite are possible. From the pairs of points 1, 3; 1, 4; and 2, 4, the respective ranges are -336.38 to -336.90; -335.78 to -335.80; and -335.30 to -339.85. The values do not all overlap, but the discrepancy is not significantly large. The adopted mean value of $S_f{}^0$ is -335.79 ± 0.2 Gb/gf; the narrow uncertainty range is deceptive and results from the values of the pair of points 1, 4. The entropy of wairakite at 298 K and 1 bar is 110.86 ± 1.0 Gb/gf, where an arbitary but more realistic estimate of the uncertainty has been given.

The entropy value is considerably greater than the "oxide sum" estimate of 81.2 Gb/gf when the entropy contribution of H_2O is taken to be 10 Gb/gf. Part of the unusually high entropy of wairakite can be attributed to the low density of the phase (see Fyfe *et al.*, 1958, p. 117 for discussion). However, the bulk of the anomaly must be associated with the loosely attached zeolitic water in the structure. If we assign all the "excess" entropy to such a cause without correcting for density, we get 15 Gb/gf of H_2O, so that the H_2O contribution to the wairakite entropy would be about 25 Gb/gf, a value greater than that of liquid water, 16.7 Gb/gf.

The comparison may seem speculative because of uncertainties in

the validity of the computed entropy value itself, or in the possibility that the wairakite equilibrated in Liou's experiments was not stoichiometric, especially in its H_2O content. However, the same effect is found in the entropy of analcime, to which wairakite is structurally analogous except for slight distortions that reduce the symmetry from cubic to monoclinic. The entropy of analcime, $NaAlSi_2O_6 \cdot H_2O$, calorimetrically obtained by Kelley and King (1961; see Robie and Waldbaum, 1968), is 56.03 Gb/gf at 298 K and 1 bar. The oxide sum value, using 10 Gb/gf for H_2O, is 44.8 Gb/gf, and the deviation is 11 Gb/gf, which resembles the 15 Gb/gf excess computed for wairakite, and the H_2O contribution to entropy likewise is higher than the entropy of liquid water. A dehydrated wairakite could be expected to show anomalously low entropy instead. It appears that in both wairakite and analcime the molecular H_2O exists in the structure in a highly mobile state, having fewer or looser bonds to other H_2O molecules than in the short-range structured liquid water.

Because of the lack of overlap of entropy values, no internally consistent set of adjusted temperatures is possible. The mean temperatures reported by Liou (1970) therefore were used directly for Gibbs free energy calculations. The deviations from this cause are negligible. From the mean entropy value, the G_f^o of wairakite is computed to be $-1,477.29 \pm 1.54$ kcal; the individual values of the four p-T brackets are -1477.30, -1477.28, -1477.26, and -1477.32 kcal. The H_f^o of wairakite is -1577.41 ± 1.63 kcal.

An independent check of the thermochemical parameters for wairakite can be obtained because another reaction involving this phase has been studied:

$$\underset{\text{wairakite}}{CaAl_2Si_4O_{12} \cdot 2H_2O} = \underset{\text{lawsonite}}{CaAl_2Si_2O_7(OH)_2 \cdot H_2O} + \underset{\text{quartz}}{2SiO_2}$$

This reaction, involving only solids, has been studied by Liou (1971b) who gave two reversed points: 305°C, 3.4 kbar, and 390°C, 4.4 kbar. These points give an entropy value of 90 Gb/gf for wairakite, which is much too low compared with the value of 110.9 Gb/gf obtained from the wairakite-anorthite reaction. Because the control on the points is inferior to that on the wairakite-anorthite reaction this value is rejected, even though it is still reasonable compared with the 81 Gb/gf estimate from the oxide sums.

If we used the value 110.9 Gb/gf for wairakite, the G_f^o of wairakite can be calculated from the wairakite-lawsonite reaction. The mean result is -1479.3 kcal, which is about 2 kcal too negative compared with the data obtained from the wairakite-anorthite reaction. Using

the entropy of wairakite derived from the wairakite-lawsonite reaction would make this value about 6 kcal more negative.

