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Thermodynamic properties of anthophyllite and talc: Corrections and discussion of calorimetric data

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ABSTRACT

Arithmetic errors in calculating heat capacity values (Krupka, 1984; Krupka et al., 1985a) for anthophyllite and several errors in the Hess cycles utilized to derive enthalpies of formation of anthophyllite and talc are identified, and revised values are reported. The corrected values are: for anthophyllite, $S^0_{298} - S^0_0 = 554.2 \pm 3$ J/mol·K and $\Delta_f H^0_{298} = -12163 \pm 8$ kJ/mol·K for the composition $Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$; and $S^0_{298} = 534.5 \pm 3.5$ J/mol·K, $\Delta_f H^0_{298} = -12070 \pm 8$ kJ/mol and $\Delta_f G^0_{298} = -11343 \pm 8$ kJ/mol for the composition $Mg_7Si_8O_{22}(OH)_2$; and for talc [$Mg_3Si_4O_{10}(OH)_2$], $\Delta_f H^0_{298} = -5900 \pm 2$ kJ/mol and $\Delta_f G^0_{298} = -5520 \pm 2$ kJ/mol. Corrected heat capacity equations for anthophyllite are: for $Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$

$$C^0_P = 1285.774 + 0.011\,648T - 8602.01T^{-0.5} - 11\,178\,000T^{-2}$$

and for $Mg_7Si_8O_{22}(OH)_2$

$$C^0_P = 1259.938 + 0.018\,884T - 8127.40T^{-0.5} - 11\,642\,700T^{-2}$$

in J/mol·K, with the valid range 298.15 to 1200 K. The revised calorimetric values are in good agreement with evaluations by linear and mathematical programming (Day et al., 1985; Berman et al., 1986; Berman, 1988), and they support the values determined by solubility studies (Hemley et al., 1977a, 1977b; Bricker et al., 1973).

INTRODUCTION

Knowledge of the thermodynamic properties and hence of the stability of hydrous minerals is important for models of the origin and evolution of metamorphic H_2O as well as for processes that may involve metamorphic H_2O (e.g., the formation of ore bodies and the elastic or nonelastic response of rocks under stress). Enthalpies and Gibbs free energies of formation for anthophyllite and talc are in question because results derived from aqueous solubility studies (Hemley et al., 1977a, 1977b; Bricker et al., 1973; Hostetler et al., 1971) differ from those obtained from aqueous HF (Weeks, 1956; Bennington, 1956; Barany, 1963) and molten salt (Kiseleva and Ogorodova, 1984) calorimetry by about 16–23 kJ/mol. Day et al. (1985), Berman et al. (1986), and Berman (1988) have evaluated thermodynamic properties for these phases using the techniques of linear and mathematical programming and combining the calorimetric and solubility data with available phase equilibrium data. The optimized results selected in these studies agree with the values obtained from solubility studies (e.g., Hemley et al., 1977a, 1977b). However, Day et al. (1985) have shown that the experimental data can be fitted in such a way that good agreement with the calorimetric data results, albeit with somewhat larger residuals. Because solubility and phase equilibrium experiments measure properties through surface reactions and calorimetric experiments measure properties of the bulk sample, disparate data must be examined to determine whether some measurements are in error or whether a process other than that thought to be measured has occurred. Therefore, a reevaluation of the calorimetric Hess cycles is indicated.

The entropy and molar heat capacities for anthophyllite of the composition $Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$ (Krupka, 1984; Krupka et al., 1985a, 1985b) are in error. This fact was discovered simultaneously and independently by Bernard Evans of the University of Washington and the author. These data are recalculated in this study.

EXPERIMENTAL HEAT CAPACITIES AND ENTROPIES FOR ANTHOPHYLLITE

Molar values for the heat capacities and entropies for anthophyllite of the composition $Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$ (Krupka, 1984; Krupka et al., 1985a, 1985b) are in error because of arithmetic errors in the input data set processed with the standard computer software used in our laboratory. The specific heats for anthophyllite reported in these studies are correct. It is important to emphasize that the errors were associated only with the data set and not with the computer software. Thus no other data sets suffer the same errors. Nor do the errors result from problems in the measurement of heat capacities, instrument calibration, or other experimental detail. Rather, the errors involve the use of incorrect molar masses and an

