Magmatic Processes: Physicochemical Principles
© The Geochemical Society, Special Publication No. 1, 1987
Editor B. O. Mysen

Calorimetric studies of melts, crystals, and glasses, especially in hydrous systems

ALEXANDRA NAVROTSKY
Dept. of Geological and Geophysical Sciences, Princeton University, Princeton, N.J. 08544, U.S.A.

Abstract—Hydrous minerals, melts, and glasses may be studied by a variety of calorimetric techniques. These include measurements of heat capacities and enthalpies by adiabatic, drop, transposed-temperature-drop and differential scanning calorimetry, and the measurement of enthalpies of reaction by solution, drop-solution, and decrepitation calorimetry. Some calorimetric experiments on hydrous melts at high P and T are possible. The system $NaAlSi_3O_8$-H_2O has been studied. It shows small negative heats of mixing which may be consistent with STOLPER's model of an H_2O dissociation equilibrium.

INTRODUCTION

THE PROGRESS of experimental petrology has been limited at all stages by available technology. The problems one can attack can be exemplified by the tale of the drunkard seeking a lost key under a streetlamp on a moonless night. "Is that where you lost it?" "No, but it is the only place I have light enough to find it. And I might find some other treasure." So it is with experimental thermochemical studies of magmas. Are melts too difficult to study by structural and thermodynamic methods? Then study glasses. Are hydrous multicomponent melts at high pressure even more difficult? Then keep them dry and iron-free at atmospheric pressure. Yet much interesting science, which can be applied with care to nature's crucible, has come from such studies of simplified systems. The purpose of this paper is to review calorimetric studies of silicate systems, especially those containing H_2O, to show how such thermochemical data can be applied to petrology, to point out thermochemical studies that are now feasible, and to present some recent calorimetric results for the system albite-water.

THE USES OF CALORIMETRIC DATA IN HYDROUS SILICATE SYSTEMS

In phase equilibria involving silicate melts, the most obvious influence of H_2O is to lower liquidus temperatures very substantially. In addition, crystallization sequences can be altered and hydrous crystalline phases (*e.g.*, amphiboles and micas) can form, either on the liquidus or in subsequent reactions. These phase relations reflect the free energy relations among the phases and specifically, the lowering of the activity of aluminosilicate components in the melt by the addition of H_2O. Indeed, thermodynamic models of melt-water interactions (e.g., BURNHAM, 1981; BURNHAM and NEKVASIL, 1986; SILVER and STOLPER, 1985) often focus on these activities and seek simple phenomenological expressions for them. In general, each activity term can be separated into energetic (enthalpic) and entropic components. For a given process,

$$\mu - \mu^0 = \Delta\mu = RT \ln a = \Delta\bar{h} - T\Delta\bar{s} \qquad (1)$$

(where μ = chemical potential, a = activity, $\bar{h}$ = partial molar enthalpy, and $\bar{s}$ = partial molar entropy). The range of temperatures over which phase equilibria give estimates of activity is frequently too small and the uncertainty too large to permit an accurate separation of enthalpy and entropy terms from the temperature dependence of μ. Thus a major purpose of calorimetric studies is to determine the integral and partial molar enthalpies directly for specific reactions. One can measure the heat of formation, of reaction, of phase transition, or of dehydration of a crystalline silicate. One can obtain enthalpies of mixing in solid solutions, in glasses and melts, and in glass-water or melt-water systems (see below). One can determine enthalpies of vitrification (crystal → glass) and of fusion (crystal → liquid). One can study order-disorder processes. All the above are necessary for a complete thermodynamic description of phase equilibria.

Calorimetric studies also provide heat capacity (C_p) and heat content (H^0_T-H^0_{298}, H^0_T-H^0_0) data. In addition to providing information on the temperature dependence of heats of reaction, such data yield values for the absolute entropy (S^0_T) of a phase if the substance in question is a perfectly ordered crystal at low temperature. Heat capacities and heats of fusion are also needed to construct the heat budget of an ascending magma and its interactions with the surrounding rocks.

Furthermore, the magnitude of thermochemical parameters can give insight into structure and bonding. Mixing models of solid and liquid solutions are based on assumptions about the configurational entropy which, although it does not imply speciation directly, puts constraints on the numbers and types of entities being mixed. Thus if one can obtain entropies of mixing from a combination of activity and enthalpy of mixing data, one can compare those to values predicted by various statistical models and, in favorable cases, distinguish among or rule out some possible models (Weill *et al.*, 1980; Henry *et al.*, 1982). Systematic trends in thermochemical parameters for heats of formation (Navrotsky, 1982, 1985) and vitrification and heats of fusion (Hervig *et al.*, 1985; Stebbins *et al.*, 1984) also lend insight into structural features and permit estimates of values for other real or hypothetical phases.

From the point of view of silicate-water interactions, thermochemical data in several areas are needed. First, one would like to know the enthalpies, entropies, and free energies of all important hydrated mineral phases and their solid solutions. Second, one needs data on heats of fusion of important anhydrous silicates and heats of mixing in melts of rock-forming compositions. Third, one requires knowledge of the energetics of melt-water interactions and of the enthalpies of solution of H_2O at high P and T in aluminosilicate melts. Fourth, one wishes information on thermodynamics of aqueous fluids at high P and T. The next section describes the current possibilities and limitations for calorimetric study in these related areas.

TYPES OF CALORIMETRIC STUDIES

Heat capacities

Heat capacities at 4–300 K are measured by adiabatic calorimetry (Westrum *et al.*, 1968; Robie and Hemingway, 1972). Such studies usually require 1–30 g of sample. Heat capacities and standard entropies of a number of hydrous silicates including amphiboles and micas have been measured (see for example Perkins *et al.*, 1979, 1980; Hemingway *et al.*, 1986; Robie *et al.*, 1976; Krupka *et al.*, 1979). Heat capacities of several anhydrous aluminosilicate glasses have also been reported (Robie *et al.*, 1978; Krupka *et al.*, 1979). In glassy materials, $\int_0^T (C_p/T)dT$ gives only the vibrational contribution to the entropy; a term arising from configurational disorder, and depending on cooling history, also contributes to the total entropy. Low temperature heat capacities could be measured on a quenched hydrated glass (to the best of my knowledge this has not been done) and would provide information on the excess vibrational entropy of mixing. This excess vibrational entropy would be related to both the speciation of H_2O (Stolper, 1982) and the extent to which the aluminosilicate framework is perturbed by the dissolution of water. However, a relatively large amount (several grams) of homogeneous hydrous glass with no fluid inclusions of H_2O would be needed and the excess heat capacities might be quite small.