Laumontite

Laumontite has been experimentally studied in recent years by Crawford and Fyfe (1965), Nitsch (1968), Thompson (1970a), and Liou (1971b). All these studies pertain to the reversible reaction:

$$CaAl_2Si_4O_{12}\cdot4H_2O + CaAl_2Si_2O_7(OH)_2\cdot H_2O + 2SiO_2 + 2H_2O$$
$$\text{laumontite} \qquad \text{lawsonite} \qquad \text{quartz} \quad \text{vapor}$$

Because of large volume differences between laumontite and lawsonite, the p-T projection of this univariant reaction is nearly parallel to the temperature axis. The results of Thompson agree with those of Nitsch, but the results of Liou lie at a slightly higher pressure. The curve of Crawford and Fyfe (1965) is discordant with all the others and will not be considered.

A second reaction involving laumontite was also studied by Liou: It is the breakdown of laumontite to form wairakite:

$$CaAl_2Si_4O_{12}\cdot4H_2O = CaAl_2Si_4O_{12}\cdot2H_2O + 2H_2O$$
$$\text{laumontite} \qquad \text{wairakite} \qquad \text{vapor}$$

We will examine these two reactions to deduce thermochemical parameters for laumontite, and then compare the results from Liou's data with those to be obtained from Nitsch's and Thompson's data.

For the laumontite-lawsonite reaction, Liou (1971b) gave two p-T brackets, at $210 \pm 5°C$, 3 kbar, and $250 \pm 5°C$, 3.2 kbar[1]. Using these values, the poorly-controlled $S_f°$ of laumontite becomes -440.6 Gb/gf, corresponding to an entropy of 118 Gb. The $G_f°$ of laumontite is then -1600.1 kcal, and the $H_f°$, -1731.7 kcal. No meaningful estimate of uncertainties is possible.

Liou (1971b) also gave five reversed p-T brackets for the dehydration of laumontite to form wairakite. Using the data previously derived for wairakite, an independent set of values for laumontite can be derived. The p-T brackets are: (1) $235 \pm 5°C$, 0.5 kbar; (2) $255 \pm 5°C$, 1 kbar; (3) $282 \pm 5°C$, 2 kbar; (4) $297 \pm 5°C$, 3 kbar; and (5) $327 \pm 5°C$, 6 kbar[2]. A problem arose when pairs of brackets were used to calculate the entropy of laumontite. The entropy ranges for different pairs are wide, and different ranges do not overlap; the

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[1] Note that the T-value for the 3.2 kbar point given in the abstract (Liou, 1971b) is apparently in error.

[2] Again, note that the p-T values in the abstract (Liou, 1971b) are not the same as those in the main text.

entropies calculated seem to become more negative as the p-T values of the brackets increase. This fact suggests some systematic experimental error; as the calculation of wairakite did not lead to such a trend, the suspicion is that the laumontite compositions may have differed systematically in Liou's experiments. Using the pairs of brackets 1, 3; 1, 4; 1, 5; and 2, 5, however, the calculated $S_f{}^0$ is -439.0 ± 4.6 Gb/gf; the uncertainty is formal and obviously too low because the individual values range from -424 to -457 Gb/gf. It is interesting to note, though, that the mean value is nearly same as the value obtained from the laumontite-lawsonite equilibrium. The entropy of laumontite at 298 K, 1 bar is 119.3 ± 4.6 Gb/gf.

The lack of a consistent entropy made it necessary to calculate the $G_f{}^0$ of laumontite using the mean p-T values. The $G_f{}^0$ values are -1596.46, -1596.68, -1596.97, -1596.82, and -1595.98 kcal; the average value is -1596.6 ± 1.8 kcal, and the $H_f{}^0$ -1727.5 ± 2.2 kcal. It must be stressed again that the data above are not "consistent" in the sense used in this paper. However, the values derived from the two reactions by Liou do overlap within the uncertainties.

Thompson (1970a) determined a p-T bracket for the reaction laumontite = lawsonite + quartz + vapor by using the weight-loss method, at 250°C, 2.75 ± 0.25 kbar. If we accept an entropy of 119.3 Gb/gf for laumontite from Liou's study of the same reaction (an assumption that seems reasonable because the slopes of Liou's curve and the one preferred by Thompson (1970a, p. 271) are parallel; note that Thompson's slope was obtained by circuitous extrapolation from Crawford and Fyfe's (1965) data), we obtained the $G_f{}^0$ of laumontite of -1599.5 kcal, in fair agreement with the values obtained from Liou's data, despite the fact that Thompson's p-T value is obviously at lower pressure than Liou's curve for the same reaction.

