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A reevaluation of the calorimetric data for the enthalpy of formation of some K- and Na-bearing silicate minerals[1]

by

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Abstract

Calorimetric data from aqueous HF and molten-salt calorimetry have been reviewed for the phases microcline, sanidine, muscovite, analcime, sodium aluminate, low albite, jadeite, and analbite. The review was conducted to evaluate the suggestion by Sverjensky et al. (1991) that the calorimetric data for K- and Na-bearing phases was in error by -6.69 and -6.80 kJ•mol^{-1}, respectively; and the suggestion by Johnson et al. (1992) that silicalite replace quartz as the Si reference phase in aqueous HF calorimetry. Our examination of the data set does not support either suggestion. Our recommended values for the enthalpies of formation from the elements at 298.15 K for muscovite, analcime, sodium aluminate, low albite, jadeite, and analbite (-5974.8 ± 4.9, -3309.8 ± 3.3, -1135.6 ± 1.4, -3935.0 ± 2.6, -3029.3 ± 2.5, and -3923.6 ± 2.6 kJ•mol^{-1}) are essentially identical to the generally accepted calorimetric values given by Hemingway and Robie (1977) or Robie et al. (1979). However, our recommended values for the enthalpy of formation from the elements of microcline and sanidine are -7.2 and -6.3 kJ more stable than the values given by those sources. Our analysis suggests that the enthalpy of solution of aluminum chloride hexahydrate in aqueous HF was the probable source of error. Our recommended values for the enthalpy of formation from the elements at 298.15 K for microcline, sanidine, and $KAlSi_3O_8$ glass are -3974.6 ± 3.9, -3965.6 ± 4.1, and -3920.8 ± 4.2 kJ•mol^{-1}, respectively.

Introduction

A recent article by Sverjensky et al. (1991) has called for the addition of -6.69 and -6.80 kJ to the enthalpies of formation of all K- and Na-bearing silicate minerals, respectively, calculated by Berman (1988) from an analysis of phase equilibrium data. They base this recommendation on an analysis of their solubility data for K-bearing silicate assemblages and corrected data for Na-bearing silicate assemblages (Montoya and Hemley, 1975) together with the properties of the aqueous species calculated by Shock and Helgeson (1988). Because Berman (1988) selected calorimetric data as the reference data from which to calculate the enthalpies of formation he reported, Sverjensky et al. (1991) are suggesting that the calorimetric data are in error by the amounts given above. Alternatively, either the properties of the aqueous species or the solubility data could be in error. The properties of the aqueous species developed by Shock and Helgeson (1988) are based upon analysis of data for a number of simple compounds and agreement between varied data sets supports the accuracy of the properties. On the other hand, significant differences exist in phase equilibrium data for muscovite solubility and dehydration reactions (Haselton and Cygan, 1988; Haselton et al., 1993). In this study, we shall review the calorimetric data for some of the K- and Na-bearing silicate minerals.

Sverjensky et al. (1991) were unable to identify a particular calorimetric reaction that could be the cause of the disparity between the calorimetrically and solubility derived thermodynamic data. They suggested that the cause might lie in the value used for the enthalpy of solution of quartz in aqueous HF. This seems unlikely since Hemingway et al. (1981) have shown that their value for the enthalpy of formation of low albite derived from aqueous HF calorimetry and based on quartz agrees with the value reported by Navrotsky et al. (1980) derived from molten-salt calorimetry and also based on quartz. If there is an error as suggested by Sverjensky et al. (1991), the calorimetric data can be adjusted only if the error is associated with a specific reference reaction for an element (contrary to the procedure followed by Sverjensky et al., 1991). For example, if an error was detected in a reference reaction for Na, K, or Al, the full correction suggested by Sverjensky et al. (1991) would be applied for each Na, K, or Al in the formula of the phase to be corrected. On the other hand, if the error were in a reference reaction for Si, only 1/3 of the correction would be applied per Si in the phase to be corrected (e.g., the correction for low albite would be larger than for jadeite). The experimental data analyzed by Sverjensky et al. (1991) only examined feldspar and mica reactions where the Na or K/Al/Si was constant at 1/1/3. Thus their analysis can not discriminate between the corrections listed above.

It has been more than 15 years since the last review was made of the calorimetric data for K- and Na-bearing silicate minerals (Hemingway and Robie, 1977). Some questions could not be resolved completely at that time. New calorimetric data reported in the intervening years provides independent measurements for some of these phases and allows resolution of some of the questions.

Calorimetric reaction schemes for microcline, sanidine, muscovite, analcime, sodium aluminate, albite, analbite, and jadeite

The calorimetric data examined in this study are derived from two types of solution calorimetry, aqueous HF and molten-salt calorimetry. Each type of calorimeter can be operated in two modes, one in which the sample and the solvent are maintained at the same temperature (e.g., Hemingway and Robie, 1977, Navrotsky et al., 1980 and Johnson et al., 1982), and the other in which the sample is maintained at room temperature and the solvent at a higher temperature (Barany, 1962 and 1964). In the latter method, the sample must be dropped into the calorimeter. The calorimetric reactions are shown in abbreviated form in Tables 1-5, and are discussed below.