At temperatures from about 100°C to near 800°C, commercial differential scanning calorimeters can measure heat capacities on samples of 10–200 mg. Heat capacities of a number of minerals and of aluminosilicate glasses have been measured (Stebbins *et al.*, 1984; Krupka *et al.*, 1979). The upper end of this range samples the glass transition region for anhydrous glasses and the beginning of decomposition (dehydration) for hydrated minerals and glasses. Because DSC is usually done at fairly rapid scanning rates (1–10°C per minute), kinetic factors may dominate the decompositions seen. In combination with thermogravimetric analysis (TGA), such DSC measurements provide useful data on the heat capacities, decomposition rates, and decomposition kinetics of hydrous crystals and glasses. Although no commercial DSC units currently operate above 827°C, this limitation is more a matter of market demand (mostly for polymer-related work) and the softening point of the silver block commonly used than of any other major technical obstacle. A DSC for work with small samples to at least 1000°C should be possible. Differential thermal analysis (DTA) provides transition temperatures and qualitative indication of heat effects up to ~2000°C using commercially available instruments.

Above 800°C, heat capacities are generally derived from measurements of heat contents (H^0_T-H^0_{298}) either by conventional drop calorimetry (dropping a sample from a furnace into a calorimeter at room temperature) (Stebbins *et al.*, 1982, 1983, 1984) or by transposed-temperature-drop calorimetry (dropping a sample from room temperature into a hot calorimeter). The upper temperature limit of the former is ~1700°C with normal Pt-wound furnaces (Stebbins *et al.*, 1982, 1984) and ~2300°C with specially designed furnaces (Stout and Piwinskii, 1982). The method requires 5–50 g of sample. One must be concerned about the energetic state of glassy samples quenched from different temperatures (Stebbins *et al.*, 1983, 1984; Richet *et al.*, 1982; Richet and Bottinga, 1984). A commercial transposed-temperature-drop calorimeter operates to 1500°C. It requires samples of <100 mg and, because the final state of the sample is melt at high temperature, the potential variability in the glassy state can be avoided.

To study the high temperature heat capacities and enthalpies of hydrous systems one must apply pressure to maintain H_2O as a dense fluid or a dissolved phase. KASPER *et al.* (1979) measured the heat content of aqueous $NaCl$-H_2O solutions by dropping sealed Pt capsules of solution from room temperature into a calorimeter operating at 184, 263, or 712°C. The entire system inside the calorimeter and extending from the hot zone within the thermal sensing elements (at the bottom) to the cold pressure head containing the sample to be dropped (at the top) was held at 0.5 to 1.0 kbar argon pressure. Although the experiments were successful, the geometrical arrangement with hot zone at the bottom resulted in very substantial convection and limited the sensitivity of the method.

CLEMENS and NAVROTSKY (1986) used a variant of conventional drop calorimetry to study the heat contents of hydrous albite glass and melt. By placing an internally heated pressure vessel above a calorimeter operating near room temperature (see Figures 1 and 2), and allowing a long cold-finger of the vessel to extend down into the calorimeter, they could drop samples from temperatures of up to 1033°C to room temperature within a system maintained at pressures to 1.5 kbar. Convection was decreased by having the hot zone on top and better results were obtained. The upper temperature was limited by the location and material of seals in the internally heated vessel. It should be possible with some modification to achieve somewhat higher temperatures. At temperatures below the liquidus at each H_2O content, albite crystallized rapidly, limiting the utility of the measurements to the stable liquid range. The results for Ab-H_2O are discussed below.

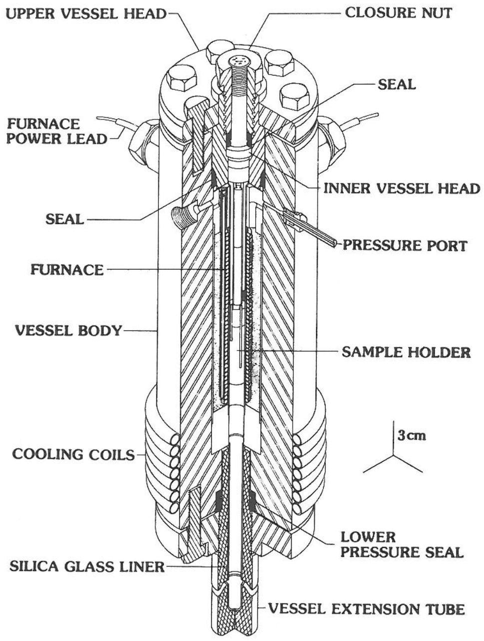

FIG. 1. Schematic longitudinal section through the pressure vessel used for high pressure drop experiments (CLEMENS and NAVROTSKY, 1986). The vessel extension tubes reaches into the calorimeter roughly 90 cm below the furnace.

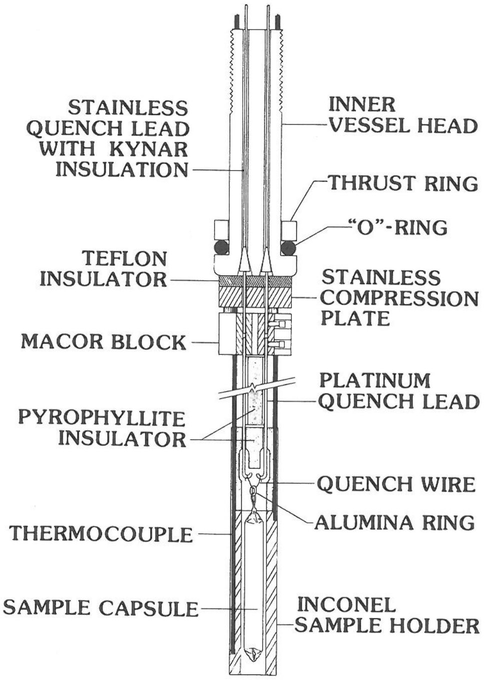

FIG. 2. Schematic section through the inner portion of the pressure head showing the sample assembly for drop calorimetry of hydrous melts (CLEMENS and NAVROTSKY, 1986).

Heats of fusion

Since most rock forming silicates melt above ~1000°C, their heats of fusion require the use of drop or transposed-temperature-drop methods. Drop calorimetry works most conveniently when the melt crystallizes rapidly, releasing the latent heat in the calorimeter. The heat of fusion of fayalite has been measured in this manner (STEBBINS and CARMICHAEL, 1984). When the melt forms a glass on rapid cooling, the enthalpy difference between glass and crystal must be measured by solution calorimetry (see below) and a thermochemical cycle involving this heat of vitrification and the heat capacities of glass, liquid, and crystal must be used to calculate the heat of fusion. This has been done for a number of rock-forming silicates (STEBBINS *et al.*, 1982, 1983, 1984; RICHET *et al.*, 1982; RICHET and BOTTINGA, 1984). A general conclusion is that the heat of fusion can depend quite strongly on temperature because the heat capacity of the liquid can be substantially greater than that of the crystal. This effect can be quite important in thermochemical calculations of phase equilibria.

