

## Correlated free energy values of anthophyllite, brucite, clinochrysotile, enstatite, forsterite, quartz, and talc

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### Abstract

Among the thermochemical data for rock-forming minerals in the system  $\text{MgO-SiO}_2\text{-H}_2\text{O}$ , those for orthoenstatite and for talc are highly uncertain. The tightly-bracketed reactions (1) talc = 3 enstatite + quartz + steam, and (2) talc + forsterite = 5 enstatite + steam permit the simultaneous calculation of the standard Gibbs free energies of formation for both orthoenstatite and talc:  $-1457.27 \pm 4 \text{ kJ mol}^{-1}$  and  $-5516.37 \pm 10 \text{ kJ mol}^{-1}$ , respectively. Using the calculated free energies of talc and enstatite and six reversed brackets for four reactions involving anthophyllite (Greenwood, 1963), the standard Gibbs free energy of formation of anthophyllite was recomputed to be  $-11,331.8 \text{ kJ mol}^{-1}$  with an estimated uncertainty of  $\pm 17 \text{ kJ mol}^{-1}$ ; this value is more positive than previous estimates because of the revised value for enstatite.

The reversed brackets of Johannes (1968) for the reaction clinochrysotile + brucite = 2 forsterite + 3 steam were used to calculate the free energy of formation of clinochrysotile. The value obtained ( $-4,030.84 \pm 4.0 \text{ kJ mol}^{-1}$ ) agrees well with published values. As an independent check, the free energy of talc was calculated, using the calculated free energy of clinochrysotile and a single reversed bracket for the reaction 5 clinochrysotile = 6 forsterite + talc + steam (Chernosky, 1973). The result,  $-5,522.91 \pm 15.62 \text{ kJ mol}^{-1}$ , is in satisfactory agreement with the above-cited value.

Our results confirm the geometry of the  $P$ - $T$  diagram for anthophyllite, enstatite, talc, forsterite, quartz, and steam suggested by Greenwood, through inconsistencies in the slopes of Chernosky's experimental results and those of Greenwood remain to be resolved. Nevertheless, our results indicate that an internally consistent  $P$ - $T$  net, using the experimental data of Chernosky (1976) and Greenwood (1963) for anthophyllite, enstatite, talc, forsterite, and quartz, should be possible.

### Symbols and notations

A, anthophyllite,  $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$

B, brucite,  $\text{Mg}(\text{OH})_2$

F, forsterite,  $\text{Mg}_2\text{SiO}_4$

E, orthoenstatite,  $\text{MgSiO}_3$

Chr, clinochrysotile,  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$

Tc, talc,  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$

Q, quartz,  $\text{SiO}_2$

W, steam,  $\text{H}_2\text{O}$

$G_f^\circ$ , standard Gibbs free energy of formation (298.15 K, 1 bar) of a phase from the elements, in joules

$S_f^\circ$ , standard entropy of formation (298.15 K, 1 bar)

of a phase from the elements, in  $\text{J mol}^{-1}$

$S$ , third-law entropy of a phase

$V$ , volume

$\Delta V_s$ , volume change of the solid phases for a given reaction

$\Delta S_s$ , change of the entropy of formation of the solid phases for a given reaction

$G^*$ , Gibbs free energy of  $\text{H}_2\text{O}$  at  $T$  and  $p$  according to Burnham *et al.*'s (1969) data, consistent with the standard state of 298.15 K and 1 bar

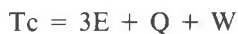
$\sigma$ , the conventional thermochemical uncertainty, sigma, stated as two standard errors

1 thermochemical calorie = 4.1840 joules

### Introduction

The free energy of formation of various hydrous and anhydrous magnesium silicate phases has been a topic of lively discussion in recent petrologic literature (Hostetler and Christ, 1968; Hostetler *et al.*, 1971; Christ *et al.*, 1973; Bricker *et al.*, 1973; Hemley *et al.*, Parts I and II, 1976). One major source of uncertainty is that the heat of formation for talc (Barany, 1963) results in a value for the free energy of formation that is too negative (talc too stable) compared with recent phase equilibrium and solubility measurements. Another problem is the uncertainty in the value for the free energy of formation of enstatite. The values listed in Robie and Waldbaum (1968) and in Stull and Prophet (1971) are for clinoenstatite, yet in making calculations, workers have been forced to apply these values to orthoenstatite.

Chernosky (1974) recently redetermined the two equilibria



and

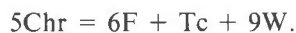


by hydrothermal methods, in which the reversals of the equilibria were carefully established. Assuming that Chernosky's reversed  $P$ - $T$  brackets are correct and that the locations of the two equilibria are mutually consistent and deal with phases in the same structural states (so that the thermodynamic properties of each phase are functions of  $P$  and  $T$  alone), we were able to extract new thermodynamic data for talc and for enstatite by simultaneous solution of the equations for the above reactions; thence, by application to Greenwood's (1963) experimental data, we obtained thermodynamic data for anthophyllite and obtained a "consistent" set of values.

The calculated free energy for talc was checked by the following procedure. We used the bracketing data of Johannes (1968) for the reaction



to calculate the free energy of formation of clinochrysotile. Using this value, the free energy of formation of talc was calculated from the bracketing data of Chernosky (1973) for the reaction



This paper reports the results of the calculations and some comments derived from them. The standard state for the enthalpies and Gibbs free energies of

formation of a phase,  $\Delta H_f^\circ$  (298.1) and  $\Delta G_f^\circ$  (298.1), refer to the standard state of the elements at 298.15 K and 1 bar. These quantities are simply abbreviated as  $H_f^\circ$  and  $G_f^\circ$  without further specification of  $T$  (=298.15 K) or  $P$  (= 1 bar).