A second univariant reaction studied by Thompson (1970a) was the direct dehydration of laumontite to anorthite:

$$\underset{\text{laumontite}}{CaAl_2Si_4O_{12}\cdot 4H_2O} = \underset{\text{anorthite}}{CaAl_2Si_2O_8} + \underset{\text{quartz}}{2SiO_2} + \underset{\text{vapor}}{4H_2O}$$

for which four p-T brackets were given: (1) $310 \pm 10°C$, 1 kbar; (2) $317 \pm 10°C$, 2 kbar; (3) $338 \pm 10°C$, 4 kbar; and (4) $347 \pm 10°C$, 6 kbar. Using the pairs 1, 3; 1, 4; and 2, 4, I obtained a straight arithmetic mean $S_f{}^0$ of laumontite of -454.9 ± 6.3 Gb/gf, and a range from -444.3 to -629 Gb/gf. The wide range reflects in part the narrow temperature difference between brackets and the formal uncertainty is meaningless. However, the mean value of entropy implies an entropy of 103 Gb/gf, which is low in view of the fact that the oxide-sum estimate, using 10 gb for H_2O, is 104 Gb, and a zeolite

should certainly have an entropy exceeding the oxide sum. The value of -444 Gb/gf would give an entropy in close agreement with that derived from Liou's data. Using this last value gives a G_f^0 of laumontite of -1599.5 kcal. The Gibbs free energy is not sensitive to the entropy (hence, p-T slope) values and the closely agreeing values should be fairly reliable. The recommended value and uncertainty are given in Table 2.

The entropy of 119.3 Gb/gf for laumontite from Liou's data leads to an "excess" entropy of H_2O of 4 Gb/gf, much smaller than that in wairakite or analcime. The magnitude of the "excess" agrees with that of leonhardite (Robie and Waldbaum, 1968), which is equivalent to a laumontite that has lost 1/8 of the molecular H_2O: for leonhardite the anomaly is 3.3 Gb/gf H_2O.

This discussion underscores the problem of hydrothermal phase equilibrium studies involving zeolites which could have variable amounts of H_2O: How would one ascertain the amount of H_2O in the zeolite along a particular "univariant" reaction curve, and how would one ascertain that the amount remains uniform for all experiments that define the curve? As far as I know this problem has not been tackled, and to that extent all existing hydrothermal data involving zeolites are of ambiguous significance. On the basis of the preceding discussion, one might conclude that the consistency of Liou's data using laumonitie-lawsonite (not a zeolite) relations and using laumontite-wairakite relations, and the consistency of his data using laumontite-wairakite relations and using wairakite-anorthite relations, suggest that he indeed dealt with the same zeolites having the same states of hydration. Comparison of the anomalous entropy values with the oxide-sum estimate and with the values for leonhardite suggests further that Liou probably dealt with the fully hydrated laumontite as well as wairakite, whereas Thompson may not have.

Nitsch (1968) did not publish his p-T data for the breakdown of laumontite to lawsonite, and his figure showing the experimental data does not allow accurate estimate. As his data agree closely with those of Thompson (1970a, p. 273), no further calculation seems warranted.

Clinochlore

The thermodynamic parameters for the low-Al, pure Mg-end member of chlorite, clinochlore, have been estimated from the breakdown curve reported by Fawcett and Yoder (1966) according to the reaction:

$$Mg_5Al_2Si_3O_{10}(OH)_8 = Mg_2SiO_4 + 2MgSiO_3 + MgAl_2O_4 + 4H_2O$$

clinochlore   forsterite   enstatite   spinel   vapor

E-AN ZEN
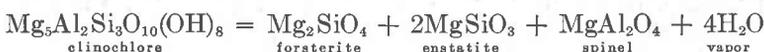
Unfortunately there is only one good reversed point, at $831 \pm 6°C$ and 10 kbar, and a questionably reversed[1] point at $785 \pm 15°C$, 5 kbar. Accepting these two $p\text{-}T$ brackets at their face values, one could get an essentially uncontrolled estimate of the entropy of clinochlore. Using the mean temperatures, we obtain a $S_f°$ of -547 Gb/gf, or a $S°$ value of 85 Gb/gf. This value seems low because the oxide-sum estimate is about 114 Gb/gf. Next, I adjusted the 5 kbar temperature to that of the lower limit, at $770°C$, and the 10 kbar value to the upper limit at $837°C$. These adjustments result in a value of $S_f°$ of -523 Gb/gf, corresponding to a $S°$ value of 109 Gb/gf, which is more reasonable. The corresponding $G_f°$ of clinochlore is -1974 kcal, and the $H_f°$ is -2130 kcal.