Transposed temperature drop calorimetry can measure heats of fusion to ~1500°C; results for diopside are shown in Figure 3 (ZIEGLER and NAVROTSKY, 1986). They confirm the previous measurements using a thermochemical cycle involving the glassy state (STEBBINS *et al.*, 1983; RICHET and BOTTINGA, 1984) and prove the utility of the commercial instrument. Direct measurement of the heats of fusion of other silicates, of multicomponent systems and of model rock compositions and/or rocks should be feasible. The calorimeter can operate under controlled low oxygen fugacity, making the control of oxidation state feasible. However, the small size of the calorimeter makes it unsuitable for work under high pressure, so heat contents and heats of fusion of hydrous systems cannot be studied in it. Rapid dehydration reactions (decrepitation) can be studied readily; one can pick a temperature at which decomposition occurs rapidly but not violently.

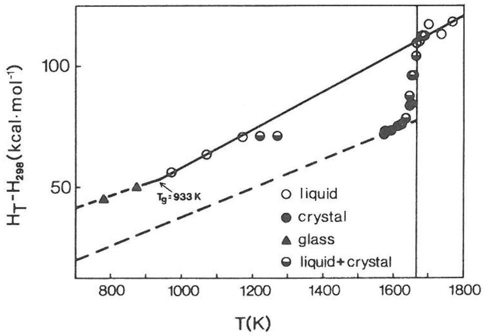

FIG. 3. Enthalpy vs. temperature for $CaMgSi_2O_6$ crystal, glass, and liquid crystal. The calorimetric data for glass have been corrected to the crystalline reference state by adding the enthalpy of vitrification. The line through the crystal data is that given by STEBBINS *et al.* (1983). The line through the liquid data is the best fit line for the data shown by open circles. The different symbols represent the state of the sample at the upper temperature, *T*. Open circles—liquid, closed circles—crystal, half-filled circles—crystal + liquid, triangles—glass. The figure shows that diopside melts incongruently. From ZIEGLER and NAVROTSKY (1986).

Enthalpies of formation and of mixing

To relate the energetics of one phase assemblage to that of another (oxide mixture versus compound, end-member versus solid solution) when one cannot be transformed rapidly to the other in the calorimeter, a thermochemical cycle must be used. This cycle usually involves the dissolution of reactants and products in a solvent where the final dissolved state is the same for both. The primary measurement is then of a heat of solution. Two classes of solution calorimetry have commonly been in use for silicates: dissolution in aqueous acid (usually HF) near room temperature (ROBIE and HEMINGWAY, 1972) and dissolution in a molten oxide (usually $2PbO \cdot B_2O_3$) at 700–800°C (NAVROTSKY, 1977, 1979). Each has some advantages and disadvantages. Hydrous minerals have generally been studied using aqueous HF for the following reasons. They often dissolve readily in that solvent, they frequently decompose below 700°C and the final state of the water which would contact lead borate melt at 700°C is unknown. However, HF calorimetry requires several grams of sample, alumina-rich samples do not always dissolve well, and much data on analogous anhydrous compositions have been obtained by oxide melt calorimetry. Thus more direct interrelation of the two methods and exploration of the applicability of oxide melt calorimetry to hydrous systems appears highly desirable. We have begun exploration of such possibilities and present several preliminary findings.

For phases which contain OH^-, such as micas and amphiboles, the fluoride analogues can be studied by oxide melt calorimetry and the systematics of cation-substitution energetics can be applied to the hydroxy materials. This was exploited by WESTRICH *et al.* (1981) for fluorpargasite, fluorapatite and fluorphlogopite and more recently by GRAHAM and NAVROTSKY (1986) for the fluortremolite-fluoredenite solid solution series, for which heat of solution data are shown in Figure 4.

Not all phases containing water decompose rapidly at 700°C. Well-crystallized pargasite and phlogopite persist unchanged for 24 hours in the calorimeter and appear to give reproducible heats of solution in $2PbO \cdot B_2O_3$ (N. ROSS, J. D. CLEMENS and A. NAVROTSKY, unpublished). There is some evidence that when ~30 mg of a hydrous phase containing 2–5 weight percent H_2O is dissolved in 30 g of $2PbO \cdot B_2O_3$ at 700°C, the H_2O stays in

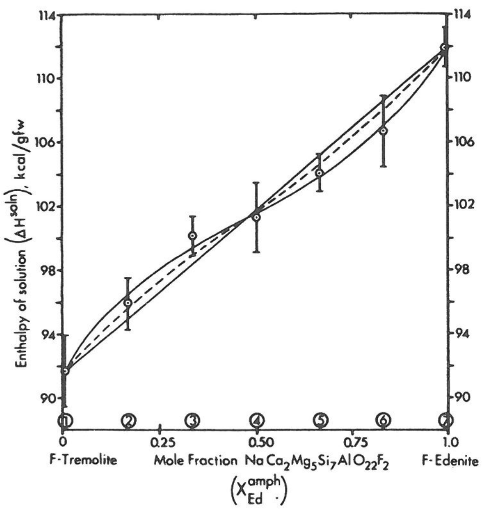

FIG. 4. Enthalpies of solution of synthetic fluortremolite-fluoredenite amphiboles. Brackets indicate standard deviations. Solid curve is least squares fitted third-order polynomial through all the data, consistent with subregular solution model. Dashed curve is for subregular model with W^{H}_{tr} and W^{H}_{ed} fixed at lower magnitude limits permitted by uncertainties at the 95% confidence interval. Solid straight line indicates ideal mixing (GRAHAM and NAVROTSKY, 1986).

solution, corresponding to an H_2O solubility on the order of 50 ppm or greater, but this needs further study. Preliminary data for the heat of formation of phlogopite using its heat of solution in lead borate (J. D. CLEMENS and A. NAVROTSKY, unpublished) look reasonable. These same studies also suggest the feasibility of studying the energetics of stacking disorder in layer silicates by solution calorimetry. An exploratory study of the heats of solution along the F-pargasite-OH-pargasite join (N. ROSS and A. NAVROTSKY, unpublished) also is promising. Problems and limitations seem to arise more from sample quality (phase purity, structural state and homogeneity) than from calorimetric difficulties.

Thermochemical cycles can be devised to deal with phases which decompose if left at 700°C in the calorimeter to equilibrate prior to dissolution. The first of these can be called "drop-solution" calorimetry. In it, the sample is dropped from room temperature into molten lead borate in the calorimeter, whereupon it dissolves. The enthalpy measured is its heat content plus its heat of solution. Subtraction of the heat content gives the heat of solution. A similar approach has been taken to calorimetry of high pressure phases which do not persist metastably at 700°C and atmospheric pressure (AKAOGI and NAVROTSKY, 1985).

"Drop-solution" calorimetry on MgO and $Mg(OH)_2$ has been used to estimate the heat of solution of H_2O in lead borate melt at 700°C and 1 atm (S. CIRCONE and A. NAVROTSKY, unpublished). An exothermic enthalpy of solution of -5.7 ± 0.7 kcal/mole has been estimated. This value can be used in other thermochemical cycles to calculate heats of formation of hydrous minerals from "drop-solution" calorimetry and to correlate data obtained by high temperature oxide melt calorimetry and by HF solution calorimetry. Though still preliminary, this work opens the way to many other studies of hydrous phases.