The larger portion of calorimetric values for the enthalpy of formation of silicate minerals were calculated from experiments reported by workers at the U.S. Bureau of Mines (e.g., Barany, 1962 and 1964). Therefore, some of the discussion below is referenced to that work and to the procedures used in their laboratory.

Microcline, sanidine, and muscovite

The enthalpy of solution and formation reactions selected for the extraction of the recommended calorimetric enthalpies of formation of microcline, sanidine and muscovite are listed in Table 1. Each reaction represents dissolution in 20.1% HF by the drop method and is discussed below. The reaction schemes for these phases are those developed by Hemingway (unpublished data, 1976). The resultant value for muscovite was used by Hemingway and Robie (1977), however, the values for microcline and sanidine listed in that publication were consensus values obtained by averaging the unpublished values from Hemingway (where the aluminum reference phase was gibbsite) and those of Waldbaum (1968) and Robie and Waldbaum (1968) (where the aluminum reference phase was aluminum chloride hexahydrate).

Reaction 1 was taken from Bennington and Brown (1982). The value used for this reaction by Barany (1964) in the reaction scheme for muscovite was taken from the study of King (1951), and that value is thought to be in error (too negative) because the quartz sample was ground to a very fine particle size. Hemingway et al. (1988) and references therein have shown that dissolution of fine grained quartz results in an excess enthalpy of solution. Bennington and Brown (1982) used the same calorimeter, the same temperature of dissolution, the same concentration of acid and the same molar ratio of SiO_2 as was used by King (1951). The results of the two studies should be identical within experimental error. Since they are not, one value must be in error. The value reported by Bennington and Brown (1982) is equivalent to that used by Hemingway and Robie (1977) in their reevaluation of the calorimetric data for silicate minerals and that value was recommended by Hemingway et al. (1988) following their review of the calorimetric data for the enthalpy of solution of quartz. This value is also equivalent to that recommended by NIST (formerly NBS, Kilday and Prosen, 1973). The enthalpy of this reaction (dissolution at 73.7°C) has been reproduced by several calorimetric systems and thus should not be in significant error as proposed by Sverjensky et al. (1991) who compared the data for the dissolution of quartz at lower temperatures, reactions that do not effect these results.

Reaction 2 was taken from Barany (1964) who used the value reported by Barany and Kelley (1961). The value for this reaction has been verified by the work of Koehler et al. (1961), Hemingway and Robie (1977), Hemingway et al. (1978), Hovis (1982), Johnson et al. (1982), Hemingway et al. (1988), Donahoe et al. (1990), and Johnson et al. (1992) which suggests that the result should not be in significant error.

Reaction 3 was taken from Barany (1964) who used the result reported by Kelley et al. (1959). This reaction does not appear to have been duplicated.

Reaction 4 was calculated from the data of Hemingway and Robie (1977) for the enthalpy of solution of H_2O in HF at 346.85 K (73.7° C) (also see Hemingway et al., 1988) and the enthalpy of warming water from 298.15 K (25° C) to 346.85 K, -39 and 3669 $J{\bullet}mol^{-1}$, respectively. Values for this reaction as reported in the literature vary significantly. The following values have been reported (referenced to dissolution of 1 mole of H_2O for comparison purposes): 3.507 kJ (Barany and Kelley, 1961), 3.513 kJ (Barany, 1962), 3.600 kJ (Barany, 1962), and 3.431 kJ (Bennington and Brown, 1982). The value of 3.600 kJ reported by Barany (1962) is in fair agreement with the calculated value accepted here. Of course, there should be but a single value for this reaction. The differences seen in these values likely arise from the samples having temperatures other than 298.15 K (25° C) at the time they were dropped into the calorimeter. Each 1 degree represents a difference of about 75 $J{\bullet}mol^{-1}$ in this value. Such differences would tend to cancel out in the reaction schemes used by the U.S. Bureau of Mines workers if the same temperature difference occurred throughout the time the measurements of the full reaction scheme were performed. For example, for the microcline reaction scheme, ΔC_p, the difference in heat capacities for the products and reactants, is 320 J assuming a 1 degree difference for all materials, while for $HCl{\bullet}12.731H_2O$ and for $11.731H_2O$ the differences would be 880 and 882 J, respectively. Problems can arise if the temperature error is not constant for all materials studied in the reaction scheme. Because Barany (1962, 1964) and other workers at the U.S. Bureau of Mines relied on enthalpies of solution from earlier studies, there is concern that drop temperatures for samples may have been different.