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incorrect value for the mass of Fe_2O_3. Preliminary heat capacities were calculated by Krupka during initial data collection using a molar mass of 780.82 g for the natural anthophyllite sample. When corrections were made for deviations of the sample composition from $Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$, the specific heats were recalculated using a value for the molar mass of 801.638 g instead of 780.82 g. The specific heats calculated in this manner were too small, and this calculation represents the primary error. Other errors of lesser consequence were: (1) summation of the correction terms yielded a value of 801.506 g rather than 801.638 g, (2) the molar mass was reported to be 802.900 g when the calculations were based upon a value of 801.506 g, and (3) the correction for Fe_2O_3 should have been 5.0 g rather than the 5.7 g used. The heat capacity and entropy of the natural anthophyllite sample at 298.15 K are 644.2 and 540.7 J/mol·K, respectively, based upon a molar mass of 780.82 g and integration of the data given in Table 3 of Krupka et al. (1985a). The specific heat and entropy are 0.8250 and 0.6925 J/g·K.

The heat capacity and entropy of $Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$ at 298.15 K may be calculated using 881.858 g for the mass of 1 mol of the natural sample (anthophyllite plus impurities) and subtracting the contribution of the following components (correction terms in moles of substance): 0.2325 SiO_2, 0.0477 Al_2O_3, 0.0318 Fe_2O_3, 0.0564 $NaAlSi_3O_8$, 0.0124 $KAlSi_3O_8$, 0.0980 $CaSiO_3$, 0.1461 Mg_2SiO_4, 0.0075 Mn_2SiO_4, 0.0070 Ni_2SiO_4, 0.0018 P_2O_5, 0.0018 CO_2, 0.0009 TiO_2, 0.0062 Cr_2O_3, and 0.0293 H_2O. For $Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$ of mass 802.906 g, the heat capacity and entropy are 665.3 ± 1.5 and 554.2 ± 3.0 J/mol·K, respectively. The corrected values are significantly larger than 647.2 ± 1.5 and 538.9 ± 3.0 J/mol·K reported by Krupka (1984) and Krupka et al. (1985a) for the heat capacity and entropy, respectively. Heat capacity and entropy data for the component phases are somewhat different from those used by Krupka et al. (1985a) and were taken from Robie et al. (1979, 1982a, 1984) and Krupka et al. (1985a). Data for albite and microcline were used in these calculations rather than the data for the glasses of these compositions that were used by Krupka (1984) and Krupka et al. (1985a).

The heat capacity and entropy of magnesio-anthophyllite at 298.15 K were calculated in a similar manner using 926.269 g as the mass of 1 mol of the natural sample and subtracting the contributions from the following components (in moles): 0.1409 amosite (Bennington et al., 1978), 0.0447 Al_2O_3, 0.0253 Fe_2O_3, 0.0600 $NaAlSi_3O_8$, 0.0132 $KAlSi_3O_4$, 0.1040 $CaSiO_3$, 0.0021 Mn_2SiO_4, 0.0075 Ni_2SiO_4, 0.0019 P_2O_5, 0.0019 CO_2, 0.0009 TiO_2, and 0.0066 Cr_2O_3. The amosite sample measured by Bennington et al. (1978) was a mixed Mg-Fe crystal. The correction listed above is based upon removal of all Fe^{2+} and some Fe^{3+}, Al, and Mn using the amosite data. The use of the amosite data also results in removal of Mg, Si, and OH in excess. Therefore, 0.0454 $Mg(OH)_2$, 0.0844 Mg_2SiO_4, and 0.2972 SiO_2 must be added. The use of thermodynamic data for amosite rather than that of a phase like fayalite is justified on the basis of the similar magnetic contribution of Fe at low temperatures in anthophyllite and amosite. For $Mg_7Si_8O_{22}(OH)_2$ of mass 780.82 g, the heat capacity and entropy at 298.15 K are 662.4 ± 2.0 and 534.3 ± 3.5 J/mol·K, respectively. The correction was also calculated using the data for grunerite (Anovitz et al., 1988) rather than that for amosite. This calculation yielded 534.7 ± 3.5 J/mol·K for the entropy of magnesio-anthophyllite, in good agreement with the first calculation. The average of these values is recommended.

The results of the latter calculations are of greatest importance because the entropy and heat capacity of magnesio-anthophyllite are the primary thermodynamic values that have been utilized. The change from the heat capacity given by Krupka et al. (1985a) to the heat capacity at 298.15 K as corrected in this study is negligible. The entropy at 298.15 K is 0.5% lower than that calculated by Krupka (1984) and Krupka et al. (1985a) but is within the reported uncertainty. The difference in these values largely reflects the difference in the correction procedure for Fe used in each study.