Another approach to high temperature calorimetry of hydrous phases not persisting near 700°C is direct measurement of heat of dehydration by transposed-temperature-drop calorimetry. This method works well when samples dehydrate rapidly and we have called it decrepitation calorimetry. The enthalpy of dehydration is measured as the difference between first and second drop experiments on an unsealed Pt capsule containing powdered material. Weight change is monitored to check for complete H_2O loss and the dehydrated product is characterized by X-ray and optical means and by a normal heat of solution measurement in $2PbO \cdot B_2O_3$ at 700°C. This heat of solution permits a comparison of the energetics of the fine-grained and often amorphous or poorly crystalline dehydration product with that of a crystalline anhydrous phase assemblage or a previously melted glass. From these data, a thermochemical cycle calculates the enthalpy of dehydration to well-characterized products. The results of such studies for glasses in the system albite-water are discussed below. The method should be applicable to a variety of synthetic and also possibly natural hydrous materials. Changes in oxidation state of iron during dehydration present a complication and experiments are best confined to samples with low iron contents.

Oxide melt solution calorimetry using $2PbO \cdot B_2O_3$ near 700°C has been used extensively in anhydrous silicate systems to study heats of formation (NAVROTSKY and COONS, 1976), phase transition (AKAOGI and NAVROTSKY, 1985), solid solution formation (CARPENTER *et al.*, 1985) and vitrification and mixing in the glassy state (NAVROTSKY *et al.*, 1980). It is now an essentially routine procedure for phases containing SiO_2, Al_2O_3, Fe_2O_3, GeO_2, alkali and alkaline earth oxides, CoO, NiO, ZnO and can be applied, with care under a non-oxidizing atmosphere to compounds containing Mn^{2+}, Cr^{3+}, and to some Fe^{2+}-silicates (AKAOGI and NAVROTSKY, 1985; NAVROTSKY *et al.*, 1979; WOOD and KLEPPA, 1984). Combined with the methods discussed above, hydrous crystals and glasses containing these same oxides can be studied. More rigorous oxygen fugacity control for calorimetry of iron-bearing phases can be achieved in an alkali borate solvent near 750°C (CHATILLON-COLINET *et al.,* 1983). This melt is also useful for calorimetry of titanates and zirconates (E. MUROMACHI-TAKAYAMA and A. NAVROTSKY, in preparation) which form insoluble precipitates on reaction with lead borate. The calorimetric behavior of samples containing small amounts of Ti^{4+} and/or Fe^{2+} has not been explored in detail.

The growing data base of mixing properties of aluminosilicate glasses has been extrapolated to provide enthalpy of mixing data for the melts. The validity of such extrapolations from glass to melt has been discussed extensively (NAVROTSKY *et al.,* 1982; STEBBINS *et al.,* 1982, 1983, 1984; BOETTCHER *et al.,* 1982; RICHET *et al.,* 1982; RICHET and BOTTINGA, 1984). The verdict is not in yet but the evidence seems to suggest that when ΔC_p terms are known, such comparisons can be made with reasonable accuracy. Direct measurement of heats of mixing in silicate melts at 1000–1400°C would be very desirable. Conventional oxide melt solution calorimetry is not readily extended into that range because of problems of calorimeter stability, volatility of solvent, corrosion of ceramic and SiO_2-glass parts, and other technical difficulties. Transposed temperature drop calorimetry, using closed capsules of mixtures of phases which melt in the calorimeter, is potentially capable of getting heats of fusion and heats of mixing in melts. We are currently investigating the applicability of this method to melts in the system albite-anorthite-diopside at 1100–1500°C.

The simultaneous application of high pressure to contain H_2O and temperatures of 800–1500°C, necessary for direct calorimetric study of mixing in hydrous silicate melts, is very difficult. Other than the heat content measurements by drop calorimetry described above, there is little hope, in my opinion, for immediate progress in this area. Qualitative methods, such as DTA at high pressure (ROSENHAUER, 1976) offer some possibilities, but they are more useful in mapping out phase relations, including those in hydrous systems, than in attempts to obtain quantitative thermochemical data.

Aqueous fluids at high P and T

Despite the importance of the aqueous phase in geothermal systems, hydrothermal and magmatic ore deposits, late stage magmatism and pegmatites, and explosive volcanism, thermochemical data for aqueous fluids, especially away from the vapor saturation curve, are largely lacking. Calorimetric data are difficult to obtain above ~100°C. KASPER *et al.* (1981), as mentioned above, obtained some heat content data on NaCl-H_2O at 0.5 and 1 kbar up to 700°C. H. FUKUYAMA, J. R. HOLLOWAY and A. NAVROTSKY (unpublished) designed and operated a mixing cell for use to ~350°C at pressures of up to 1 kbar. Some heat of dilution data in the system NaCl-H_2O were obtained but the cell, which contained inconel bellows assemblies to equalize internal pressure to that of the external argon medium, proved prone to mechanical failure when used with salt solutions. Both the heat content and heat of dilution measurements were time- and labor-intensive; each calorimetric experiment had to be assembled, pressurized, equilibrated at high temperature, run, disassembled, and cleaned. Thus even under optimum conditions, productivity in such experiments was limited to one run per day. After these experiences, it appears that future calorimetric studies at high temperature should concentrate on methods which maintain a continuous high P, T regime while measuring enthalpy changes associated with aqueous solutions passing through the system, that is, flow calorimetry. Such calorimeters have been in use for a number of years for both heat capacity measurements and heats of mixing at the low end of the needed temperature range, namely up to about 200°C and at pressures either along the vapor saturation curve or up to a few hundred bars (MESSIKOMER and WOOD, 1975; PERRON *et al.,* 1975; PICKER *et al.,* 1971; BUSEY *et al.,* 1984; SIMMONS *et al.,* 1985). It should be technologically feasible to extend the range to ~1 to 2 kbar and 500–600°C.

THERMOCHEMISTRY OF GLASSES AND MELTS IN THE SYSTEM ALBITE-WATER AND A MODEL GRANITE

To illustrate the application of the methods described above to a specific petrologic system, this section summarizes recently completed work on the system albite-water and a model hydrous granite (CLEMENS and NAVROTSKY, 1986). The purpose of this study was to characterize the energetics of dissolution of H_2O into framework silicate melts. Samples were prepared at appropriate high P and T conditions (900–1200°C, 1–5 kbar) to give liquids with H_2O-contents between 1.5 and 9 weight percent (mole fraction H_2O in $NaAlSi_3O_8$-H_2O in the range 0.05 to 0.59). The P-T conditions were chosen, for a given H_2O-content, to be at temperatures above the liquidus and at water contents below H_2O-saturation, so that quenched melts would not trap H_2O bubbles. Samples were quenched to glasses and H_2O-contents were determined by TGA. The quenched glasses were generally clear and showed no indication of exsolved water either prior to or after drop calorimetry at high pressure. Three types of calorimetric measurements were performed: "decrepitation" calorimetry mainly at 795°C (some experiments also at 700°C), heat of solution measurements in $2PbO \cdot B_2O_3$ at 700°C of decrepitated glasses, and drop calorimetry at 1 kbar of one anhydrous and one hydrous samples with the furnace at 983°C and 1033°C, the calorimeter at 85°C. Similar decrepitation experiments were run for a model hydrous granite.