Reaction 5 has been studied several times: 42.101, 44.141, 43.820, 43.053, 45.313 kJ, respectively, from Kelley et al. (1959), Barany and Kelley (1961, 2 values), Barany (1962) and Barany (1964). Again, as noted above, there should be but a single value for this reaction. This value may be calculated from the heat capacity of $HCl{\bullet}12.731H_2O$ derived from the values of Parker (1965) and the enthalpy of solution of $HCl{\bullet}12.731H_2O$ in HF at 346.85 K (73.7° C), 3.628 $kJ{\bullet}mol^{-1}$, from Hemingway and Robie (1977). Parker provides tables of the heat capacity of HCl in aqueous solutions from which the heat capacity of $HCl{\bullet}12.731H_2O$ may be calculated using the relation

$$\Phi_C = [(1000 + mM_2)C - 1000C^\circ]/m$$

where Φ_C is the heat capacity of HCl in aqueous solution tabulated by Parker

(1965), *C* and *C*° are the specific heats of the solution and the pure solvent, respectively, M_2 is the molecular weight of the solute, and *m* is the molality. Parker's values are limited to 288.15 to 303.15 K (15° to 30° C). The data were fit to a Maier-Kelley (1932) type equation and extrapolated to 346.85 K. The heat capacities were calculated and fit, and the resulting equation integrated to obtain the enthalpy of warming $HCl \bullet 12.731H_2O$ from 298.15 to 346.85 K, 42.986 kJ. Combining these values gives 46.614 kJ for reaction 5.

Reaction 6 was calculated from an extrapolation to 346.85 K of the 4 enthalpy of solution measurements of microcline in 20.1% HF at 322.85 K (49.7° C) and 332.85 K reported by Waldbaum and Robie (1971) and the enthalpy of warming microcline from 298.15 to 346.85 K. Hovis (1971, also see Hovis, 1982) reported an equivalent enthalpy of solution at 322.85 K to that given by Waldbaum and Robie (1971), but he provided no information on the temperature dependence of the enthalpy of solution.

Reaction 7 is the enthalpy of formation of microcline and $HCl \bullet 12.731H_2O$ from the reference reactant phases calculated from the Hess' Law summation of the preceding reactions, that is, $\Delta_7H = \Delta_1H + \Delta_2H + \Delta_3H + \Delta_4H - \Delta_5H - \Delta_5H$.

Reactions 8 - 12 represent the enthalpies of formation of quartz, gibbsite, sylvite, water, and HCl in 12.731 H_2O. The values for reactions 8, 10, and 11 are from Robie et al. (1979). The value for reaction 9 was calculated from the data in Robie et al. (1979). The value for reaction 12 was calculated from the data in Wagman et al. (1982).

Reaction 13 is the enthalpy of formation of microcline from the elements calculated by Hess' Law as follows: $\Delta_{13}H = \Delta_7H + \Delta_8H + \Delta_9H + \Delta_{10}H + \Delta_{11}H - \Delta_{12}H$. The resulting value differs considerably from an earlier value of -3967.69 ± 3.37 (Robie et al., 1979) principally due to the fact that the latter value was an averaged value derived from two independant reaction schemes, one based on aluminum chloride hexahydrate (see below) and the other based on gibbsite (as shown above).

Reaction 14 is the enthalpy of transition of microcline to sanidine as given by Hovis (1988). The value is based upon the difference in the enthalpies of solution of microcline and sanidine in 20.1% HF at 322.85 K. The value is supported by results reported by Waldbaum and Robie (1971). The difference in the heat content ($H^\circ_{322.85} - H^\circ_{298}$) for the two feldspars is about 0.1 kJ and far less than the uncertainty in the difference in the enthalpies of solution for the phases. The value of 11.088 kJ used by Berman (1988) is incorrect (Hovis, 1988).

Reaction 15 is the enthalpy of formation of sanidine from the elements and represents the sum of reactions 13 and 14.

Reaction 16 is the enthalpy of solution of natural muscovite taken from Barany (1964) who applied a correction of -4.435 kJ for the chemical deviation from pure muscovite. However, the correction term has been recalculated because new data are available for Fe_2O_3 and the details of the correction calculation were not made clear by Barany (1964). The chemical analysis was used to calculate an impure muscovite having an excess of 0.1580, 0.0815, 1.3117, 0.1328, and 0.0990 moles of SiO_2, $Mg(OH)_2$, H_2O, total Fe as Fe_2O_3, and NaCl, respectively, and a deficiency of 0.0563, 0.2795, and 0.0765 moles of KCl, $Al(OH)_3$, and $HCl \bullet 12.731H_2O$ (needed to balance the reactions), respectively. The enthalpies of solution of $Mg(OH)_2$ and Fe_2O_3 were taken from Torgeson and Sahama (1948) and Bennington and Brown (1982), respectively. The remaining reactions are taken from the values listed in Table 1. The correction is -5.004 kJ.

Reaction 17 is the enthalpy of formation of muscovite and water from microcline and gibbsite calculated as $\Delta_{17}H = \Delta_6H + 2\Delta_2H - (2/11.731)\Delta_4H - \Delta_{16}H$.