### Basic data and calculations

The basic thermochemical constants available for the phases involved in the calculations are presented in Table 1. The heats of formation, and hence free energies, of clinochrysotile, forsterite, and talc were adjusted to take into account the actual state of  $\alpha$ -quartz when the heats of solution of these phases (Hemingway and Robie, unpublished data) were measured in a mixture of 10.05 weight percent HF and 10.05 weight percent HCl. The correction factor is +1.25 kJ mol<sup>-1</sup> of SiO<sub>2</sub> in the silicate. For forsterite, the free energy selected was based on the heat-of-formation data (corrected by Hemingway and Robie) obtained on a synthetic sample by King *et al.* (1967) rather than on the data obtained by Torgeson and Sahama (1948) and reported in Robie and Waldbaum (1968). The free-energy value for brucite reported by Robie and Waldbaum (1968),  $-834.53 \pm 3.30$  kJ ( $-199,458 \pm 790$  cal) mol<sup>-1</sup>, was used in preference to the value  $-831.49$  kJ mol<sup>-1</sup> calculated from the solubility-product constant of brucite by McGee and Hostetler (1973). Robie and Waldbaum's value was selected because it is in better agreement with the value calculated by Fisher and Zen (1971),  $-836.97 \pm 2.9$  kJ ( $-200,040 \pm 690$  cal) mol<sup>-1</sup>, from the hydrothermal bracketing data of Barnes and Ernst (1963).

Values for  $G^*(\text{H}_2\text{O})$ , the standard Gibbs free energy of water, are from the tabulation by Fisher and Zen (1971), which is based on the  $P$ - $V$ - $T$  data of Burnham *et al.* (1969). The volumes of the phases are those given by Robie *et al.* (1967); the volume of anthophyllite was determined by Greenwood (1963) and has been used previously by Zen (1971).

The method of calculation is identical with that used by Fisher and Zen (1971) and by Zen (1972). The "summation method" to calculate the entropy term (Zen, 1972) was used, provided that the entropy for each solid phase participating in a reaction was known as a function of temperature; third-law entropies tabulated by Robie and Waldbaum (1968) have been converted to entropies of formation from the elements by Zen (1972).

The entropy of orthoenstatite is unknown, so the value for clinoenstatite, measured by Kelley (1943), was used. Since there is no order-disorder transition

TABLE 1. Thermodynamic parameters of phases

	$H_f^\circ(298,1)$ kJ/mol		$G_f^\circ(298,1)$ kJ/mol		$S_f^\circ(298,1)$ kJ/mol/deg		$V(298,1)$ joule/bar/gf	
Anthophyllite $Mg_7Si_8O_{22}(OH)_2$	-12,083.9	(2)	-11,365.06 ± 16	(2)	-2.411	(2)	26.446	(8)
			-11,368.68	(6)				
			-11,331.82 ± 17 <sup>†*</sup>	(4)				
Brucite $Mg(OH)_2$	-925.58 ± 3.3	(1)	-834.53 ± 3.3	(1)	-0.3051	(2)	2.4635 ± .0067	(9)
			-831.49	(10)				
Clinochrysotile $Mg_3Si_2O_5(OH)_4$	-4,361.37 ± 4.2	(3)	-4,034.00 ± 4.2 <sup>*</sup>	(3)				
			-4,030.8 ± 4 <sup>*</sup>	(4)	-1.098	(4)	10.715 ± .029	(4)
Clinoenstatite $MgSiO_3$	-1,548.92 ± 4	(5)	-1,462.07	(5)	-.2913	(4)	3.1476 ± .0050	(9)
	-1,548.67 ± 1.8	(1)	-1,461.86 ± 1.9	(1)				
Enstatite $MgSiO_3$			-1,457.27 ± 4 <sup>*</sup>	(4)				
	-1,547.29	(11)	-1,460.43	(11)				
Forsterite $Mg_2SiO_4$	-2,170.166 <sup>*</sup>	(12)	-2,051.70 ± 1.9 <sup>*</sup>	(12)	-.3990	(2)	4.3786 ± .0029	(9)
Quartz $SiO_2$	-910.648 ± 1.7	(1)	-856.239 ± 1.72	(1)	-.1825	(2)	2.2689 ± .0003	(9)
Talc $Mg_3Si_4O_{10}(OH)_2$	-5,916.20 ± 7.2 <sup>*</sup>	(3)	-5,536.63 ± 7.2 <sup>*</sup>	(1)	-1.273	(2)	13.6252 ± .0259	(9)
			-5,522.9 ± 8.4	(7)				
			-5,518.7	(13)				
			-5,516.37 ± 10.5 <sup>†*</sup>	(4)				

Number in parentheses refers to source of data: (1) Robie and Waldbaum (1968); (2) Zen (1972); (3) calculated from King et al. (1967); (4) this study; (5) Stull and Prophet (1971); (6) Mel'nik and Onoprienko (1969); (7) Bricker et al. (1973); (8) Zen (1971); (9) Robie et al. (1967); (10) McGee and Hostetler (1973); (11) calculated from Newton et al. (1974); (12) Hemingway and Robie (unpub. data); (13) Hostetler et al. (1971).

\*Values corrected in accordance with the revised value for the heat of solution of quartz used to compute calorimetric data of the silicate phases.

†Value refers to orthoenstatite.

or problem of site occupancy in pure  $MgSiO_3$  polymorphs, the entropy difference between the ortho and clino varieties of enstatite should be mainly one of configurational contributions involving second-order neighbors, and this difference should be small. An error of, say, 5 J deg<sup>-1</sup> mol<sup>-1</sup> could introduce an error in the Gibbs free energy of a few kJ per mole of enstatite. Although Chernosky's experiments cover relatively small spans of temperature, any sizable sys-

tematic error in the entropy of enstatite should nevertheless be detectable by a systematic change in the calculated value for  $G_f^\circ$  as a function of the equilibrium temperature. For the reaction  $Tc + F = 5E + W$ , five moles of E are involved and the temperature span is 79°; if the error in the entropy of enstatite is 4 J mol<sup>-1</sup>, there should be an error of  $5 \times 4 \times 79 =$  about 1.6 kJ. The data from the calculations will show that there is no such systematic deviation. We