These values are very rough, as their derivation pushed the meagre experimental data beyond warranted limits. However, consistent with the experimental data, the entropy is a maximum measure, and the Gibbs free energy and enthalpy, correspondingly, the most positive value. Therefore, it is of interest to compare the Gibbs free energy value with the only other published estimate (Helgeson, 1969, p. 784) for Mg-chlorite derived from solubility measurements made by Mackenzie and Garrels (1965). The value of Third Law entropy was estimated by Helgeson to be 112 Gb/gf, and the $G_f°$ was -1954.8 kcal, nearly 20 kcal less negative than my results. The difference could drastically affect predictions of course of phase reactions involving chlorite. Because in Mackenzie and Garrels' work (1965, fig. 1) equilibrium was approached only from the supersaturation direction, Helgeson's Gibbs free energy value is, if anything, too positive, and the value of -1974 kcal may be a better estimate of the true value.

Muscovite

The Gibbs free energy of formation of muscovite was determined by Barany (1964), using conventional calorimetry, and by Reesman and Keller (1965), using solubility measurements. The standard values at 298 K and 1 bar are, respectively, -1330.1 kcal and -1328.7 kcal. Routine calculations using reversed hydrothermal equilibrium data (Velde, 1966; Day, 1970), however, revealed unexpected inconsistencies.

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[1] The question is prompted by two considerations. First, oxide mixtures rather than the product/reactant phases were used in some runs, thus delineating synthesis rather than stability fields; second, the plotted points in Fawcett and Yoder's Figure 2 do not all correspond to the runs listed in their Table 2. The discrepancy is not explained, and includes the questionable 5-kbar point.

Velde (1966) studied the equilibrium:

$$\underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_2} = \underset{\text{sanidine}}{KAlSi_3O_8} + \underset{\text{corundum}}{Al_2O_3} + \underset{\text{vapor}}{H_2O}$$

He gave five p-T brackets for the equilibrium: (1) $560 \pm 10°C$, 1 bar; (2) $620 \pm 10°C$, 160 bars; (3) $660 \pm 10°C$, 1 kbar; (4) $688 \pm 13°C$, 2 kbar; and (5) $730 \pm 10°C$, 8 kbar. As the entropy of muscovite has been calorimetrically determined to high temperatures, no separate determination of the entropy was attempted. Rather, the entropy term was calculated by the summation method. Using these values, those of Tables 1 and 2, and those of Fisher and Zen (1971), the G_f^0 of muscovite turns out to be, in order of p-T listing above, -1348.1 kcal, -1341.9 kcal, -1340.2 kcal, -1340.0 kcal, and -1338.1 kcal. The spread is 10 kcal, much greater than expected.

In corresponding with Velde, it was brought out that the point at 1 bar is quite unreliable, and so it is disregarded in the ensuing discussion. The four remaining Gibbs free energy values are in a much tighter grouping, averaging at -1340.1 ± 1.5 kcal, including the uncertainty due to the temperature brackets, less than 0.2 kcal. Using the mean value, a H_f^0 is computed to be -1431.1 ± 1.5 kcal.

Anderson (1970) also discussed the problem of deriving consistent thermodynamic parameters of muscovite from hydrothermal data, using the work of Velde as an example. Anderson derived an internally consistent univariant curve, and showed that one such curve passes through the following four p-T points, all within Velde's stated uncertainties: $620°C$, 0.16 kbar; $655°C$, 1 kbar; $680°C$, 2 kbar; and $729°C$, 8 kbar. Using these values, the corresponding G_f^0 of muscovite are -1341.9 kcal, -1340.4 kcal, -1339.8 kcal, and -1338.1 kcal, with a mean of -1340.0 kcal.

There is no sensible difference between these values and those obtained by using the means of Velde's temperature brackets, again showing the general insensitivity of calculated Gibbs free energies to the precise location of the p-T points. The persistence of a 3 kcal spread in the Gibbs free energy value in using Anderson's adjusted data, however, remains a puzzle. Polymorphism of the feldspar or muscovite at different p-T brackets could be a cause of the data scatter, but this is entirely speculative, and its seems doubtful that polymorphism could account for 3 kcal of discrepancy. Use of the assumption of constant ΔV_s is not the cause, for even at a pressure of 8 kbar the pV term amounts to only about 1 kcal.