The entropy reported here for magnesio-anthophyllite is in excellent agreement with the value obtained by Berman et al. (1986) in their derivation of an internally consistent thermodynamic data set for the system $MgO\text{-}SiO_2\text{-}H_2O$. However, the reactions limiting anthophyllite stability show significant curvature in P-T space, and the experimental phase reversal data exhibit significant scatter and spread. Thus, entropies (which are slope terms in the calculations) calculated in this manner are subject to large uncertainties. Therefore, the agreement may only be viewed as encouraging.

Specific heats for anthophyllite measured by differential scanning calorimetry (Krupka, 1984; Krupka et al., 1985b) have been corrected using the procedures and components discussed above. Additional values have been estimated to 1200 K. The heat capacities of the two corrected compositions were separately fitted by least squares to an equation of the form suggested by Haas and Fisher (1976). For each fit, the average deviation between the data and the equation was 0.4%. For the temperature interval 298.15 to 1200 K, the heat capacities (in J/mol·K) may be calculated from

$$C_P^0 = 1285.774 + 0.011\,648T - 8602.01T^{-0.5} - 11\,178\,000T^{-2}$$

for $Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$ and from

$$C_P^0 = 1259.938 + 0.018\,884T - 8127.40T^{-0.5} - 11\,642\,700T^{-2}$$

for $Mg_7Si_8O_{22}(OH)_2$. As discussed earlier, the heat capacities for the composition $Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$ differ significantly from those given in Krupka (1984) and Krupka et al. (1985b), being 2.8% larger at 298.15 K and 2.4% larger at 700 K. Heat capacities calculated for $Mg_7Si_8O_{22}(OH)_2$ differ by less than 0.2%.

TABLE 1. Thermodynamic properties for anthophyllite and talc from selected sources

Reference	$\Delta_f H^\circ_{298}$ kJ/mol	$\Delta_f G^\circ_{298}$ kJ/mol	S°_{298} J/mol·K	Method
		Anthophyllite		
Weeks (1956)	−12086.8	−11358.3*	—	HF calorimetry
Naumov et al. (1974)	−12090.9	−11364.6	534.7	Evaluation
Helgeson et al. (1978)	−12086.5	−11361.4	538.1	Evaluation
Hemley et al. (1977b)	−12072.7*	−11344.2	—	Solubility
Day et al. (1985)	−12072.8	−11345.0	537.0	Evaluation
	−12093.5	−11365.7	537.0	Evaluation
Berman et al. (1986)	−12072.4	−11345.9	535.0	Evaluation
Berman (1988)	−12069.0	−11342.6	535.2	Evaluation
This study	−12070.0	−11343.3	534.5	HF calorimetry
		Talc		
Bennington (1956)	−5881.8	−5501.8*	—	HF calorimetry
Barany (1963)	−5922.5	−5543.0	260.83	HF calorimetry
Hostetler et al. (1971)	−5898.7*	−5518.7	—	Solubility
Bricker et al. (1973)	−5895.3	−5521.6	280.58	Evaluation
	−5902.4	−5528.7	280.58	Solubility
Naumov et al. (1974)	−5922.9	−5543.4	260.79	Evaluation
Hemley et al. (1977a)	−5904.6*	−5524.6	—	Solubility
Helgeson et al. (1978)	−5903.3	−5523.7	260.83	Evaluation
Robie et al. (1979)	−5915.9	−5536.0	260.83	Evaluation
Kiseleva and Ogorodova (1984)	−5922.4	−5542.4*	—	Molten salt
Day et al. (1985)	−5898.2	−5518.2	260.83	Evaluation
	−5909.2	−5529.2	260.83	Evaluation
Berman et al. (1986)	−5899.5	−5519.6	260.76	Evaluation
Berman (1988)	−5897.4	−5517.7	261.19	Evaluation
This study	−5900.0	−5520.0	260.83	HF calorimetry

* Calculated from the measured value and the entropy used in this study.

ENTHALPY OF FORMATION OF ANTHOPHYLLITE AND TALC

The stability of magnesio-anthophyllite is in question because results for the enthalpies and consequently the Gibbs free energy of formation from two experimental techniques differ significantly. Early estimates of the enthalpies and Gibbs free energies of formation of magnesio-anthophyllite were based upon the calorimetric results given in Weeks (1956) (e.g., Naumov et al., 1974; Helgeson et al., 1978). More recently, the solubility data of Hemley et al. (1977b) have been utilized (e.g., Day et al., 1985; Berman et al., 1986; Berman, 1988). These disparate results (see Table 1) appear to be the critical values upon which the enthalpies and Gibbs free energies of formation of magnesio-anthophyllite are based.