TABLE 2. Gibbs energy difference functions for two equilibria in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O

(1) Tc = 3E + Q + W

$$G_f^\circ(Tc) - 3G_f^\circ(E) = G_f^\circ(Q) + \Delta V_s \Delta P - \Sigma \Delta S_s \Delta T + G^*(H_2O)$$

P, kbar	T° C	G <sub>f</sub> <sup>o</sup> (Tc) - 3G <sub>f</sub> <sup>o</sup> (E), kJ/mol		
		Med. temp.	Lower temp. limit	Upper temp. limit
0.5	660 ± 12	-1144.32	-1143.11	-1145.52
1.0	700 ± 20	-1144.68	-1142.89	-1146.42
2.0	733 ± 7	-1144.70	-1144.13	-1145.25
Average and standard error		-1144.56 ± .21	-1143.38 ± .66	-1145.76 ± .66

(2) Tc + F = 5E + W

$$G_f^\circ(Tc) - 5G_f^\circ(E) = -G_f^\circ(F) + \Delta V_s \Delta P - \Sigma \Delta S_s \Delta T + G_f^*(H_2O)$$

P, kbar	T° C	G <sub>f</sub> <sup>o</sup> (Tc) - 5G <sub>f</sub> <sup>o</sup> (E), kJ/mol		
		Med. temp.	Lower temp. limit	Upper temp. limit
0.5	611 ± 10	1770.27	1771.20	1769.34
1.0	647 ± 10	1769.84	1770.64	1769.04
2.0	652 ± 12	1771.30	1772.15	1770.45
3.0	677 ± 15	1768.97	1771.35	1769.30
4.0	696 ± 10	1769.49	1770.14	1768.83
Average and standard error		1769.97 ± .88	1771.10 ± .76	1769.39 ± .62

	Med. temp.	Lower temp. for (1) Upper temp. for (2)	Upper temp. for (1) Lower temp. for (2)
G <sub>f</sub> <sup>o</sup> (E) (298,1), kJ/mol	-1457.27 ± 4.2	-1456.39	-1458.43
G <sub>f</sub> <sup>o</sup> (Tc) (298,1), kJ/mol	-5516.37 ± 10.5	-5512.54	-5521.04

Bracketing data from Chernosky (1974) except for 2 kbar entry of (1) from Skippen, 1971.

therefore assume that the entropy of clinoenstatite is a good approximation for orthoenstatite with an uncertainty of no more than 1-2 Jdeg<sup>-1</sup>mol<sup>-1</sup>.

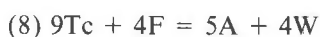
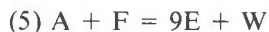
Another major source of uncertainty is the entropy of anthophyllite. The low-temperature heat capacity of anthophyllite has not been measured. The entropy value used by Zen (1971) was calculated by Mel'nik and Onoprienko (1969) from the experimental data of Greenwood (1963). This entropy value is therefore suspect. Again, however, the consistency of the calculated results to be presented suggests that error introduced by this source is probably not serious.

Using these data, difference functions (Thompson, 1973) for the two reactions: (1) G<sub>f</sub><sup>o</sup>(Tc) - 3G<sub>f</sub><sup>o</sup>(E), and (2) G<sub>f</sub><sup>o</sup>(Tc) - 5G<sub>f</sub><sup>o</sup>(E) were computed (Table 2). The median temperature of Chernosky (1976) and Skippen (1971), for reaction 1 at 2kbar<sup>1</sup> was used to calculate the initial set of values, and the average values for each reaction were then used to solve the

<sup>1</sup> Skippen's study was made under Ni-NiO buffer conditions, implying a lower reaction temperature than if no buffer were used. The activity of H<sub>2</sub>O must have been greater than 0.998, and the thermochemical correction is too small to concern us, as the error on the chemical potential of H<sub>2</sub>O must be less than 10 cal/mol.

two simultaneous equations to obtain the median values of  $G_f^\circ$  (Tc) and  $G_f^\circ$  (E). No adjustment of temperatures seems warranted, because the initial set of median values shows sufficiently good clustering [-1,144,562 J, with an observed range (o.r.) of 213 J for reaction 1 and +1,769,974 J, with o.r. of 883 J for reaction 2]. Next, we calculated the difference functions for the lower and upper temperature brackets for each pressure and each reaction. We thus obtained the average values for each reaction at both temperature limits; the clustering was good enough to justify use of these averages for further manipulations [o.r. = 661 J for (1) and 761 J for (2), low-temperature limits; o.r. = 661 J for (1) and 623 J for (2), high-temperature limits]. Using the low-temperature value of one reaction and the high-temperature value for the other to solve the simultaneous equations, we obtained estimates of the range of  $G_f^\circ$  (E) as o.r. = 1.3 kJ, and for  $G_f^\circ$  (Tc) as 4.6 kJ. These ranges, together with the uncertainties in the other quantities in the calculations, then led to our estimated  $\sigma$  uncertainty in the final values:  $G_f^\circ$  (E) =  $-1457.3 \pm 4.2$  kJ mol<sup>-1</sup>, and  $G_f^\circ$  (Tc) =  $5516.4 \pm 10.5$  kJ mol<sup>-1</sup>. These values refer, of course, to 298.15 K and 1 bar.

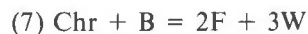
Next, the results of the preceding calculations were applied to four reactions bracketed by Greenwood (1963) that involve anthophyllite (Table 3):



The median temperature values for Greenwood's brackets and the entropy value of Mel'nik and Onoprienko (1969) were used in the calculations (Table 3). The mean and standard error for  $G_f^\circ$  (A) at 298,1 are  $-11,331.84 \pm 1.70$  kJ mol<sup>-1</sup>. The small magnitude of the standard error, which measures the scatter of results from individual brackets from the mean, is gratifying, considering the fact that the four reactions were experimentally totally independent of one another and considering the uncertainties of Greenwood's  $P$ - $T$  values. These results show no discernible correlation with the equilibria, temperature, or pressure.