Next, I used the data of Day (1970) for the breakdown of muscovite in the presence of quartz:

$$\underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_2} + \underset{\text{quartz}}{SiO_2} = \underset{\text{sanidine}}{KAlSi_3O_8} + \underset{\text{sillimanite}}{Al_2SiO_5} + \underset{\text{vapor}}{H_2O}$$
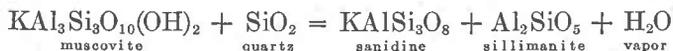
Day gave three p-T brackets at $595 \pm 15°C$, 1 kbar; $640 \pm 10°C$, 2 kbar; and $662 \pm 6°C$, 3 kbar; he did not otherwise specify experimental methods or other details. Nonetheless, using the same method applied to Velde's data, the G_f^0 of muscovite are computed to be, respectively, -1339.8 kcal, -1340.1 kcal, and -1339.9 kcal, with a mean at -1339.9 ± 1.7 kcal. The H_f^0 of muscovite is -1431.0 ± 1.7 kcal. These values are in excellent agreement with those derived from Velde's data. The uncertainty due to the temperature bracket is at most 0.4 kcal, which is to be added to the uncertainty of 1.5 kcal from the thermochemical data input.

Both Velde's and Day's data point to a Gibbs free energy (and an enthalpy value) for muscovite which disagrees with that determined by Barany, -1330.1 kcal, and by Reesman and Keller, -1328.7 kcal. One's first thought is that the entropy value for muscovite, determined by Weller and King (1963), might be questioned because the chemical analysis of the sample they used showed 3.2 percent Fe_2O_3, 0.5 percent FeO, and 0.8 percent MgO, which were not corrected for in their calculations. However, this cannot be the major source of discerpancy because the same entropy value was used in my calculations. The next possibility is that despite its unlikelihood, microcline was the real equilibrium phase in the hydrothermal work. To check this, I recalculated Day's results by assuming equilibrium with microcline. The resulting G_f^0 of muscovite is -1337.4 ± 1.4 kcal, and the H_f^0 is -1428.5 ± 1.5 kcal. The smaller uncertainty reflects the fact that the entropy of microcline was measured whereas that of sanidine was calculated (Waldbaum, 1968). The values are somewhat closer to the calorimetric value, but the gap is still wide. We will come back to this problem in a later section.

Paragonite

The upper thermal stability limit of paragonite was recently studied by Chatterjee (1970). The reaction is:

$$\underset{\text{paragonite}}{NaAl_3Si_3O_{10}(OH)_2} = \underset{\text{albite}}{NaAlSi_3O_8} + \underset{\text{corundum}}{Al_2O_3} + \underset{\text{vapor}}{H_2O}$$

Chatterjee reported six reversed p-T brackets as follows: (1) $540 \pm 10°C$, 1 kbar; (2) $565 \pm 10°C$, 2 kbar; (3) $590 \pm 10°C$, 3 kbar; (4) $633 \pm 8°C$, 5 kbar; (5) $635 \pm 15°C$, 6 kbar; and (6) $660 \pm 10°C$, 7 kbar. It is obvious, from points (4) and (5), that the mean temperatures are not mutually consistent. Using the mean for the entropy, the final adjusted tempertures adopted are, respectively, $541°C$, $567°C$,

587°C, 630°C, 641°C, and 661°C. These points still show some inconsistency (mainly point 5) but no further refinement was attempted.

The entropy of formation of paragonite was next calculated, using the pairs of points 1,6; 1,5; 2,4; 2,6; and 3,6. The calculation assumed that high albite was the equilibrium phase. Chatterjee (1970) gave no information on this point, but subsequent examination (N. D. Chatterjee, 1971, oral communication) showed that the cell parameters of the product albite are nearly those of high albite. The mean value of S_f^0 of paragonite turns out to be -305.08 ± 4.6 Gb/gf and a spread from -298.5 to -314.7 Gb/gf. The implied entropy S^0 of paragonite is 66.1 ± 5 Gb/gf, which uncertainty includes those due to data input. The oxide sum, using 10 Gb/gf for H_2O is 67.6 Gb/gf.