Phase equilibrium reactions (e.g., Reactions 1–5) provide constraints on the thermodynamic properties of magnesio-anthophyllite:

magnesio-anthophyllite
= 7 enstatite + quartz + H_2O (1)

3 magnesio-anthophyllite + 4 quartz + 4 H_2O
= 7 talc (2)

magnesio-anthophyllite + forsterite
= 9 enstatite + H_2O (3)

5 magnesio-anthophyllite + 4 H_2O
= 9 talc + 4 forsterite (4)

magnesio-anthophyllite = talc + 4 enstatite. (5)

Because of the large stoichiometric coefficients, phase equilibrium reactions cannot be utilized to resolve the disparity discussed above (see also Day et al., 1985). For example, a change of −2 kJ/mol in the enthalpy of formation of enstatite (a change well within the uncertainty of the value) would require a change of −14 kJ/mol (for Reaction 1) or −18 kJ/mol (for Reaction 3) in the enthalpy of formation of magnesio-anthophyllite.

A similar disparity exists between aqueous HF and molten salt calorimetric data (Barany, 1963; Bennington, 1956; Kiseleva and Ogorodova, 1984) and solubility data (Hemley et al., 1977a; Bricker et al., 1973; Hostetler et al., 1971) for talc. Because talc enters into several of the phase equilibrium reactions, a review of the data for talc may help resolve the disparate data for anthophyllite.

Three determinations of the Gibbs energy of formation of talc by solubility methods (Hemley et al., 1977a; Bricker et al., 1973; Hostetler et al., 1971) show good agreement but estimate a Gibbs free energy of formation for talc that is 20 kJ less stable than that derived by HF and molten salt calorimetry. The consistency of the results argues against a systematic error in the studies. If the calorimetric data were considered correct, then the solubility data could be reinterepreted as representing equilibration with a phase less stable than talc, for example, vermiculite. However, before resorting to such an interpretation, a review of the calorimetric thermodynamic cycles is in order.

The cycle used by Barany (1963) appears to contain an error in the enthalpy of solution of MgO and thus will be considered first. The thermodynamic cycles followed in the studies of Bennington (1956) and Barany (1963) are slightly different, with Bennington (1956) using $Mg(OH)_2$ rather than MgO and with dissolution in a different solvent.

Barany (1963) measured the enthalpies of solution of talc and of the constituent oxides and reported −187.8 ± 1.4 kJ for the enthalpy of the reaction

$$4SiO_2 + 3MgO + H_2O = Mg_3Si_4O_{10}(OH)_2 \quad (6)$$

in a mixture of 10.05% HCl and 10.05% HF. Barany (1963) reported the following enthalpies of solution: for talc, −849.94 ± 0.80; SiO_2, −143.70 ± 0.27; MgO, −155.02 ± 0.11; and H_2O, 2.09 ± 0.21, all in kJ/mol. King et al. (1967) have also reported values for the enthalpies of solution of two of the oxides in a solvent of the same composition, at the same temperature (dissolution at 73.7 °C), and in the same equipment. A different sample of MgO was used in the latter study. The results reported by King et al. (1967) are: for MgO, −148.31 ± 0.21 and for H_2O, 2.82 ± 0.08, both in kJ/mol. These values differ significantly from the earlier results reported by Barany (1963); however, the authors provide no discussion of this fact.

The results provided for the enthalpies of solution of MgO and H_2O by King et al. (1967) are preferred for the following reasons. The enthalpy of formation of forsterite has been determined in several studies, and good agreement between these results and those of King et al. (1967) is found (e.g., King et al., 1967, −2171.7; Torgeson and Sahama, 1948, −2177.1 and −2174.9; Charlu et al., 1975, −2175.1; Kiseleva et al., 1979, −2171.9; Robie et al., 1982b, −2170.4; Brousse et al., 1984, −2172.0; all in kJ/mol with an uncertainty of about ±2.5 kJ/mol or less). If the reactions reported by Barany (1963) were substituted for those used by King et al. (1967), the resulting enthalpy of formation for forsterite would be −2185.1 kJ/mol, a value in poor agreement with other studies.

The enthalpies of solution of MgO reported in the two studies are significantly different. The result reported by Barany (1963) is considered to be in error (too large) because the sample was very fine grained (reagent grade material). Taylor and Wells (1938) have shown that fine-grained MgO has an excess enthalpy of solution. King et al. (1967) specifically stated that macrocrystalline MgO was used in their study, and thus no excess enthalpy of solution is expected.