The  $\sigma$  uncertainty to be attached to the anthophyllite value was calculated, using the uncertainties given in Table 1 and the usual procedure to compute uncertainties of sums (Fisher and Zen, 1971). The final value is  $-11,332 \pm 17$  kJ mol<sup>-1</sup>.

An independent check on the  $G_f^\circ$  (Tc) value calculated earlier can be made by considering the following two experimentally bracketed dehydration reactions (Table 3):



and



$G_f^\circ$  (Chr) was calculated, using the thermodynamic data in Table 1 and the median  $P$ - $T$  coordinates for five reversed brackets (Johannes, 1968) for reaction 7. The mean value of  $G_f^\circ$  (Chr) for the five brackets is  $-4030.8 \pm 4$  kJ mol<sup>-1</sup>. Assuming this value is correct,  $G_f^\circ$  (Tc) can be calculated from the midpoint of a single bracket for reaction (8) determined by Chernosky (1973). The result,  $G_f^\circ$  (Tc) =  $-5522.9 \pm 15.6$  kJ mol<sup>-1</sup>, is in good agreement with the calculated value ( $-5516.4 \pm 10.5$  kJ mol<sup>-1</sup>).

## Discussion

### Anthophyllite

Mel'nik and Onoprienko (1969) calculated the thermodynamic constants for anthophyllite from Greenwood's (1963) bracketing data for the reaction  $A = 7E + Q + W$ . Using the heat-capacity and entropy values presented by Mel'nik and Onoprienko, Zen (1971) also calculated the free-energy and enthalpy values for anthophyllite on the basis of bracketing data for this reaction and for the reaction  $9Tc + 4F = 5A + 4W$ , also bracketed by Greenwood (1963). The calculated  $G_f^\circ$  (A) differed by 15–20 kJ mol<sup>-1</sup> depending on which reaction was used; the value preferred by Zen was  $-11,365 \pm 12$  kJ ( $-2716.3 \pm 3$  kcal) mol<sup>-1</sup>. The revised and correlated calculations now provide a more coherent group of values for all six of Greenwood's brackets for four different equilibria. The discrepancy previously mentioned is largely gone, and the difference of about 33 kJ from the earlier results stems directly from the more positive value for enstatite. An uncertainty of  $\pm 17$  kJ is retained for anthophyllite, because there is no improvement on the entropy of this phase, the single biggest source of uncertainty.

It is interesting to check the reasonableness of the present calculations by computing the quantity  $4G_f^\circ$  (E)  $- 2G_f^\circ$  (diopside) and comparing it with the quantity  $G_f^\circ$  (A)  $- G_f^\circ$  (tremolite)<sup>2</sup> because, to a first-order

<sup>2</sup>  $4\text{MgSiO}_3 - 2\text{CaMgSi}_2\text{O}_6 = \text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2 - \text{Ca}_2\text{Mg}_3\text{Si}_8\text{O}_{22}(\text{OH})_2$

TABLE 3. Gibbs energies of anthophyllite, clinochrysotile, and talc calculated from reversed equilibria in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O

(3) $A + F = 9E + W^a$			
$G_f^\circ(A) = 9 G_f^\circ(E) - G_f^\circ(F) + \Delta V_s \Delta P - \Sigma \Delta S_s \Delta T + G^*(H_2O)$			
P kbar	T°C	$G_f^\circ(A)$ , cal mol <sup>-1</sup>	$G_f^\circ(A)$ , kJ - mol <sup>-1</sup>
2.0	703	-2,708,679	-11,333.1
(4) $A = 7E + Q + W^a$			
$G_f^\circ(A) = 7 G_f^\circ(E) + G_f^\circ(Q) + \Delta V_s \Delta T - \Sigma \Delta S_s \Delta T + G^*(H_2O)$			
P kbar	T°C	$G_f^\circ(A)$ , cal mol <sup>-1</sup>	$G_f^\circ(A)$ , kJ - mol <sup>-1</sup>
2.0	765 ± 5°	-2,708,587	-11,332.7
(5) $7 Tc = 3A + 4 Q + 4 W^a$			
$3 G_f^\circ(A) = 7 G_f^\circ(Tc) - 4 G_f^\circ(Q) - \Delta V_s \Delta P + \Sigma \Delta S_s \Delta T - 4 G^*(H_2O)$			
P kbar	T°C	$G_f^\circ(A)$ , cal mol <sup>-1</sup>	$G_f^\circ(A)$ , kJ - mol <sup>-1</sup>
2.0	703 ± 9°	-2,708,850	-11,333.8
(6) $9 Tc + 4 F = 5 A + 4 W^a$			
$5 G_f^\circ(A) = 9 G_f^\circ(Tc) + 4 G_f^\circ(F) - \Delta V_s \Delta T + \Sigma \Delta S_s \Delta T - 4 G^*(H_2O)$			
P kbar	T°C	$G_f^\circ(A)$ , cal mol <sup>-1</sup>	$G_f^\circ(A)$ , kJ - mol <sup>-1</sup>
1.0	667 ± 4°	-2,707,836	-11,329.6
2.0	685 ± 10°	-2,707,967	-11,330.1
4.0	685 ± 8°	-2,708,326	-11,331.6
	Average	-2,708,043	-11,330.5
(7) $Chr + B = 2 F + 3 W^b$			
$G_f^\circ(Chr) = 2 G_f^\circ(F) - G_f^\circ(B) + \Delta V_s \Delta P - \Delta S_s \Delta T + 3 G^*(H_2O)$			
P kbar	T°C	$G_f^\circ(Chr)$ , cal mol <sup>-1</sup>	$G_f^\circ(Chr)$ , kJ - mol <sup>-1</sup>
0.5	355 ± 25	-963,321 ± 1635	-4,030.5
1.0	360 ± 10	-963,174 ± 944	-4,029.9
3.0	390 ± 10	-963,353 ± 912	-4,030.7
4.0	412 ± 18	-963,819 ± 1208	-4,032.6
7.0	427 ± 13	-963,419 ± 977	-4,030.9
	average	-963,393 ± 950	-4,030.8 ± 4.0
(8) $5 Chr = 6 F + Tc + 9 W^c$			
$G_f^\circ(Tc) = 5 G_f^\circ(Chr) - 6 G_f^\circ(F) - \Delta V_s \Delta P + \Delta S_s \Delta T - 9 G^*(H_2O)$			
P kbar	T°C	$G_f^\circ(Tc)$ , cal mol <sup>-1</sup>	$G_f^\circ(Tc)$ , kJ - mol <sup>-1</sup>
2.0	437 ± 5	-1,320,006 ± 3,733	-5,522.9 ± 15.6