A thermochemical cycle, shown in Figure 5, can be used to calculate the heat of mixing of Ab-H_2O at 25°C from the decrepitation and solution calorimetry. The results, for the reaction

$$X\,H_2O\,(\text{liquid}, 25°C) + (1-X)\,Ab\,(\text{glass}, 25°C) = \text{hydrous glass}\,(25°C) \quad (2)$$

are shown in Figure 6. A negative heat of mixing, with a minimum near $X = 0.25$, is seen. The results may also be represented as the heat of solution of one mole of H_2O in an amount of albite glass to form hydrous glass of the appropriate composition. This quantity is shown in Figure 7. The heat of solution, per mole H_2O, is also exothermic, but becomes less so with increasing H_2O content.

Analogous, though less complete, data are shown for a melt near the granite eutectic, where the "granite" component is $Ab_{0.35}Or_{0.26}4Q_{0.39}$ (see Figures 6 and 7). The heats of mixing and of solution of H_2O are much closer to zero and, though they show slight positive values at $X = 0.09$ and negative values at $X = 0.32$ and 0.55, these are near the resolution of the calorimetric data.

What do these data mean in terms of proposed thermodynamic model for H_2O solubility and speciation in glasses and melts? The model proposed by BURNHAM (1975, 1981) suggests that H_2O mixes ideally with the aluminosilicate component written on an 8-oxygen basis. Strictly speaking, ideality implies zero heat of mixing. The calorimetric data show small but significant non-zero heats of mixing in the glasses. These may be somewhat smaller (see below) in the melts. The Ab-H_2O and granite-H_2O systems behave somewhat differently from each other. Thus although the deviations from BURNHAM's model are small, they do suggest that in terms of energetics, the dissolution of H_2O is somewhat more complex than the model implies. Indeed, since a miscibility gap exists in Ab-H_2O at high values of X (saturated melt coexisting with aqueous fluid) energetic complexity must exist somewhere in the system.

BURNHAM's model is based on the assumption that all H_2O in the melt is present as OH^-. STOLPER (1982) suggests an equilibrium among H_2O and OH^- species according to the reaction:

$$H_2O\,(\text{in melt}) + O^=\,(\text{in melt}) = 2OH^-\,(\text{in melt}). \quad (3)$$

The equilibrium constant for this reaction is suggested to have virtually no temperature dependence and only a weak dependence on composition (STOLPER, 1982; SILVER and STOLPER, 1985) with a value of ~0.17 for the system albite-water (SILVER and STOLPER, 1985).

The mixing of H_2O with albite melt may be thought of as consisting of two steps. The first is the dissolution as molecular water

$$H_2O\,(\text{fluid}) = H_2O\,(\text{in melt}). \quad (4)$$

The second is the dissociation equilibrium [Eqn. (3)] above. These reactions may be rewritten as follows, with X = mole fraction total H_2O dissolved and Y = fraction of the dissolved H_2O which dissociates (Y = degree of dissociation).

$$X\,H_2O\,(\text{fluid}) = X\,H_2O\,(\text{in melt}) \quad (\Delta H_A) \quad (5)$$

$$(YX)\,H_2O\,(\text{in melt}) + (YX)\,O^=\,(\text{in melt}) = (YX)\,OH^-\,(\text{in melt}) \quad (\Delta H_B). \quad (6)$$

Assume that each of these steps has an enthalpy associated with it which depends linearly on the number of moles of H_2O undergoing the process. Then

$$\Delta H = X\Delta H_A + XY\Delta H_B \approx \Delta H^{mix} \quad (7)$$

where ΔH_A is that of reaction (5) in the text and ΔH_B is that of reaction (6).

This is approximately equal to the heat of mixing if the energetics of any perturbation of the aluminosilicate framework is also linearly dependent in energy on the amount of H_2O initially dissolved (X) and is therefore incorporated in Eqn. (5). This formulation is reasonable for relatively low water contents but obviously cannot be extrapolated to $X \rightarrow 1$. Since immiscibility intervenes at high H_2O content no formulation which ignores that feature can be valid at high water contents anyhow, as STOLPER (1982) has recognized.

One may then calculate Y, the degree of dissociation, as a function of X, the mole fraction of H_2O in $NaAlSi_3O_8$-H_2O, using the formulation of STOLPER (1982) and SILVER and STOLPER (1985). The numbers of moles of species, n, per mole of XH_2O-$(1-X)NaAlSi_3O_8$ are

$$\begin{tikzcd}
xAb \arrow[d, "\Delta H_2"] & + & (1-x)\ H_2O \arrow[r, "\Delta H_1", "298\ K,\ 1\ atm"'] \arrow[d, "\Delta H_3"] & Ab_x(H_2O)_{1-x} \arrow[d, "\Delta H_4"] \\
xAb & + & (1-x)\ H_2O \arrow[r, "\Delta H_5", "T,\ 1\ atm"'] & Ab_x(H_2O)_{1-x}
\end{tikzcd}$$

$$\begin{tikzcd}
xAb \arrow[d, "\Delta H_7"] & + & (1-x)\ H_2O \arrow[r, "\Delta H_6", "298\ K,\ 1\ kb"'] \arrow[d, "\Delta H_8"] & Ab_x(H_2O)_{1-x} \arrow[d, "\Delta H_9"] \\
xAb & + & (1-x)\ H_2O \arrow[r, "\Delta H_{10}", "T,\ 1\ kb"'] & Ab_x(H_2O)_{1-x}
\end{tikzcd}$$

Measure: $\Delta H_4 - \Delta H_3$ by decrepitation
calorimetry and $\Delta H_{solution}$ of anhydrous glass
ΔH_9 by high P drop calorimetry

Know: $\Delta H_2 = H^\circ_T - H^\circ_{298}$ of Ab glass
ΔH_3, ΔH_8 from properties of H_2O

Assume: $\Delta H_2 = \Delta H_7$, $\Delta H_1 = \Delta H_6$

Then

Calculate ΔH_1 = heat of mixing of Ab (glass) and H_2O (liquid) at 298 K and 1 atm

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_5 - \Delta H_4$$

Calculate ΔH_{10} = heat of mixing of Ab (glass or melt) and H_2O (fluid) at T and 1 kb (or other operating P)

$$\Delta H_{10} = -\Delta H_7 - \Delta H_8 + \Delta H_6 + \Delta H_9$$

FIG. 5. Thermochemical cycles used to calculate enthalpies of mixing in Ab-H_2O glasses and liquids.