The enthalpy of formation of talc may now be calculated from a Hess cycle that includes the enthalpy of solution of talc from Barany (1963) and the enthalpies of solution of the component oxides from King et al. (1967). The enthalpy of formation of talc from the oxides is −166.97 ± 1.5 kJ/mol and from the elements is −5900.07 ± 2.1 kJ/mol.

Bennington (1956) determined the enthalpy of formation of talc from the oxides (−148.66 ± 1.51 kJ/mol). Bennington (1956) measured the enthalpy of solution of talc (−845.11 ± 1.27 kJ/mol) in a solution of 10% HCl and 10% HF at 81 °C. The ancillary enthalpies of solution required for his cycle represented dissolutions in acid of another composition.

Problems in the Hess cycle used by Bennington (1956) are obvious from a comparison of the accepted enthalpies of solution of SiO_2 (Barany, 1963) and MgO (King et al., 1967) in a solution of 10% HCl and 10% HF and the values of −137.70 ± 0.13 kJ/mol for SiO_2 (20.1% HF) and −146.11 ± 0.61 kJ/mol for MgO (20% HCl and 5% HF) used by Bennington (1956). The values used by Bennington are for dissolution at 81 °C, whereas those of King et al. (1967) represent dissolution at 73.7 °C. Based upon the studies of Kilday and Prosen (1973) and Hemingway et al. (1988), we can estimate a correction of −1.1 kJ to Bennington's (1956) value for quartz dissolution, giving 73.7 °C. A similar correction for MgO would be required.

We may substitute Bennington's (1956) enthalpy of solution of talc for that of Barany (1963) in the Hess cycle described above. In addition, we must assume no significant change in the enthalpy of solution of talc between 73.7 and 81 °C, and we must correct for the heat content ($H^0_{81} - H^0_{73.7}$) of talc. The corrected enthalpy of talc dissolution is −847.82 ± 4 kJ/mol. The enthalpies of formation of talc derived from this value are −169.09 ± 4 and −5902.19 ± 4 kJ/mol from the oxides and elements, respectively.

The calorimetric values derived from the corrected Hess cycles described above are in good agreement among themselves and with estimates made from evaluation of experimental data or by using other experimental techniques (see Table 1). Thermodynamic properties for talc at 1 bar and based upon the CODATA key values for the elements (Cox et al., 1989) are listed in Table 2.

Recently, molten salt solution calorimetry has been applied to hydrous phases, and the enthalpy of formation of talc may be derived from data contained in three studies (Kiseleva and Ogorodova, 1984; Akaogi et al., 1984; Clemens et al., 1987). Kiseleva and Ogorodova (1984) determined the enthalpy of formation of talc at 298.15 K (−5922.4 ± 5.6 kJ/mol) from Reaction 7 with dissolution

$$2MgO + 4SiO_2 + Mg(OH)_2 = Mg_3Si_4O_{10}(OH)_2 \quad (7)$$

at 973 K. Clemens et al. (1987) determined the enthalpy of formation of phlogopite from measurements at 987 K. Values were reported for the enthalpies of solution for MgO, SiO_2, and $Mg(OH)_2$ that may be substituted into the Hess cycle listed above, yielding −5913.1 ± 5 kJ/mol for the enthalpy of formation of talc at 298.15 K. The Hess cycle may be modified slightly by substituting the enthalpy of solution of forsterite (Akaogi et al., 1984) for $2MgO + SiO_2$. This version of the Hess cycle yields −5911.9 ± 5 kJ/mol. In the latter calculations, the enthalpy of solution of talc at 987 K was calculated from the value given by Kiseleva and Ogorodova (1984) through the addition of the enthalpy difference $H_{987} - H_{973}$ and from the enthalpy of formation of forsterite from King et al. (1967). The enthalpy of solution of talc was assumed to be constant over the temperature interval of 973 to 987 K. If the enthalpy of solution of talc changed in accordance with changes observed for the enthalpies of solution of MgO and SiO_2 (Shearer and Kleppa, 1973), the calculated enthalpies of formation of talc would increase by −2.5 kJ/mol.