Reaction 18 is the enthalpy of formation of gibbsite from Hemingway and Robie (1977). The value for this reaction is equivalent (within experimental error) to that given by Gross et al. (1970, in 40% HF) and by Johnson et al. (1992, in 24.4% HF). The values are -1.1 and -1.8 $kJ \bullet mol^{-1}$, respectively, more negative than the value selected here. Selecting either of these alternative values would increase the stability of muscovite by -2 to -4 kJ.

Reaction 19 is the enthalpy of formation of muscovite from the elements calculated as $\Delta_{19}H = \Delta_{13}H + \Delta_{18}H - 4\Delta_{11}H + \Delta_{17}H$. This value differs slightly from the value of -5976.74 ± 3.24 $kJ \bullet mol^{-1}$ (Hemingway and Robie, 1977) principally due to the recalculation of the impurity correction in reaction 16.

The muscovite used by Barany (1964) was obtained from W. S. Fyfe, but further information regarding locality or paragenesis was not given. If Al/Si tetrahedral order is variable, as in the alkali feldspars, this knowledge may help to explain differences in the enthalpy of formation derived from phase equilibrium studies involving synthetic muscovite from the value recommended from calorimetric data. For example, if a muscovite with substantially more disorder were dissolved, $\Delta_{16}H$ would be more negative, $\Delta_{17}H$ would be more positive, and Δ_fH for muscovite would be less negative. Fyfe (oral communication, November, 1993) recalled that the sample provided to Barany was from the University of California, Berkeley collection and it is likely to be pegmatitic in origin.

Robie and Waldbaum (1968), Waldbaum (1968) and Waldbaum and Robie (1971) gave values for the enthalpy of formation of microcline and sanidine based upon calorimetric data available at that time, but with out publishing the reaction scheme. Table 2 provides the reaction scheme used in those studies. A brief description of the reactions follows.

Reactions 20, 23, 30, and 31 are from the same source as reactions 6, 3, 11, and 12, respectively. Reactions 21 and 24 are taken from Kelley et al. (1959), 25 from Barany and Kelley (1961), 28 is taken from Barany and Kelley (1961) and Coughlin (1957), and 29 is from Robie and Waldbaum (1968). Reaction 26 is calculated as $\Delta_{26}H = \Delta_{22}H + \Delta_{23}H + \Delta_{24}H + \Delta_{25}H - \Delta_{20}H - \Delta_{21}H$. Reaction 27 is from Robie and Waldbaum (1971).

The two reaction schemes described above for microcline use essentially the same data for the enthalpy of solution of microcline, but differ in the aluminum reference phase and consequent changes in auxillary reactions. The major differences that can be observed between the common reactions from this reaction scheme and that presented in Table 1 lie in the values for reactions 21, 22 and 25. However, the differences noted largely cancel out in the reaction scheme. That means that one of the reactions for the aluminum reference phases must be systematically different (in error) with respect to the presumed reference state.

The calorimetrically derived values may be compared with values derived from phase equilibrium studies. Krupka et al. (1979) made such a comparison using ancillary thermodynamic data from Robie et al. (1979). If we substitute our value for the enthalpy of formation of sanidine and the enthalpy of formation of andalusite from Hemingway et al. (1991) for the values used by Krupka et al. (1979), we obtain -5974.9 and -5973.6 kJ•mol^{-1}, respectively for the enthalpy of formation of muscovite from the reaction brackets for muscovite + quartz = sanidine + andalusite + steam and muscovite = sanidine + corundum + steam given by Chatterjee and Johannes (1974) and assuming muscovite to be fully disordered. The agreement with the calorimetrically derived value of -5974.8 kJ•mol^{-1} is excellent, however, the slope of the calorimetrically derived reaction boundary differs substantially from that inferred from the reaction brackets of Chatterjee and Johannes (1974). Agreement is not as good when the calorimetric values are compared to values obtained by Berman (1988) and by Holland and Powell (1990) from their analyses of phase equilibrium data. Berman (1988) used the calorimetric value for the enthalpy of formation of muscovite (Hemingway and Robie, 1977) as a fixed reference value and calculated values that are 4 and 6 kJ•mol^{-1}, respectively, less negative for the enthalpies of formation of microcline and sanidine. Berman (1988) obtained agreement between his calculated slope for the reaction boundary and the reaction brackets of Chatterjee and Johannes (1974) by considering muscovite and sanidine to be substantially and partially ordered, respectively. Holland and Powell (1990) used calorimetric values only as loose constraints in their analysis of both calorimetric and phase equilibrium data. Their values for the enthalpy of formation of microcline and sanidine are essentially equivalent to those given by Berman (1988), but their value for muscovite is about 5 to 6 kJ•mol^{-1} more negative than that given by Berman (1988) or in this study. The values derived by Berman (1988) agree with our results within the expected error of the values, but those of Holland and Powell (1990) lie outside this range.