Bracketing data from a, Greenwood (1963); b, Johannes, (1968); and c, Chernosky, (1976).

approximation, the structural environment of the  $M_2$  and  $M_4$  cation sites and their associated  $\text{SiO}_4$  tetrahedra should be the same in enstatite and anthophyllite and in diopside and tremolite, respectively. In addition to the uncertainty in the free energy of anthophyllite and enstatite, the free energies of diopside and tremolite are also questionable.  $G_f^\circ$  (tremolite) given by Robie and Waldbaum (1968) is  $-11,627 \pm 18 \text{ kJ mol}^{-1}$ , a rather large uncertainty; Zen (1972) on the basis of Boyd's (1959) experiments estimated  $-11,611 \pm 12 \text{ kJ mol}^{-1}$ .  $G_f^\circ$  (diopside) value given by Robie and Waldbaum is  $-3036 \pm 9 \text{ kJ mol}^{-1}$ , again a large uncertainty. The value itself is simply the mean of two disparate measurements, one on a natural non-end-member diopside of good crystallinity, the other a synthetic and presumably stoichiometric end-member diopside of uncertain crystal structure and phase purity. Using the values just cited (and the  $-11,611 \text{ kJ mol}^{-1}$  value for tremolite) we get a result of  $-121 \text{ kJ mol}^{-1} \text{ Ca}$  for  $4G_f^\circ(\text{E}) - 2G_f^\circ(\text{D})$  and  $-138 \text{ kJ mol}^{-1} \text{ Ca}$  for  $G_f^\circ(\text{A}) - G_f^\circ(\text{tremolite})$ . The difference is well within the errors.

### Clinochrysotile

The  $G_f^\circ(\text{Chr})$  calculated from Johannes' bracketing data (Table 3),  $-4030.8 \pm 4.0 \text{ kJ mol}^{-1}$ , is  $3.9 \text{ kJ mol}^{-1}$  more positive (chrysotile less stable) than the value calculated from the heat of formation value, corrected for 2 moles of  $\text{SiO}_2$ , obtained by King *et al.* (1967); the results are compatible within the errors of calculation. Hostetler and Christ (1968) determined the activity-product constant of clinochrysotile; however, the  $G_f^\circ(\text{Chr})$  value they cited is based on a recalculation of King's value rather than on their own experimental data. A revised value, using the experimental data but not corrected for the heat of solution of quartz, is  $-4038.35 \text{ kJ}$  (Hemley *et al.*, Part I, 1976).

If McGee and Hostetler's (1973) value for  $G_f^\circ(\text{B})$  is assumed correct, a value of  $-4027.13 \text{ kJ mol}^{-1}$  is obtained from the bracketing data of Johannes for reaction 7 (Table 3). This value may be too positive (clinochrysotile less stable).

### Enstatite

The enstatite value calculated from Chernosky's data represents a significant change from the value tabulated for clinoenstatite in Robie and Waldbaum (1968). Assuming the mutual consistency of Chernosky's two curves, and bearing in mind the possibility of an entropy error of as much as  $2 \text{ J mol}^{-1}$

$\text{deg}^{-1}$ , a  $\sigma$ -uncertainty of  $6 \text{ kJ}$  seems reasonable for the free energy value. Skippen (1971) and Williams (1971) have estimated that the Gibbs free energy of enstatite should be more negative than the clinoenstatite value by about  $4 \text{ kJ}$  ( $1 \text{ kcal}$ ); certainly a more negative value is expected because the ortho-form is more stable at  $298 \text{ K}$  and  $1 \text{ bar}$ . Our results deviate in the opposite direction by about  $2.4 \text{ kJ mol}^{-1}$ . However, this is not too distressing because of the poor quality of the value for clinoenstatite. The same synthetic material was used by Kelley (1943) for low-temperature heat capacity measurements and by Torgeson and Sahama (1948) for heat of solution measurements. The sample was synthesized from powdered periclase ("c.p. magnesium oxide") and "powdered silica" in 1:1 ratio, heated repeatedly at  $1300^\circ\text{C}$ , and ground in between heating. The final product "analyzed 92.0% magnesium metasilicate, 5.6% magnesium orthosilicate, and 2.4% uncombined silica" (Kelley, 1943). The results of calorimetric measurements were then corrected for these phase impurities. The proportions of the "orthosilicate," "metasilicate" and "uncombined silica" were determined by chemical analysis. Uncombined  $\text{MgO}$  was dissolved in dilute  $\text{HCl}$ ; uncombined silica was dissolved in  $\text{NaOH}$ , and "orthosilicate" was dissolved in  $0.2\text{N HCl}$  on a steambath for  $1\frac{1}{2}$  hour (Jander and Wuhler, 1936). The chemical analyses were not, as far as can be ascertained, supported by other means to determine the phase purity of the product or the nature of the "clinoenstatite."<sup>3</sup> Finally, Stull and Prophet (1971) pointed out that Torgeson and Sahama (1948) appear to have made the water-adsorption correction to the heat of solution of  $\text{SiO}_2(\text{c})$  in the wrong direction. They revised the  $G_f^\circ(\text{E})$  value to  $-1462.07 \text{ kJ mol}^{-1}$ , which is  $4.8 \text{ kJ mol}^{-1}$  more negative (clinoenstatite more stable) than the value calculated earlier (Table 2).