Enthalpies of formation of talc calculated from the results of molten salt calorimetry are significantly more negative than are those derived from solubility data and the corrected Hess cycle based upon aqueous HF calorimetry. However, the values are not internally consistent, although all are based upon the same value for the enthalpy of solution for talc. The results represent early efforts to study hydrous minerals or minerals containing volatile components, and they suggest that systematic errors may be present. The enthalpy of formation of forsterite may be calculated from the enthalpy of solution of forsterite (Akaogi et al., 1984) and from the enthalpies of solution of MgO and SiO_2 taken from Clemens et al. (1987, −2172.9 kJ/mol) and from Kiseleva and Ogorodova (1984, −2177.2 kJ/mol). For the anhydrous phase, forsterite, the results are in reasonable agreement with values determined by other methods (cited above).

There are several experimental problems in the application of the molten salt solution calorimeter to the study of hydrous or volatile component bearing phases that may limit the usefulness of the technique. For example, the reference phase, $Mg(OH)_2$, decomposes at a temperature lower than that of the molten salt solvent, but talc dehydrates at a temperature above that used for dissolution. Thus the processes involved in the dissolution of each phase may be different and result in a different final state for each process (essentially a failure to maintain stoichiometry through a failure to match the concentration of the volatile component dissolved in the solvent). In addition, accumulation of H_2O vapor within the calorimeter will result in a change in the thermal conductivity of the cell and, therefore, a change in the calibration of the energy equivalent of the calorimeter. It is not clear that a valid Hess cycle can be established for hydrous phases using the molten salt solution technique. It is clear that the enthalpy of formation of talc derived by the molten salt technique deviates significantly from results of other techniques and is probably in error as a consequence of undetected systematic errors.

The calorimetric data for magnesio-anthophyllite must be in error if the calorimetric values for forsterite and talc (discussed above) are correct and the phase equilibrium data for Reactions 2 and 4 are correct. Two procedures followed by Weeks (1956) may be faulted. Like Bennington (1956), Weeks (1956) used a mixed acid (20% HCl and 5% HF) for sample dissolution. However, Weeks (1956) used the dissolution of quartz in a solution of 20.1% HF as part of his Hess cycle. The anthophyllite sample used by Weeks (1956) contained Fe. Weeks (1956) used a questionable graphical technique to correct the enthalpy of solution of anthophyllite for the effect of Fe.

Table 2. Thermodynamic properties for talc, $Mg_3Si_4O_{10}(OH)_2$

Temperature K	Heat capacity	Entropy	Enthalpy function	Gibbs energy function	Formation from elements: Enthalpy	Formation from elements: Gibbs energy
	J/mol·K				kJ/mol	
298.15	321.71	260.830	0.000	260.830	−5900.0	−5520.0
	±0.63	±0.63			±2.0	±2.0
300	323.17	262.825	1.988	260.836	−5900.1	−5517.8
350	359.20	315.448	50.538	264.909	−5901.2	−5454.0
400	386.60	365.298	90.925	274.373	−5901.2	−5390.1
450	406.22	412.030	124.929	287.102	−5900.3	−5326.2
500	420.63	455.610	153.811	301.799	−5899.0	−5262.5
550	432.51	496.268	178.617	317.651	−5897.5	−5198.9
600	444.26	534.398	200.258	334.141	−5895.7	−5135.5
650	457.93	570.479	219.535	350.944	−5893.5	−5072.2
700	475.20	605.020	237.154	367.866	−5890.9	−5009.2
750	497.49	638.533	253.735	384.798	−5887.5	−4946.3
800	525.95	671.513	269.824	401.689	−5883.2	−4883.7

The enthalpy of solution of quartz used by Weeks (1956) appears to be fairly good despite the difference in acids used. Weeks (1956) reported and used a value of −137.70 kJ/mol for the enthalpy of solution of quartz in 20.1% HF at 81 °C. Neuvonen (1952) measured the enthalpy of solution of "extremely fine quartz powder" and reported −139.75 kJ/mol for the enthalpy of dissolution in 20% HCl and 5% HF at 75 °C. The difference of −2 kJ/mol is well within the range of excess enthalpy of solution that can be expected for fine quartz powder (Hemingway and Robie, 1977; Hemingway et al., 1988). For further verification, the enthalpy of solution of quartz in 20% HCl and 5% HF may be calculated from the enthalpy of formation from the oxides of chrysotile (King et al., 1967) and the enthalpies of solution of chrysotile and ancillary components in 20% HCl and 5% HF as reported by Bennington (1956). The result of this calculation is −138.38 kJ/mol for the enthalpy of solution of quartz.