Using the mean entropy value and again the data for high albite, the G_f^0 of paragonite was next computed. The mean value is -1328.37 ± 1.9 kcal, and the individual values are respectively -1328.32, -1328.34, -1328.39, -1328.47, -1328.34, and -1328.42 kcal. The H_f^0 of paragonite is -1419.33 ± 2.1 kcal. No uncertainty due to the p-T brackets is given because this is included in the uncertainty for entropy.

The above thermochemical parameters for paragonite may be compared with the values obtained by Chatterjee (1970), based on the same experimental data, but calculated by a procedure modified from Weisbrod (1968), involving a direct linear extrapolation of the data points rather than on a point-by-point calculation as is done here. Chatterjee's values are: For entropy, 67.8 ± 3.9 Gb; for Gibbs free energy, -1327.4 ± 4.0 kcal; for enthalpy, -1417.9 ± 2.7 kcal. The agreement is very good. This comparison makes clear that if enough good experimental brackets are available, reliable thermochemical parameters can be obtained by any sound method. However, unless there are enough good points to fix a straight line, extrapolatory procedure can lead to large thermochemical errors, and point-by-point calculations are preferable.
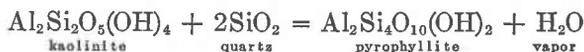
Chatterjee (in press) recently determined the equilibrium relations of the reaction

paragonite + quartz = high albite + andalusite + vapour

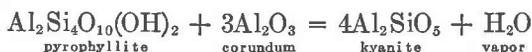and deduced thermochemical data for paragonite. The values are in good agreement with those given above.

Pyrophyllite

The value of G_f^0 of pyrophyllite from hydrothermal data was calculated by Zen (1969). Since then, new data have appeared that necessitate revision of previous values and some new conclusions.

Three reactions were considered (Zen, 1969):

$$Al_2Si_2O_5(OH)_4 + 2SiO_2 = Al_2Si_4O_{10}(OH)_2 + H_2O$$
$$\text{kaolinite} \qquad \text{quartz} \qquad \text{pyrophyllite} \qquad \text{vapor}$$

$$Al_2Si_4O_{10}(OH)_2 = Al_2SiO_5 + 3SiO_2 + H_2O$$
$$\text{pyrophyllite} \qquad \text{andalusite} \qquad \text{quartz} \qquad \text{vapor}$$

and

$$Al_2Si_4O_{10}(OH)_2 + 3Al_2O_3 = 4Al_2SiO_5 + H_2O$$
$$\text{pyrophyllite} \qquad \text{corundum} \qquad \text{kyanite} \qquad \text{vapor}$$

For the calculations, I used an oxide-sum estimate of the Third Law entropy value of pyrophyllite of 63.6 Gb/gf, given by Fonarev (1967). The Gibbs free energy value of pyrophyllite based on the kaolinite reaction turned out to be about 7 kcal more positive than given by the andalusite reaction, the value within each group is tightly clustered regardless of the source of data, and the value based on the corundum-kyanite reaction is similar to that based the andalusite reaction. The Gibbs free energy value based on solubility measurements (Reesman and Keller, 1968) is comparable to that from the andalusite reaction. Despite these facts, the value based on the kaolinite reaction cannot be ruled out as invalid because this value, in fact, when combined with the Gibbs free energy value for muscovite of Barany (1964), predicts mineral assemblages in accord with petrographic experience, whereas the value based on the andalusite reaction clearly does not.

The Third-Law entropy of pyrophyllite was recently measured by King and Weller (1970). The pyrophyllite was a natural sample, its source was not stated, but its chemical analysis is comparable with the theoretical value for pyrophyllite. The slightly low value of SiO_2 and high value of H_2O might suggest some kaolinitic contamination, but the amount is small and probably can be neglected, as was done by the authors.

The Third law entropy is 56.6 ± 0.5 Gb/gf. This is 6.7 Gb/gf less than the oxide-sum estimate, comparable with the discrepancy of 7.2 Gb/gf between the measured entropy of talc and the oxide sum. The oxide sum is the same as that obtained by adding together the entropies of 2 boehmite and 4 quartz (62.7 Gb/gf), whereas the measured value is same as that obtained by adding together the entropies of 2 diaspore and 4 quartz (56.4 Gb/gf).