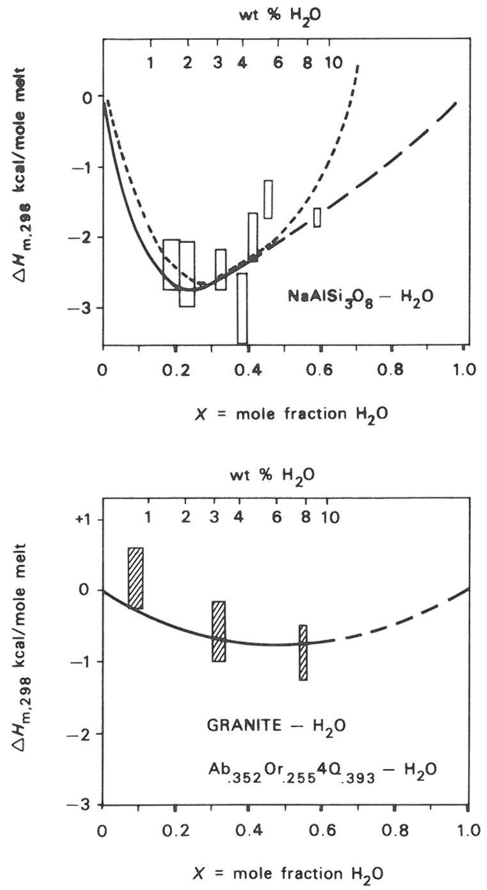

FIG. 6. Enthalpies of mixing at 25°C for the systems albite-water and "granite"-water. Rectangles are data points, showing uncertainties, from CLEMENS and NAVROTSKY (1986). Solid and long-dashed curves are visual estimates of smooth curves which approach $\Delta H^{mix} = 0$ at $X = 0$ and $X = 1$. Short-dashed curve is calculated using STOLPER's (1982) model and $K = 0.17$ (SILVER and STOLPER, 1985). See text.

$$
\begin{aligned}
nOH^- &= 2XY \\
nH_2O &= X(1-Y) \qquad (8) \\
nO^= &= 8(1-X) - XY = 8 - 8X - XY
\end{aligned}
$$

and the equilibrium constant, K, for the dissociation (STOLPER's K_2) is:

$$
K = \frac{(2XY)^2}{X(1-Y)(8-8X-XY)} = \frac{4XY^2}{(1-Y)(8-8X-XY)} \approx 0.17. \qquad (9)
$$

For any value of X one can solve for Y, then Eqn. (7) can be rewritten, per mole of H_2O dissolved as

$$
\Delta H/X = \Delta H_A + Y\Delta H_B. \qquad (10)
$$

A least squares fit of $\Delta H^{mix}/X$ versus Y gives, $\Delta H_A = 10.71 \pm 2.54$ kcal, and $\Delta H_B = -33.8 \pm 4.74$ kcal, with a correlation coefficient of 0.946. Using the same approach with $K = 0.085$ and 0.34 (half and twice STOLPER's values) gives different parameters with a slightly worse fit. The calculated heat of mixing is shown as the dotted curve in Figure 6; the values of $\Delta H^{mix}/X$ calculated from the fit are shown by the solid curve in Figure 7. Note that although $\Delta H^{mix}/X$ is assumed to be a linear function of Y (Eqn. 10), $\Delta H^{mix}/X$ varies nonlinearly with X because X and Y are related by the nonlinear function given by the equilibrium constant K (Eqn. 9).

The calorimetric data for mixing in Ab-H_2O glasses thus appear to be consistent with STOLPER's proposed speciation reactions. The minimum in the heat of mixing appears to arise from the balance of two factors: an endothermic heat of dissolution of molecular H_2O and an exothermic heat of dissociation, with the degree of dissociation decreasing with increasing H_2O content. For $X > \sim 0.7$, Eqns. (9) and (10) suggest positive heats of mixing (see Figure 6). It may be coincidental that the compo-

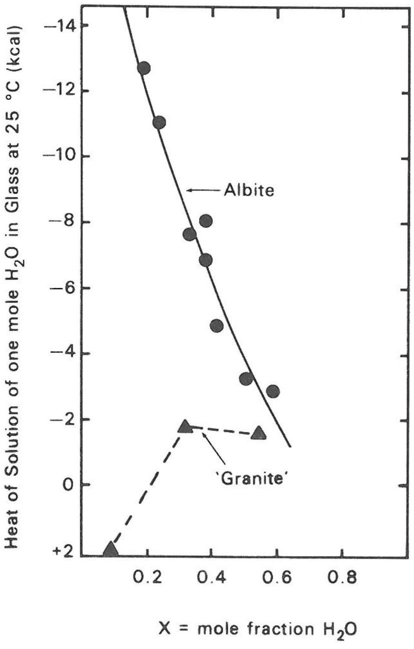

FIG. 7. Enthalpy of solution of one mole of water in glass at 25°C for system albite-water and "granite"-water. Data are from CLEMENS and NAVROTSKY (1986). Circles are data points for $NaAlSi_3O_8$-H_2O, triangles for $Ab_{0.352}Or_{0.255}4Q_{0.393}$-$H_2O$. Solid curve is calculated using STOLPER's (1982) model, see text. Dashed line simply connects "granite" data points.

sition where ΔH^{mix} becomes positive corresponds to the two-phase (saturated melt plus vapor) region, but the trend toward positive enthalpies is interesting.

However, this general interpretation suffers one serious problem. For reaction (3), STOLPER proposes an equilibrium constant of 0.17 to 0.2; we suggest an enthalpy on the order of −34 kcal. Since $\Delta G^0 = -RT \ln K$, and $K < 1$, ΔG^0 is positive regardless of what temperature (that of melt, quenched glass, or some intermediate temperature at which the speciation is frozen in) one associates with STOLPER's values of K. A small positive ΔG^0 and a large negative ΔH^0 imply a large negative ΔS^0 (on the order of −30 to −40 cal K^{-1} mol^{-1}, depending on the value of T chosen for the dissociation equilibrium). Though such large negative ΔS^0 and negative ΔH^0 values are seen for some acid dissociation reactions in aqueous solutions which produce charged species (DASENT, 1981), it is not clear that the reaction of H_2O in silicate melts bears any real analogy. Furthermore, the large magnitudes of ΔH^0 and ΔS^0 are very difficult to reconcile with a temperature-independent dissociation constant. Indeed, the values of ΔH and ΔS would suggest that the equilibrium shifts toward molecular water with increasing temperature. Further study is needed.

STOLPER's model is quite simple and neglects both positive interactions leading to immiscibility and energetic differences among differently bonded oxygen species in the melt. Though the present calorimetric data appear to be described adequately, except for the problem discussed above, one might expect that higher resolution in future calorimetric studies could require more complex models. At present the overall quality of models and data are well matched in that both are fairly crude first approximations.