Thus it would appear that the enthalpy of solution of quartz in 20.1% HF and in 20% HCl and 5% HF are nearly equivalent at 70–80 °C, but the value measured in 10% HCl and 10% HF is larger. This may explain why Bennington's (1956) Hess cycle for chrysotile (reactions in 20% HCl and 5% HF except quartz in 20.1% HF) yields a value for the enthalpy of formation of chrysotile in good agreement with other studies, but his Hess cycle for talc (talc dissolution in 10% HCl and 10% HF and other reactions as above) yields an erroneous result.

The graphical solution used by Weeks (1956) to correct his measured enthalpy of solution of anthophyllite for the effect of Fe is questionable because Hemingway and Robie (1973) have shown that the enthalpy of solution of CaO varies with the amount of MgO dissolved in an HCl solvent. Using a plot of enthalpy of solution vs. sample Fe content, Weeks (1956) plotted the enthalpies of solution of natural anthophyllite, tremolite, and ferrotremolite. He connected the values for the two tremolite compositions and then constructed a line parallel to this line through the value for the natural anthophyllite. Weeks (1956) used the constructed line to estimate the enthalpy of solution of magnesio-anthophyllite. Because tremolite contains both Ca and Mg and because the Mg content of the model sample increases as Fe is replaced by Mg, the enthalpic effect of the interaction between Ca and Mg can be expected to increase. This effect would not be present

TABLE 3. Thermodynamic properties for magnesio-anthophyllite, $Mg_7Si_8O_{22}(OH)_2$

Temperature K	Heat capacity	Entropy	Enthalpy function	Gibbs energy function	Formation from elements: Enthalpy	Formation from elements: Gibbs energy
	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol
298.15	663.90	534.500	0.000	534.500	−12070.0	−11343.3
	±2.0	±3.5			±8.0	±8.0
300	667.00	538.616	4.104	534.513	−12070.0	−11338.8
350	737.08	647.005	104.093	542.911	−12069.6	−11216.8
400	788.36	748.937	186.572	562.364	−12067.0	−11094.8
450	827.81	844.163	255.717	588.446	−12063.1	−10973.1
500	859.34	933.071	314.558	618.513	−12058.1	−10851.7
550	885.28	1016.229	365.298	650.931	−12052.5	−10730.7
600	907.13	1094.221	409.565	684.656	−12046.3	−10610.0
650	925.87	1167.588	448.578	719.011	−12039.8	−10489.8
700	942.21	1236.814	483.266	753.548	−12031.0	−10368.0
750	956.63	1302.321	514.353	787.968	−12025.9	−10250.5
800	969.51	1364.479	542.405	822.075	−12018.6	−10131.4
850	981.11	1423.609	567.875	855.734	−12011.3	−10012.8
900	991.65	1479.991	591.130	888.861	−12003.9	−9894.5
950	1001.29	1533.868	612.467	921.401	−12056.3	−9774.7
1000	1010.17	1585.457	632.133	953.323	−12049.1	−9653.7
1100	1026.04	1682.498	667.239	1015.260	−12033.4	−9412.4
1200	1039.90	1772.382	697.728	1074.654	−12016.0	−9173.0

in anthophyllite and thus invalidates Weeks' (1956) model.

A comparison may be made of the enthalpies of solution of Fe-Mg analogue pairs with no Ca as a system component. The enthalpies of solution of $MgTiO_3$ and $FeTiO_3$ in 10.05% HCl and 10.05% HF (Kelley et al., 1954) are −2023.4 and −1311.6 J/g, respectively. The enthalpy of solution of Mg_2SiO_4 in the same acid (King et al., 1967) is −2717.5 J/g, and that for Fe_2SiO_4 in 20% HCl and 5% HF (King, 1952) is −1654.4 J/g. These results suggest that the enthalpy of solution per gram of the Mg-bearing phase should be larger than that of the Fe-bearing analogue. Weeks (1956) used −2162.3 and −2169.6 J/g, respectively, for the enthalpies of solution of tremolite and ferrotremolite.

The enthalpy of solution of anthophyllite reported by Weeks (1956) may be corrected for the effect of Fe and minor Ca by a Hess cycle utilizing the enthalpies of solution of $MgTiO_3$, $FeTiO_3$, and $CaTiO_3$ (Kelley et al., 1954). The corrections are: 205.35 J for $FeTiO_3$, 36.90 J for $CaTiO_3$, and −283.80 J for $MgTiO_3$. A correction of 0.35 J is also necessary for Al (see Weeks, 1956). Summation of these values yields −2368.73 J/g for the enthalpy of solution of magnesio-anthophyllite (or −1849.55 kJ/mol).