Newton *et al.* (1974) measured the heat of solution of phase-pure orthoenstatite in a lead borate melt at  $968 \text{ K}$ . Their high-temperature value,  $37.45 \pm 1.38 \text{ kJ mol}^{-1}$ , when recalculated to a heat of formation from the elements at  $298 \text{ K}$ , is  $-1547.29 \text{ kJ mol}^{-1}$ . Assuming that this value is correct and that the entropy of clinoenstatite closely approximates that of orthoenstatite, we obtain a value of  $-1460.43 \text{ kJ mol}^{-1}$  for  $G_f^\circ$  (orthoenstatite). This value is only  $3.2 \text{ kJ mol}^{-1}$  more negative than the value calculated from

<sup>3</sup> For example, a product consisting of 99.5% clinoenstatite with an assumed  $G_f^\circ$  of  $-1457.7 \text{ kJ}$  and 0.5% of forsterite with  $G_f^\circ$  of  $-2052.6 \text{ kJ}$  would lead to a bulk, apparent  $G_f^\circ$  of  $-1460 \text{ kJ}$ .

the hydrothermal bracketing data and, interestingly, is also more positive than the value tabulated by Robie and Waldbaum (1968).

### Talc

Robie and Waldbaum (1968) reported the calorimetrically determined  $G_f^\circ$  (Tc) value as  $-5541.65 \pm 7.20$  kJ ( $-1,324,486 \pm 1720$  cal)  $\text{mol}^{-1}$  and the third law entropy as  $260.8$   $\text{Jmol}^{-1}\text{deg}^{-1}$  ( $62.34$   $\text{gb mol}^{-1}$ ). This entropy value,  $S_{\text{calor.}}$ , is much lower than the oxide sum value,  $S_{\text{oxide}}$ , of  $290.8$   $\text{Jmol}^{-1}\text{deg}^{-1}$  ( $69.5$   $\text{gb/mol}$ ) ( $S_{\text{calor.}} - S_{\text{oxide}} = -30$   $\text{Jmol}^{-1}\text{deg}^{-1}$  or  $-7.2$   $\text{gb mol}^{-1}$ ), but the anomalously low entropy is corroborated by similarly low entropy for its structural analog, pyrophyllite ( $S_{\text{calor.}} - S_{\text{oxide}} = -28.0$   $\text{Jmol}^{-1}\text{deg}^{-1}$ ; see King and Weller, 1970; Zen, 1972). This fact, together with the observation that  $S_{\text{calor.}}$  for other layer silicates does not agree with  $S_{\text{oxide}}$  (for example, chrysotile, for which  $S_{\text{calor.}} - S_{\text{oxide}} = -31.4$   $\text{Jmol}^{-1}\text{deg}^{-1}$ ) does not support Bricker *et al.*'s (1973) contention that the entropy of talc obtained by oxide summation is superior. The magnitude of the free energy value for talc, however, continues to worry geochemists, because it does not seem to agree with values derived by other methods or by consideration of natural stability relations (Bricker *et al.*, 1973; Hostetler and Christ, 1971). The two  $G_f^\circ$  (Tc) values calculated from bracketing data,  $-5516.4 \pm 10.5$  kJ  $\text{mol}^{-1}$  (Table 2) and  $-5522.9 \pm 15.6$  kJ  $\text{mol}^{-1}$  (Table 3), agree with the values calculated from solubility studies,  $-5523 \pm 8$  kJ  $\text{mol}^{-1}$  (Bricker *et al.*, 1973) and  $-5518.7$  kJ  $\text{mol}^{-1}$  (Hostetler *et al.*, 1971). Hemley *et al.* (Part II, 1976) gave  $-5524.6 \pm 5.9$  kJ  $\text{mol}^{-1}$ .

Robie and Stout (1963) calculated the equilibrium  $\text{Tc} = 3\text{E} + \text{Q} + \text{W}$  over the range 600–1100 K and found the results, using the thermodynamic constants of clinoenstatite, in agreement with Bowen and Tuttle's (1949) experimental data for this system. The results of Bowen and Tuttle are now demonstrated to be in error because the reactions were not reversed (compare Bowen and Tuttle, 1949, with Chernosky, 1974). Also, if the more positive values for  $G_f^\circ$  (E) were used, the agreement between Robie and Stout's calculations and the results of Bowen and Tuttle would disappear.

### The phase diagram

The phases A, Tc, F, E, Q, and W are pure stoichiometric phases (except for W, which we assume to be stoichiometric in hydrothermal experiments) in the ternary system  $\text{MgO-SiO}_2\text{-H}_2\text{O}$ . A multisystem having one degree of negative freedom is

present. Assuming Q and F do not coexist under the conditions of hydrothermal equilibria, only those invariant points, indifferent crossings, and univariant lines that do not imply the existence of the reaction  $\text{F} + \text{Q} = 2\text{E}$  can be admitted. This leaves the invariant points (Q), (F) and the indifferent crossing  $(\text{Q}, \text{Tc}) \times (\text{E}, \text{F})$ . The anhydrous reaction  $\text{Tc} + 4\text{E} = \text{A}$  involves a net volume increase to the right. The volume change,  $0.23$  J/bar, is significantly larger than the sums of the uncertainties of the volumes of the phases, so the sign of the  $\Delta V_s$  term seems real, and anthophyllite appears to be truly on the low-pressure side of this reaction.

Greenwood (1963) suggested a  $P$ - $T$  net to account for his experimental data; this is given by Figure 1. All the curves except  $\text{Tc} + 4\text{E} = \text{A}$  have been experimentally determined by Chernosky (1974) and Greenwood (1963); as shown these curves are mutually consistent to the extent that they produce a set of acceptably consistent free-energy values for the phases. This consistency is a rather stringent test, because only Chernosky's curves were used to get the values for enstatite and talc, and if Greenwood's curves were not mutually consistent and also consistent with Chernosky's curves, large discrepancies in the computed values would have resulted.