The revised entropy value of pyrophyllite means that the Gibbs free energy also will be more negative. The new results for G_f^0 for pyrophyllite are given in Table 3, which uses also the new Gibbs free energy data for H_2O (Fisher and Zen, 1971) and new experimental determinations of the stability of pyrophyllite (Thompson, 1970b).

The point previously attributed to Hemley for the kaolinite-pyrophyllite reaction is replaced by the better and more recent data point of 300°C ± 10°C, 1 kbar (Reed and Hemley, 1966).

Table 3 shows that use of the new entropy value for pyrophyllite leads to nearly uniform changes of the G_f^0 values, so that the difference between the mean of the kaolinite + quartz reaction and the mean of the andalusite + quartz reaction remains at 7 kcal (compare Zen, 1969), and the result of the corundum-kyanite reaction is more negative than the result of either of the other two reactions. The more negative values are close to the measurements of Reesman and Keller (1968) of −1258.7 kcal. Reesman, on the basis of additional experiments, now prefers a value of about −1263.5 kcal (A. L. Reesman, letter, September, 1969).

Table 3. Standard (298 K, 1 bar) Gibbs free energy of formation of pyrophyllite from elements

T, °C	$P_t = P_{H_2O}$, bars	G_f^0, kcal	Reference
I. Kaolinite + 2 quartz = pyrophyllite + H_2O			
290	667	−1253.49 ± 1.27*	R. O. Fournier, 1969, oral communication
300 ± 10	1000	−1253.41 ± 1.37	Reed and Hemley, 1966
325 ± 20	1000	−1253.18 ± 1.48	Thompson, 1970b
345 ± 10	2000	−1253.09 ± 1.38	same
375 ± 15	4000	−1252.86 ± 1.20	same
390 ± 10	2000	−1252.62 ± 1.39	Althaus, 1966
405 ± 5	7000	−1253.60 ± 1.33	same
	Average	−1253.2 ± 1.3 kcal	

Average standard (298 K, 1 bar) enthalpy of formation from the elements −1342.7 ± 1.3 kcal

II. pyrophyllite = andalusite + 3 quartz + H_2O			
400 ± 15	1000	−1260.14 ± 1.55	Hemley, 1967
410 ± 15	1800	−1259.97 ± 1.52	Kerrick, 1968
430 ± 15	3900	−1259.52 ± 1.52	same
490 ± 5	2000	−1261.20 ± 1.38	Althaus, 1966
525 ± 5	7000	−1260.04 ± 1.37	same
	Average	−1260.2 ± 1.5 kcal	

Average standard (298 K, 1 bar) enthalpy of formation from the elements −1349.7 ± 1.5 kcal

III. pyrophyllite + 3 corundum = 4 kyanite + H_2O			
520 ± 5	7000	−1262.83 ± 2.45	Matsushima et al., 1967

Standard (298 K, 1 bar) enthalpy of formation from the elements −1352.3 ± 2.5 kcal

*No bracket information available.

Discussion: Muscovite, Paragonite, Pyrophyllite Data

The inconsistency in the value of the Gibbs free energy of pyrophyllite could be resolved by assigning a 7 kcal error in the Gibbs free energy for the aluminum silicate phases, as previously discussed (Zen, 1969). The known phase relations of kyanite, andalusite, and sillimanite indicate that their relative free energies cannot be in error by more than a very few hundred calories, so if one Gibbs free energy value is off by 7 kcal, all the polymorphs will be off by as much. The concordant Gibbs free energy value of pyrophyllite, calculated from the reaction pyrophyllite + 3 corundum = 4 kyanite + vapour then suggests that the value for corundum may be off by a similar amount. This conclusion, that the corundum value and the values for the aluminum silicate polymorphs are internally consistent, is borne out by the consistent Gibbs free energy of both muscovite and paragonite calculated from the "quartz present" reaction (Day, 1970; Chatterjee, in press) and from the "quartz absent" reaction (Velde, 1966; Chatterjee, in press also discussed the same point).

Thus if it is indeed true that the sillimanite value and corundum value are off by 7 kcal, then the discrepant Gibbs free energy of muscovite, based on hydrothermal data and on calorimetry, can be reconciled. As 7 kcal per two gram atoms of Al (as in andalusite and corundum) means 10 kcal per three gram atoms of Al (as in muscovite), the change would eliminate all of the present discrepancy of 10 kcal.