The fact that negative heats of mixing are seen argues for chemical interaction between glass and H_2O. Were the water present only as species having the characteristics of pure H_2O (e.g., as microbubbles) then a zero heat of mixing (that of a mechanical mixture) would be expected. Thus, regardless of details of speciation, our data suggest that H_2O is interacting energetically on a microscopic (atomistic) scale as a truly dissolved entity.

The drop calorimetric experiments from high P and T allow estimates of the heat of mixing at high P and T for the composition studied by using the thermochemical cycle in Figure 5. The results for $x = 0.388$ are shown in Figure 8. The heat of mixing becomes less exothermic with increasing temperature. However, this is at least partly a result of increasing the molar volume of H_2O with increasing T (at 1000°C and 1 kbar, the volume of H_2O is roughly 5 times the volume of liquid water at 25°C). When the PV work done to compress the H_2O back to its original volume is subtracted, the resulting heat of mixing (open circles in Figure 8) shows a temperature dependence which is not outside experimental error. This suggests that the interactions within the melt or glass phase may not be very temperature dependent.

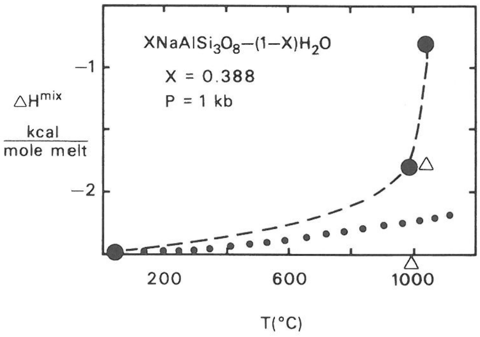

FIG. 8. Enthalpy of mixing of Ab-H_2O at $X_{H_2O} = 0.388$ at different temperatures. Solid circles are points calculated using thermochemical cycle in Figure 5. Triangles are calculated from these by subtracting the term $P(V_{H_2O(P,T)} - V_{H_2O(1\ atm,\ 25°C)})$ with P = 1 kbar. These then refer to mixing of water at a constant volume. Uncertainties are about ±0.4 kcal at 25°C and ±0.8 to ±1.0 kcal at high temperature.

CONCLUSIONS

Calorimetric study of hydrous crystals and glasses is possible utilizing thermochemical cycles involving solution calorimetry, drop and transposed-temperature-drop calorimetry, and direct study of water release. Direct calorimetric data on silicate melts may be obtainable by transposed temperature drop calorimetry. Calorimetric study of hydrous melts at high P and T is feasible for fairly limited heat content studies. Calorimetry of aqueous fluids at 200–600°C can be developed. Many of these methods are new and exploratory. The next few years should provide many new advances.

Acknowledgements—This work has been supported by the U.S. Dept. of Energy (Grant DE-FG02-85ER-13437) and the National Science Foundation (Grant EAR-8513916).

REFERENCES

AKAOGI M. and NAVROTSKY A. (1985) Calorimetric study of high pressure polymorphs of $MnSiO_3$. *Phys. Chem. Min.* **12,** 317–323.

BOETTCHER A. L., BURNHAM C. W., WINDOM K. E. and BOHLEN S. R. (1982) Liquids, glasses, and the melting of silicates at high pressure. *J. Geol.* **90,** 127–138.

BURNHAM C. W. (1975) Water and magmas: a mixing model. *Geochim. Cosmochim. Acta* **39,** 1077–1084.

Burnham C. W. (1981) The nature of multicomponent aluminosilicate melts. In *Chemistry and Geochemistry of Solutions at High Temperatures and Pressures* (eds. D. T. Rickard and F. E. Wickman), *Physics and Chemistry of the Earth,* Vol. 13–14, 197–229, Pergamon Press.

Burnham C. W. and Nekvasil H. (1986) Equilibrium properties of granite pegmatite magmas. *Amer. Mineral.* **71,** 239–263.

Busey R. H., Holmes H. F. and Mesmer R. F. (1984) The enthalpy of dilution of aqueous sodium chloride to 373 K using a new heat flow and liquid flow microcalorimeter. Excess thermodynamic properties and their pressure derivatives. *J. Chem. Thermo.* **16,** 343–372.

Carpenter M. A., McConnell J. D. C. and Navrotsky A. (1985) Enthalpies of Al-Si ordering in the plagioclase feldspar solid solution. *Geochim. Cosmochim. Acta* **49,** 947–966.

Chatillon-Colinet C., Kleppa O. J., Newton R. C. and Perkins D. (1983) Enthalpy of formation of $Fe_3Al_2Si_3O_{12}$ (almandine) by high temperature alkali borate solution calorimetry. *Geochim. Cosmochim. Acta* **47,** 439–444.

Clemens J. D. and Navrotsky A. (1986). Mixing properties of $NaAlSi_3O_8$ melt-H_2O: New calorimetric data and some geological applications. *J. Geol.* (In press).

Dasent W. E. (1981) *Inorganic Energetics.* 167–171. Cambridge Univ. Press.

Graham C. M. and Navrotsky A. (1986) Thermochemistry of the tremolite-edenite amphiboles using fluorine analogues, and applications to amphibole-plagioclase-quartz equilibria. *Contrib. Mineral. Petrol.* **93,** 18–32.

Hemingway B. S., Barton M. D., Robie R. A. and Haselton H. T. (1986) Heat capacities and thermodynamic functions for beryl, phenakite, euclase, bertrandite and chrysoberyl. *Amer. Mineral.* **71,** 557–568.

Henry D. J., Navrotsky A. and Zimmermann H. D. (1982) Thermodynamics of plagioclase-melt equilibria in the system albite-anorthite-diopside. *Geochim. Cosmochim. Acta* **46,** 381–391.

Hervig R. L., Scott D. and Navrotsky A. (1985) Thermochemistry of glasses along joins of pyroxene stoichiometry in the system $Ca_2Si_2O_6$-$Mg_2Si_2O_6$-Al_4O_6. *Geochim. Cosmochim. Acta* **49,** 1497–1501.

Kasper R. B., Holloway J. R. and Navrotsky A. (1979) Direct calorimetric measurement of enthalpies of aqueous sodium chloride solutions at high temperatures and pressures. *J. Chem. Thermo.* **11,** 13–24.

Krupka K. M., Robie R. A. and Hemingway B. S. (1979) High-temperature heat capacities of corundum, periclase, anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophillite, $KAlSi_3O_8$ glass, grossular, and $NaAlSi_3O_8$ glass. *Amer. Mineral.* **64,** 86–101.

Messikomer E. E. and Wood R. H. (1975) The enthalpy of dilution of aqueous sodium chloride at 298.15 to 373.15 K, measured with a flow calorimeter. *Jour. Chem. Thermo.* **7,** 119–130.

Navrotsky A. (1977) Recent progress and new directions in high temperature calorimetry. *Phys. Chem. Min.* **2,** 89–104.