A corrected enthalpy of formation for magnesio-anthophyllite may be calculated from the corrected enthalpy of solution of anthophyllite and the Hess cycle used by Weeks (1956) and, for comparison, from a Hess cycle based upon the enthalpy of solution of chrysotile (Bennington, 1956). The revised enthalpy of formation of magnesio-anthophyllite from the oxides is −288.59 kJ/mol and −12070 ± 8 kJ/mol from the elements. The enthalpy of formation of magnesio-anthophyllite also may be calculated from the reaction

$$2Mg_3Si_2O_5(OH)_4 + MgO + 4SiO_2 = 3H_2O + Mg_7Si_8O_{22}(OH)_2. \qquad (8)$$

The Hess cycle based upon Reaction 8 yields a value of 42.25 kJ for the enthalpy of the reaction and −12073 kJ/mol for the enthalpy of formation of magnesio-anthophyllite (from the elements and using −4364.3 kJ/mol for the enthalpy of formation of chrysotile, e.g., Berman, 1988).

The corrected values for the enthalpy of formation of magnesio-anthophyllite are in good agreement with the values predicted by Berman et al. (1986, −12072 kJ/mol) and Berman (1988, −12069 kJ/mol). The results support the value derived by Hemley et al. (1977b, −12069 kJ/mol). Thermodynamic properties for magnesio-anthophyllite at 1 bar and based upon the CODATA key values for the elements (Cox et al., 1989) are listed in Table 3.

The enthalpy of formation of $Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$ may be calculated using a similar procedure to that described above for magnesio-anthophyllite. Corrections to the observed enthalpy of solution of anthophyllite are: 34.22 J for $FeTiO_3$, 36.90 J for $CaTiO_3$, and −80.67 J for $MgTiO_3$. The enthalpy of solution of 802.906 g of anthophyllite is −1876.21 kJ/mol. The enthalpy of formation from the elements is derived from the reaction

$$6.3MgO + 0.35Fe_2SiO_4 + 7.65SiO_2 + H_2O = Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2. \qquad (9)$$

The enthalpy of Reaction 9 is −603.555 kJ based upon the enthalpies of solution for the component oxides given by Weeks (1956) and that for fayalite from King (1952). The enthalpy of formation from the elements of $Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$ is −12163 ± 8 kJ/mol based upon the enthalpies of formation of the oxides components from Robie et al. (1979) and of fayalite from Robie et al. (1982b).

SUMMARY AND CONCLUSIONS

Errors in the derivation of the heat capacities and entropy of anthophyllite of the composition $Mg_{6.3}Fe_{0.7}Si_8$-

$O_{22}(OH)_2$ (Krupka, 1984; Krupka et al., 1985a, 1985b) have been documented, and revised values have been calculated. Revised equations for the heat capacity of the two anthophyllite compositions are given for the temperature interval 298.15 to 1200 K.

Separate problems in the calorimetric Hess cycles used by Barany (1963), Bennington (1956), and Weeks (1956) caused the enthalpies of formation of talc and magnesio-anthophyllite reported by these authors to be in error. These problems have been discussed, and revised calorimetric values are reported. The revised values are in agreement with solubility data (Hemley et al., 1977a, 1977b; Bricker et al., 1973; Hostetler et al., 1971) and with optimized solutions derived by the techniques of linear and mathematical programming (Day et al., 1985; Berman et al., 1986; Berman, 1988).

Analysis of the results of molten salt solution calorimetry applied to hydrous phases suggests that systematic errors may exist in the procedures. These errors may lead to incorrect values for enthalpies of solution for phases not stable at the temperature of the solvent. Further work will be required to validate the molten salt solution technique in this application.

The recommended thermodynamic properties for anthophyllite and talc derived from the calorimetric studies are: $S^0_{298} - S^0_0 = 554.2 \pm 3$ J/mol·K and $\Delta_f H^0_{298} = -12163 \pm 8$ kJ/mol for $Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$; $S^0_{298} = 534.5 \pm 3.5$ J/mol·K, $\Delta_f H^0_{298} = -12070 \pm 8$ kJ/mol, and $\Delta_f G^0_{298} = -11343 \pm 8$ kJ/mol for $Mg_7Si_8O_{22}(OH)_2$; and $\Delta_f H^0_{298} = -5900 \pm 2$ kJ/mol and $\Delta_f G^0_{298} = -5520 \pm 2$ kJ/mol for talc.

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