The Gibbs free energy of formation of K-feldspar is more negative than that of the Na-feldspar in the same structural state by about 9 kcal. Because the difference in the framework internal energy of a K-feldspar and a Na-feldspar is not expected to amount to more than a few hundred calories, the bulk of the 9 kcal should be associated with the Na-K substitution. The structures of muscovite and of paragonite are basically the same (Burnham and Radoslovich, 1964; Radoslovich, 1960), so the bulk of the free energy difference between paragonite and muscovite again could be associated with the Na-K substitution. One might expect this difference to be on the order of 8–10 kcal. The calculated difference is about 12 kcal when the high-temperature feldspar polymorphs were used. Thus one might expect that if the muscovite value is nearer −1330 than −1340 kcal, the paragonite value should be nearer −1320 than −1330 kcal. This would in fact be the case because the paragonite value also implied the same possible discrepancy in the corundum data and would be revised by precisely the same amount.

In the earlier study (Zen, 1969) it was suggested that in order to decide which of the two Gibbs free energy values of pyrophyllite was more nearly correct, two petrographic criteria could be applied. One was the breakdown of kaolinite to pyrophyllite in the presence of quartz, and the other was the reaction of pyrophyllite + microcline (a virtually unknown assemblage) to form muscovite + quartz (a ubiquitous assemblage). My discussion was partly faulty because I tacitly assumed that the chain of logical arguments can be decoupled by supposing that hydrothermal studies of the kaolinite reaction (leading to the more positive Gibbs free energy of pyrophyllite) were erroneous. It seems a bad supposition because the reactions are reported to have been reversed, and a 7 kcal error would entail a temperature error of many hundreds of degrees. The second petrographic test involving muscovite is now vitiated by the adjustment in pyrophyllite data and new uncertainties in the muscovite value itself. It appears that we could use the consistent values of −1260 kcal for pyrophyllite and −1340 kcal for muscovite, and predict that muscovite + quartz is more stable by 6 kcal, or use the value of −1253 kcal for pyrophyllite and −1330 kcal for muscovite and predict a 3 kcal margin in favor of muscovite + quartz. The combination of −1260 kcal for pyrophyllite and −1330 kcal for muscovite would imply that pyrophyllite + microcline is a more stable assemblage, contradicting all petrographic data, so these two values cannot be both correct.

One could run through a parallel series of calculations for the reaction of paragonite + quartz versus albite + pyrophyllite. The former is a common assemblage in metamorphic rocks of all grades (Zen and Albee, 1964), the latter found only rarely (Tobschall, 1969) and in rocks that include other strange assemblages such as pyrophyllite + biotite (instead of muscovite + chlorite), and thus may be out of phase equilibrium. Using values of Gibbs free energy of −1260 kcal for pyrophyllite and −1327 kcal for paragonite, the reaction at near-surface conditions is a few kcal in favour of paragonite + quartz. Analogous to the kaolinite + quartz = pyrophyllite reaction, however, changing the value of pyrophyllite to −1253 kcal would require, for consistency, changing the paragonite value to −1318 kcal, and the same conclusion on the stability of paragonite + quartz would be arrived at.

It appears that because of interdependence of the thermochemical data, no resolution of the dilemma is available short of direct calorimetric determination of the Gibbs free energy of paragonite and pyrophyllite, and redetermination of those of corundum, the aluminum silicate polymorphs, muscovite and kaolinite. This is an urgent task

Table 4.--Two sets of internally consistent Gibbs free energy of
formation values for phases. The two sets are mutually incompatible.

	Set 1		Set 2	
Andalusite	-584.13	kcal	-577.	kcal
Sillimanite	-583.60	kcal	-576.	kcal
Kyanite	-584.00	kcal	-577.	kcal
Muscovite	-1340.	kcal	-1330.	kcal
Paragonite	-1328.	kcal	-1318.	kcal
Pyrophyllite	-1260.	kcal	-1253.	kcal
Kaolinite	-910.	kcal	-902.87	kcal
Diaspore	-219.9	kcal	-216.	kcal
Corundum	-378.08	kcal	-371.	kcal

because so much of the available thermochemical data on rock-forming
minerals ultimately hinge on the correct knowledge of the thermo-
chemical parameters of corundum. Table 4 is an example of possible
sets of internally consistent data on some important minerals; one set
assumes the calorimetric corundum data to be correct, the other set
assumes the calorimetric muscovite data to be correct.

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