Navrotsky A. (1979) Calorimetry: its application to petrology. *Ann. Rev. Earth Planet. Sci.* **7,** 93–115.

Navrotsky A. (1982) Trends and systematics in mineral thermodynamics. *Berichte Bunsengesellschaft Phys. Chem.* **86,** 994–1001.

Navrotsky A. (1985) Crystal chemical constraints on thermochemistry of minerals. In *Microscopic to Macroscopic* (eds. Kieffer S. W. and A. Navrotsky), Chap. 7, pp. 225–276 Min. Soc. Amer.

Navrotsky A. and Coons W. E. (1976) Thermochemistry of some pyroxenes and related compounds. *Geochim. Cosmochim. Acta* **33,** 1281–1288.

Navrotsky A., Capobianco C. and Stebbins J. (1982) Some thermodynamic and experimental constraints on the melting of albite at atmospheric and high pressure. *J. Geol.* **90,** 679–698.

Navrotsky A., Hon R., Weil D. F. and Henry D. J. (1980) Thermochemistry of glasses and liquids in the systems $CaMgSi_2O_6$-$CaAl_2Si_2O_6$-$NaAlSi_3O_8$, SiO_2-$CaAl_2Si_2O_8$-$NaAlSi_3O_8$ and SiO_2-Al_2O_2-CaO-Na_2O. *Geochim. Cosmochim. Acta* **44,** 1409–1423.

Navrotsky A., Pintchovski F. S. and Akimoto S. (1979) Calorimetric study of the stability of high pressure phases in the systems CoO-SiO_2 and "FeO"-SiO_2 and calculation of phase diagrams in MO-SiO_2 systems. *Phys. Earth Planet. Int.* **19,** 275–292.

Perkins D., Essene E. J. and Westrum E. T. (1979) New thermodynamic data for diaspore and their application to the system Al_2O_3-SiO_2-H_2O. *Amer. Mineral.* **64,** 1080–1090.

Perkins D., Westrum E. F. and Essene E. J. (1980) The thermodynamic properties and phase relations of some minerals in the system CaO-Al_2O_3-SiO_2-H_2O. *Geochim. Cosmochim. Acta* **44,** 61–84.

Perron G., Fortier J. and Desnoyers J. E. (1975) The apparent molar heat capacities and volumes of aqueous NaCl from 0.01 to 3 mol kg^{-1} in the temperature range 274.65 to 318.15 K. *J. Chem. Thermo.* **7,** 1177–1184.

Picker P. K., Luduc P., Philip P. and Desnoyers J. E. (1971) Heat capacity of solutions by flow microcalorimetry. *J. Chem. Thermo.* **3,** 631–642.

Richet P. and Bottinga Y. (1984) Anorthite, andesine, wollastonite, diopside, cordierite, and pyrope: thermodynamics of melting, glass transitions, and properties of the amorphous phases. *Earth Planet. Sci. Lett.* **67,** 415–422.

Richet P., Bottinga Y., Danielou L., Petitet J. P. and Tequi C. (1982) Thermodynamic properties of quartz, cristobalite and amorphous SiO_2: drop calorimetry measurements between 1000 and 1800 K and a review from 0 to 2000 K. *Geochim. Cosmochim. Acta* **46,** 2639–2658.

Robie R. A. and Hemingway B. S. (1972) Calorimeters for heat of solution and low-temperature heat capacity measurements. *U.S. Geol. Survey Prof. Paper 755,* U.S. Govt. Printing Office, Washington, DC.

Robie R. A., Hemingway B. S. and Wilson W. H. (1976) The heat capacities of calorimetry conference copper and of muscovite, pyrophillite, and illite between 15 and 375 K and their standard entropies at 298.15 K. *J. Res. Nat. Bur. Stand.* **4,** 631–644.

Robie R. A., Hemingway B. S. and Wilson W. H. (1978) Low-temperature heat capacities and entropies of feldspar glasses and of anorthite. *Amer. Mineral.* **63,** 109–123.

Rosenhauer M. (1976) Effect of pressure on the melting enthalpy of diopside under dry and H_2O-saturated conditions. *Carnegie Inst. Wash. Yearb.* **75,** 648–650.

Silver L. and Stolper E. (1985) A thermodynamic model for hydrous silicate melts. *J. Geol.* **93,** 161–178.

Simmons J. M., Busey R. H. and Mesmer R. E. (1985) Enthalpies of dilution of aqueous calcium chloride at low molalities at high temperatures. *J. Phys. Chem.* **89,** 557–560.

Stebbins J. F. and Carmichael I. S. E. (1984) The heat of fusion of fayalite. *Amer. Mineral.* **69,** 292–297.

Stebbins J. F., Carmichael I. S. E. and Moret L. K. (1984) Heat capacities and entropies of silicate liquids and glasses. *Contrib. Mineral. Petrol.* **86,** 137–148.

Stebbins J. F., Weill D. F. and Carmichael I. S. E. (1983) The high temperature liquid and glass heat contents and the heats of fusion of diopside, albite, sanadine, and nepheline. *Amer. Mineral.* **68,** 717–730.

Stebbins J. F., Weill D. F. and Carmichael I. S. E. (1983) The high temperature liquid and glass heat contents and the heats of fusion of diopside, albite, sanidine, and nepheline. *Amer. Mineral.* **68,** 717–730.

Stolper E. (1982) The speciation of water in silicate melts. *Geochim. Cosmochim. Acta* **46,** 2609–2620.

Stout N. D. and Piwinskii A. J. (1982) Enthalpy of silicate melts from 1520 to 2600 K under ambient pressure. *High Temp. Sci.* **15,** 275–292.

Westrum E. F. Jr., Furukawa G. T. and McCullough J. P. (1968) Adiabatic low temperature calorimetry. In *Experimental Thermodynamics, Vol. I, Calorimetry of Non-Reacting Systems,* (eds. J. P. McCullough and D. W. Scott), pp. 133–214, Plenum, New York.

Weill D. F., Hon R. and Navrotsky A. (1980) The igneous system $CaMgSi_2O_6$-$CaAl_2Si_2O_6$-$NaAlSi_3O_8$: Variations on a classic theme by Bowen. In *Physics of Magmatic Processes,* (ed. R. B. Hargraves), pp. 49–92, Princeton Univ. Press.

Westrich H. R., Holloway J. R. and Navrotsky A. (1981) Some thermodynamic properties of fluorapatite, fluorpargasite, and fluorphlogopite. *Amer. J. Sci.* **281,** 1091–1195.

Wood B. J. and Kleppa O. J. (1984) Chromium-aluminum mixing in garnet: a thermochemical study. *Geochim. Cosmochim. Acta* **48,** 1373–1375.

Ziegler D. and Navrotsky A. (1986) Direct measurement of the enthalpy of fusion of diopside. *Geochim. Cosmochim. Acta.* **50,** 2461–2466.