Analcime

A similar difference is observed when the enthalpy of formation of analcime is calculated from reaction schemes involving gibbsite and aluminum chloride hexahydrate as the reference phase for aluminum. The unique reactions are listed in Table 3 (reactions 33 and 34 are from Barany, 1962, and reaction 36 is from Robie et al., 1979). For the reaction scheme using gibbsite, the enthalpy of formation of analcime from the elements is -3308.9 ± 2.3 kJ•mol^{-1} and is calculated as $\Delta_{37}H = 2/3\Delta_1H + \Delta_2H + \Delta_{33}H + 12.731/11.731\Delta_4H - \Delta_5H - \Delta_{34}H + 2/3\Delta_8H + \Delta_9H + \Delta_{36}H + 3\Delta_{11}H - \Delta_{12}H$ (note that the first 6 terms on the RHS yield $\Delta_{35}H$). For the reaction scheme using aluminum chloride hexahydrate, the enthalpy of formation of analcime from the elements is -3300.3 ± 2.7 kJ•mol^{-1} and is calculated as $\Delta_{39}H = 2/3\Delta_1H$ -74.935 (Barany, 1962) $+ \Delta_{33}H + 47.924/11.731\Delta_4H - 4\Delta_5H - \Delta_{34}H + 2/3\Delta_8H + \Delta_{28}H + \Delta_{36}H + 3/2\Delta_{30}H - \Delta_{31}H$

(note that the first 6 terms on the RHS yield $\Delta_{38}H$).

Johnson et al. (1982) have provided an independent calorimetric determination of the enthalpy of formation of analcime from measurements in 24.4% HF which we can compare to the values discussed above. Their result, corrected as discussed below, is -3309.8 ± 3.3 kJ•mol^{-1} and is in good agreement with the reaction scheme for analcime based upon gibbsite. This result suggests that the enthalpy of solution of aluminum chloride hexahydrate in aqueous HF is in error. Such an error could arise from two sources, non-stoichiometry of the water of crystallization in the sample or a temperature error similar to that discussed above.

Corrections were made to the reaction scheme presented by Johnson et al. (1982) because they reported their results for a non-stoichiometric composition (see reactions 40 - 47 in Table 3). Johnson et al. (1982) reported the chemical composition for their sample and noted that it was similar to that given by Barany (1962) for his sample. Barany (1962) corrected his enthalpy of solution for analcime to give the enthalpy of solution of stoichiometric analcime. To provide a proper comparison, the data of Johnson et al. (1982) need to be treated in a similar manner. The enthalpy of solution ($\Delta_{43}H$) was corrected to represent solution (-518.13 kJ•mol^{-1}) of 1 mole of analcime, and 0.12 SiO_2 and 0.04 H_2O. The correction was 16.29 kJ primarily for quartz. The remainder of reactions 40 - 47 simply restate the results of Johnson et al. (1982) for the stoichiometric composition. Reaction 40 has been verified by Hemingway et al. (1988), and reactions 41 and 42 were verified by Donahoe et al. (1990).

Sodium aluminate

Sodium aluminate, $NaAlO_2$, was used as a reference phase in determining the enthalpy of formation of albite in the studies of Hemingway and Robie (1977) and Navrotsky et al. (1980). Two values for the enthalpy of formation of sodium aluminate that differ by about 2 kJ are available in the literature; Hemingway and Robie (1977) where the experiments were conducted in aqueous HF, and Coughlin (1957) where the solvent was aqueous HCl. The reaction schemes used in each study are recalculated here to ensure internal consistency of ancillary data.

The reaction scheme used by Coughlin (1957) to calculate the enthalpy of formation of sodium aluminate is outlined in reactions 48 - 55. Reactions 48 - 54 are taken from Coughlin (1957). Reaction 50 has been verified by Hemingway and Robie (1973). Reaction 54 is the enthalpy of formation of sodium aluminate and aqueous HCl at 298.15 K, and is calculated as $\Delta_{54}H = \Delta_{48}H + \Delta_{49}H + \Delta_{50}H - \Delta_{51}H - \Delta_{52}H$ + the difference in enthalpy for the products and reactants between 303.15 and 298.15 K. Reaction 55 is the enthalpy of formation of sodium aluminate from the elements calculated as $\Delta_{55}H = \Delta_{54}H + \Delta_{36}H + 4\Delta_{11}H - \Delta_{12}H$.

The reaction scheme used by Hemingway and Robie (1977) to calculate the enthalpy of formation of sodium aluminate is outlined in reactions 56 - 63. Reactions 56 - 60 were calculated from equations fit to the data of Hemingway and Robie (1977). The same equations are used to calculate values at other temperatures for reactions involving albite and jadeite. The enthalpy of reaction 58 is calculated from the same equation as that used to derive the value for reaction 4. Reaction 62 is the enthalpy of formation of sodium aluminate and aqueous HCl at 298.15 K, and is calculated as $\Delta_{62}H = \Delta_{56}H + \Delta_{57}H + \Delta_{58}H - \Delta_{59}H - \Delta_{60}H$ + the difference in enthalpy for the products and reactants between 303.15 and 298.15 K. Reactions 62 and 54 may be compared directly, and they show the 1.9 kJ difference between the two studies. Reaction 63 is the enthalpy of formation of sodium aluminate from the elements calculated as $\Delta_{63}H = \Delta_{62}H + \Delta_{36}H + 4\Delta_{11}H - \Delta_{12}H$.