Unfortunately, mutual consistency of the derived free-energy values is only a necessary, not sufficient, condition for the consistency of the parent curves because the free energies are rather insensitive functions of the locations of the curves (a fact which makes it feasible to derive reasonable thermochemical data from hydrothermal equilibria of moderate quality). Chernosky (1974) suggested that, on the basis of the univariant scheme (Zen, 1966), Greenwood's univariant reaction  $\text{Tc} + \text{F} = \text{A} + \text{W}$  or (Q,E) should be less steep than Chernosky's univariant reaction  $\text{Tc} + \text{F} = \text{E} + \text{W}$  or (A,Q), but this is not borne out by the data, even though both curves have yielded consistent results.<sup>4</sup>

A second way to resolve the dilemma, also pointed out by Chernosky (1974), is that the  $P$ - $T$  diagram ought to be inverted. Chernosky (1974) considered this improbable because of the apparent need to conclude thereby that the reaction  $\text{T} + \text{E} \rightarrow \text{A}$  is favored by an increase in pressure. Hemley *et al.* (Part II, 1976), however, produced an ingenious reorientation of the inverted  $P$ - $T$  diagram that obviates this diffi-

<sup>4</sup> Note that the equation numbers (1), (3) on one hand and (2), (4) on the other have been accidentally reversed in Chernosky's (1974) statement of the same problem.



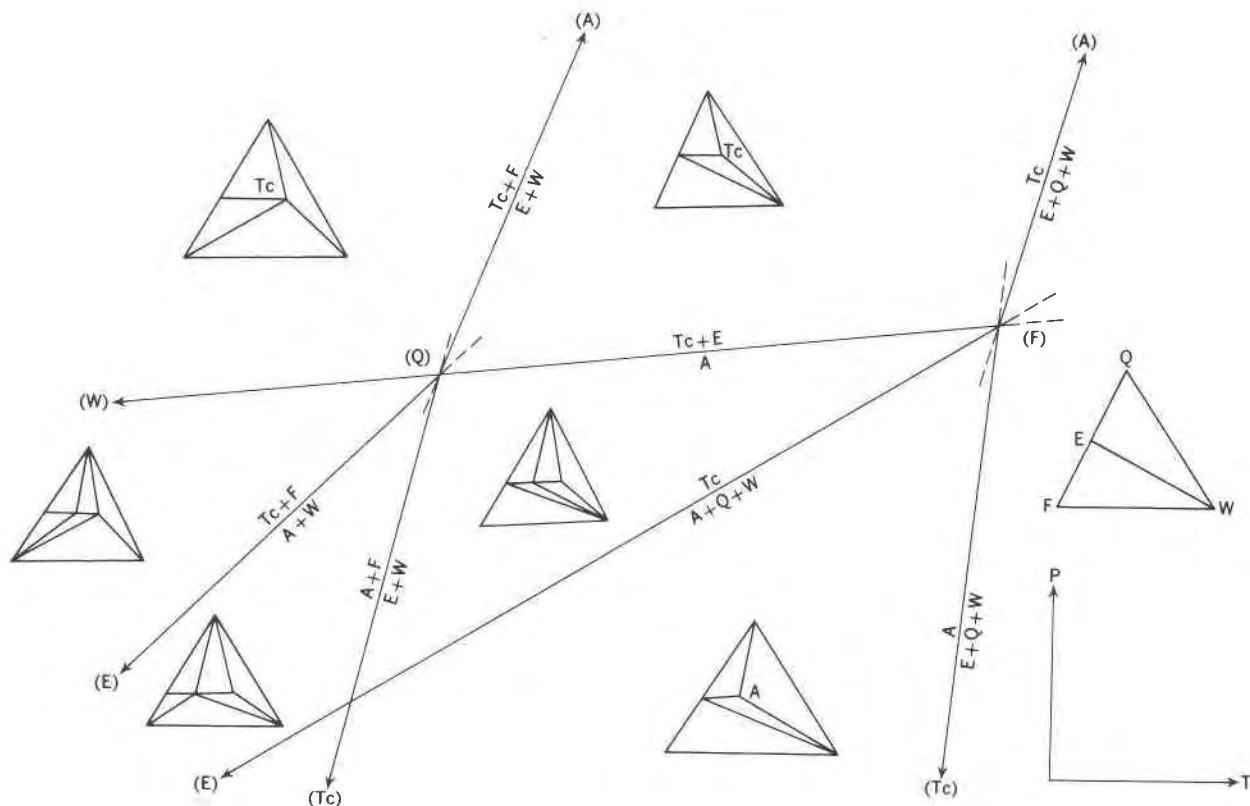


FIG. 1. Chemography about the stable invariant points (Q) and (F), modified from Greenwood (1963).

culty and that could explain many of the known experimental data, including those of Hemley *et al.* (Part II, 1976). It will be interesting to find out if further experiments can resolve the inconsistencies that remain [for instance, Greenwood's (1963) and Chernosky's (1974) data indicated that the invariant point (Q) was located at a pressure in excess of 3 kbar, but Hemley *et al.* (Part II, 1976) placed this at a few hundred bars only]. Caveat Emptor.

One lesson to be learned from this discussion is that it is impractical to calculate useful phase diagrams from thermochemical data, unless the data are consistently of extremely high quality. Because free energies are insensitive functions of the locations of the univariant curves, any small error in the free energy values will lead to large errors in the location of the curves. This can be appreciated in the following way. Such calculations, if they involve hydrous phases (and, of necessity, they usually do), basically amount to matching the sums of free-energy values of the solid phases against the free energy of  $H_2O$  until null points are obtained at particular pairs of  $P$  and  $T$  values. At typical pressure values of a few kilobars or less, the free energy of  $H_2O$  changes by about 2.5 kJ

per 20 degrees (based on Burnham *et al.*'s (1969) data; see Fisher and Zen, 1971). Thus, if an error of 20 degrees is the limit of acceptable uncertainty in the location of a calculated univariant curve, then the sums of uncertainties of the free-energy values of the solid phases, taken in the proportion they appear in the reaction, must not exceed about 2.5 kJ. This degree of accuracy of free-energy values for solid silicate phases is rarely attained.