The enthalpy of formation of sodium aluminate calculated from the data of Hemingway and Robie (1977) is preferred for reasons discussed below. Use of the value given by the data of Coughlin (1957) would result in enthalpy of formation values for Na-bearing silicate phases that are less negative by about 1.9 kJ per Na, in direct contrast to the recommendations of Sverjensky et al. (1991).

Albite and jadeite

For the minerals albite and jadeite, a comparison can be made between the results obtained from aqueous HF calorimetry and molten-salt calorimetry. Table 4 lists the unique reactions necessary for the comparisons discussed below. A brief description of each calculation follows.

Kracek et al. (1951) and Kracek and Neuvonen (1952) reported two values for the enthalpy of solution of albite in 20% HF at 347.85 K (74.7° C), one based on a sample from Varuträsk, Sweden and the other on a sample from Amelia, Virginia. The difference in the two values was about 7 $kJ\bullet mol^{-1}$, with the sample from Amelia appearing to be much less stable than that from Varuträsk.

The enthalpy of formation of low albite from the elements may be calculated from the enthalpy of solution of the Varuträsk sample of albite by using the reaction scheme for microcline and substituting the enthalpies of solution of NaCl (reaction 33) for KCl and low albite (reaction 64) for microcline, and the enthalpy of formation of NaCl (reaction 36) for that of KCl. Kracek and coworkers did not publish their directly measured values for the ancillary reactions required to calculate the enthalpy of formation of albite. Reaction 64 represents the enthalpy of solution of low albite at 346.85 K (73.7° C) as corrected from the value given by Kracek et al. (1951) for dissolution at 74.7° C. Based on the chemical analysis, the sample was calculated to be 1 mole of albite plus 0.023 and 0.007 moles of H_2O and K-feldspar, respectively. Corrections for these impurity phases and for the change in heat content were made. The calculated enthalpy of formation of low albite at 298.15 K (reaction 65) is -3935.0 ±3.7 $kJ\bullet mol^{-1}$.

The enthalpy of formation of low albite can be calculated from the data of Hovis (1988) using reactions 66 - 74 from Table 4 and some ancillary reactions. The enthalpy of formation of low albite from the elements (-3933.96 ±2.50 $kJ\bullet mol^{-1}$) is calculated by the reaction scheme used for microcline, with the substitutions listed above. Waldbaum and Robie (1971), Hovis (1982), and Hovis (1988) have reported values for the enthalpy of solution of low albite (sample from Amelia, Virginia) at 322.85 K (49.7° C) that differ by less than 250 J. The same calorimeter was used in each study. The reaction scheme is similar to that used above, but with the exception that the sample and acid were at the same temperature. Reactions 66, 67, 69 and 71 are taken from fits to the data of Hemingway and Robie (1977) and are consistent with reactions 1, 2, 4 and 5 used in the calculations above. Reaction 68 is taken from the data of Hemingway and Robie (1977). Extrapolation of this data to 346.85 K yields a somewhat less negative value than reaction 33. Hovis (1982) has reported enthalpy of solution values for gibbsite and quartz at 322.85 K (49.7° C). His value for the enthalpy of solution of gibbsite is more negative by about 0.35% (Hemingway et al., 1988) than reaction 67. The value reported by Hovis (1982) for the enthalpy of solution of quartz (-139.06 ±0.09 $kJ\bullet mol^{-1}$) is considered to be too negative by Hemingway et al. (1988) and is thought to include an enthalpy of abrasion, a consequence of a fast stirring rate for the calorimeter coupled with a hard mineral that requires a long dissolution time. Substituting Hovis' (1982) values for reactions 66 and 67 would yield a value for the enthalpy of formation of low albite that is about nine kJ more negative, but in closer agreement with the seven kJ more negative difference suggested by Sverjensky et al. (1991).

Hemingway and Robie (1977) calculated the enthalpy of formation of low albite from a reaction scheme that utilized sodium aluminate in place of gibbsite and NaCl. (However, these phases were used to derive the enthalpy of formation of sodium aluminate as discussed earlier.) The enthalpy of formation of low albite from quartz and sodium aluminate at 333.15 K is $\Delta_{78}H = \Delta_{75}H + \Delta_{76}H - \Delta_{77}H$. Correction of this reaction to 298.15 K is shown in reaction 79. Combining reaction 79 with the enthalpy of formation of quartz and sodium aluminate (-1135.64 $kJ\bullet mol^{-1}$) yields -3935.06 ±2.60 $kJ\bullet mol^{-1}$ for the enthalpy of formation of low albite. Reaction 77 represents the average of the values for the enthalpy of solution of 4 samples of low albite, one of which was reportedly a portion of the Amelia albite sample used by Kracek and coworkers (1951, 1952). The consistency of the values for the 4 samples suggests that Kracek and coworkers (1951, 1952) had a systematic error associated with their measurement of the enthalpy of solution of the Amelia albite sample.

Navrotsky et al. (1980) measured the enthalpy of solution of low albite, quartz and sodium aluminate by molten-salt calorimetry at 985 K. The enthalpy of formation of low albite can be calculated from this data and the ancillary data listed above. The enthalpy of formation of low albite from quartz and sodium aluminate at 985 K is $\Delta_{84}H = \Delta_{81}H + \Delta_{82}H - \Delta_{83}H$. Correcting this value to the reaction at 298.15 K yields reaction 85. The enthalpy of formation of low albite at 298.15 K (-3933.99 ±2.20 $kJ\bullet mol^{-1}$) is $\Delta_{86}H = \Delta_{85}H + \Delta_{63}H + \Delta_{8}H$.

The values derived above (-3935.0 ±3.7, -3933.96 ±2.50, -3935.06 ±2.60, and -3933.99 ±2.20 $kJ\bullet mol^{-1}$) represent a remarkably tight cluster of values for the enthalpy of formation of low albite from the elements. The latter 2 values are referenced to the enthalpy of formation of sodium aluminate given in reaction 63. Using the value from reaction 55 would make the latter 2 values listed above more positive by 1.9 $kJ\bullet mol^{-1}$ and increase the scatter in the results. For that reason, reaction 63 is preferred. The first 2 values listed above probably represent minimum values. Kracek and coworkers (1951, 1952) ground their samples for several hours in a power mortar and may have produced an excess in the enthalpy of solution (reaction 64) of low albite arising from surface energy contributions (e.g., Hemingway et al., 1988). Such an effect would be reflected in the reaction scheme as a decrease in the apparent stability of low albite. Based on values for the surface energy contribution to the enthalpy of solution of quartz (Hemingway and Robie, 1977), the effect for low albite would likely be less than -2 kJ. Hovis (1988, and Hovis, 1982, and Waldbaum and Robie, 1971) used a fast stirring rate and may have introduced a heat of abrasion during dissolution of their feldspar sample similar to the effect suggested by Hemingway et al. (1988) for their quartz dissolution value. The result of such an effect would be to decrease the apparent stability of low albite. It is unlikely that such an effect could be larger than -2 kJ. The value derived from the data of Navrotsky et al. (1980) may also represent a minimum value because the low albite sample may have been slightly disordered. Again, the result would be an apparent decrease in the stability of low albite. Navrotsky et al. (1980) report a value for the enthalpy of dissolution of analbite (a heat treated portion of the low albite sample) at 985 K that is about 9.8 kJ•mol^{-1} larger than the value of reaction 83. This value is about 1.7 kJ•mol^{-1} smaller than the difference recommended by Hovis (1988) for 298.15 K and about 2 kJ•mol^{-1} smaller at 985 K (data of Robie et al., 1979 used for the correction to 985 K). Because we are unsure of the amount of disorder of both the low albite and analbite samples used by Navrotsky et al. (1980) we can only note that the enthalpy of formation of low albite could be as much as -2 kJ larger. Small differences exist between the values used for the enthalpies of solution of quartz and gibbsite in the reaction scheme for Kracek and coworkers (1951, 1952) as compared to the values obtained from an extrapolation of the data of Hemingway and Robie (1977) for the same reactions. The differences largely cancel in the reaction scheme and yield a difference of 0.13 kJ. Were the data of Hemingway and Robie (1988) used in place of reaction 32, the enthalpy of formation of low albite calculated from the data of Kracek and coworkers would be less negative by about 0.7 kJ. The value selected for the enthalpy of formation of low albite from the elements is -3935.0 ±2.6 kJ•mol^{-1}. The tight cluster of these results and the relatively small size of the estimated potential systematic error of each result argues against the redefinition of thermodynamic values proposed by Sverjensky et al. (1991).

The enthalpy of formation of jadeite can be calculated from the data of Navrotsky et al. (1980), Kracek et al. (1951) and Hlabse and Kleppa (1968). In the latter case, ancillary reactions are not available, but the authors report enthalpy of solution values for quartz and low albite from which the enthalpy of formation can be calculated. The unique reactions for jadeite are listed in Table 4.

The enthalpy of formation of jadeite can be calculated from the molten salt calorimetric data of Navrotsky et al. (1980) using reactions 82, 87 - 90, 63 and 2/3 of reactions 8 and 81. The resulting value is -3029.40 ±2.10 kJ•mol^{-1}.