#### The $P_s - \mu_w$ diagram

A phase diagram that uses for the independent intensive variables the pressure on the solid phases ( $P_s$ ) and the chemical potential of  $H_2O$  can be useful (Zen, 1974) because on such a diagram the slopes of the isothermal univariant curves can be computed with fair precision from the molar volume data and the stoichiometry of the reaction. The diagram is useful for situations in which  $H_2O$  behaves as a boundary-value component (Zen, 1963). On this diagram, the ternary system is projected as a binary. The result is shown in Figure 2. The curve (Q,F) is a horizontal line; it terminates at (Q) because the prolongation in the direction of increasing  $\mu_w$  is invisible

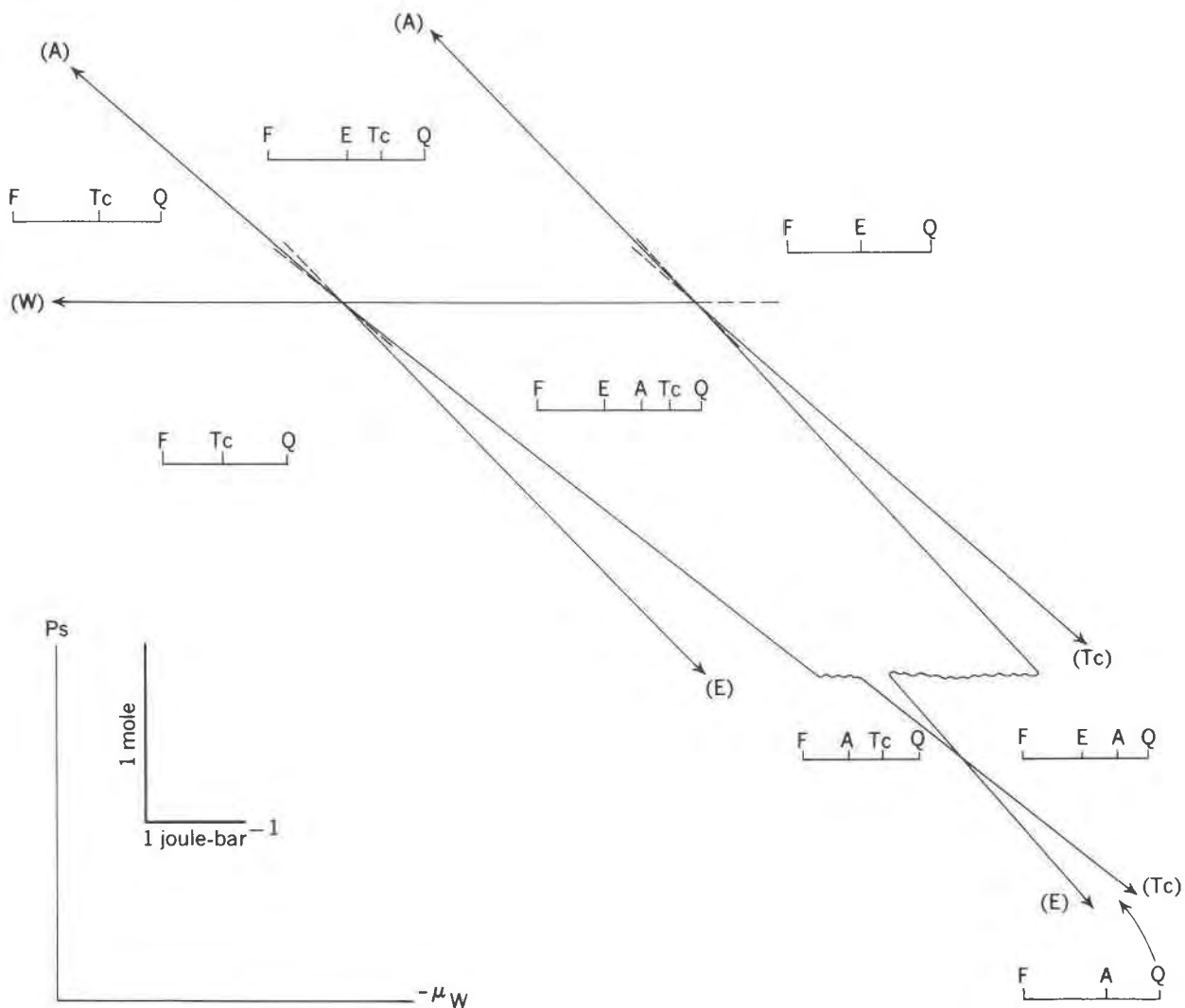


FIG. 2. Phase diagram for the system depicted on Fig. 1 using the pressure on the solid phase ( $P_s$ ) and the chemical potential of  $H_2O$  as the independent intensive variables.

from the point of projection. The possible mineral assemblages for this diagram differ from those for Figure 1 for any temperature. Comparison of predictions of these two diagrams with natural occurrences might yield information about the important external variables during metamorphism.

**Acknowledgments**

We wish to thank D. R. Wones, J. R. Fisher, J. J. Hemley, H. J. Greenwood, J. L. Haas, P. B. Hostetler, R. A. Robie, and B. S. Hemingway for encouragement and stimulating discussion during the course of this investigation. Wones, Hemley, N. D. Chatterjee, C. L. Christ, and J. S. Huebner reviewed the manuscript, and we thank them for their helpful comments.

Chernosky wishes to acknowledge the support of the National Science Foundation (Grant GA-43776) and of the Faculty Research Fund, University of Maine at Orono.

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Manuscript received, January 5, 1976; accepted for publication, May 18, 1976.