Kracek et al. (1951) reported three values (-478.44, -485.05, and -

480.99 kJ•mol-1) for the enthalpy of solution of jadeite in aqueous HF at 347.85 K (74.7° C). The first two values represent results for two portions of a single sample (Japan) that had been processed differently: each ground for several hours, one in agate and one in mullite. The other sample (Burma) was from another locality and was ground for several hours, but the mortar type was not specified. Kracek et al. (1951) note that early preparations of the ground samples were elutriated for about 10 minutes and the coarse fraction was removed. This practice led to some problems during the dissolution reaction as some dissolution reactions were slow and showed residual solid that was either unreacted sample (formation of a gel that shielded some sample) or chiolite. Thus elutriation was not performed on all portions of the jadeite samples. Kracek et al. (1951) do not explain the specific treatment for the portions of the samples for which enthalpy of solution values were reported. Because of this, we must make some assumptions. A comparison of the two values reported for the two portions of the Japanese jadeite sample shows a substantially more negative value for the enthalpy of solution of the sample ground in mullite. Assuming that Kracek et al. (1951) discarded all experiments where residual material was found following the dissolution measurement (a standard practice), then the larger enthalpy of solution would suggest a surface energy contribution from fine grinding of the sample. The enthalpy of solution per gram of quartz and jadeite are close so minor contamination by agate would not be a significant problem. There is a question as to whether mullite would dissolve in the calorimeter. Waldbaum (1965) notes that he and several others were unsuccessful in their attempts to dissolve mullite in aqueous HF, however, Neumann (1925) claims to have been successful using 40% HF. Using Neumann's (1925) data suggests that if mullite does dissolve, the enthalpy of solution per gram is significantly less negative than that for jadeite. Thus whether mullite acts as an inert impurity or dissolves in the acid, the net effect should be a less negative enthalpy of solution for jadeite than in the absence of mullite. This suggests that mullite contamination was not a problem as suggested by Kracek et al. (1951) who based their conclusion on weighing the mortar and pestle before and after each grinding of a sample. Thus, excess grinding of the sample prepared in mullite is assumed to be the cause of the larger value reported by Kracek et al. (1951) for the enthalpy of solution of this portion of the Japanese jadeite sample and that value will not be considered here.

The enthalpy of formation of jadeite can be calculated from the data of Kracek et al. (1951) for dissolution of Japanese jadeite ground in an agate mortar using a reaction scheme similar to that used above to calculate the enthalpy of formation of low albite from their data. The reaction scheme must be modified to include only 2 SiO_2. The unique reactions (91 - 93) are listed in Table 4. The resultant value is -3029.12 ±2.45 $kJ•mol^{-1}$ which is in excellent agreement with the value derived from the data of Navrotsky et al. (1980).

The enthalpy of formation of jadeite may also be calculated from the enthalpy of solution reported by Kracek et al. (1951) for the sample obtained from Burma. Reactions 94 and 95 represent the variations to the reaction scheme discussed in the preceding paragraph. Because we do not know how the jadeite sample from Burma was prepared, we consider the value of the enthalpy of solution of the jadeite to have a greater uncertainty (±2.5 kJ•mol^{-1}) than that assigned by Kracek et al. (1951, ±1.5 kJ•mol^{-1}). The enthalpy of formation of jadeite calculated from this data is -3026.56 ±3.5 kJ•mol^{-1}.

Finally, the enthalpy of formation of jadeite can be calculated from the enthalpy of solution of low albite, quartz, and jadeite in molten salt at 964 K using the data of Hlabse and Kleppa (1968) listed in Table 4 (reactions 96-101) and ancillary data discussed above. For this calculation we use -3935.0 kJ•mol^{-1} for the enthalpy of formation of low albite as recommended above. The resultant enthalpy of formation for jadeite is -3026.0 ±3.1 kJ•mol^{-1}. This value is derived from early experiments in the area of molten-salt calorimetry. As the apparatus and techniques have been refined, some revision of enthalpy of solution values for phases like quartz and corundum has occurred and suggest that similar adjustments to the values for low albite and jadeite might be necessary. This value is in good agreement with the value calculated from the data of Kracek et al. (1951) for the sample from Burma. However, both of these results are seen as more problematical than the first two calculated above.

Reasonably good agreement exist between the four values for the enthalpy of formation of jadeite calculated above as all values agree within their stated uncertainties. The recommended value is -3029.3 ±2.5 kJ•mol^{-1}. The differences in these results and the earlier values for low albite suggest that reaction 63 is the preferred value for the enthalpy of formation of sodium aluminate. Similarly, the results for jadeite support the choice of -3935.0 kJ•mol^{-1} for the enthalpy of formation of low albite.

Analbite

The enthalpy of formation of analbite may be calculated from the data of Hovis (1988) and is supported by earlier work referenced there in. Reactions 102 and 103 from Table 4 provide the necessary information. The value derived in reaction 103 is recommended.

The calorimetrically derived values for the enthalpy of formation of low albite, analbite, and jadeite are in better agreement with the results derived from phase equilibrium (Berman, 1988, and Holland and Powell, 1990) than was the case for the K-bearing phases. Berman (1988) used the calorimetric enthalpy of formation for low albite as a reference phase. His calculated values for analbite and jadeite differ from the values derived here by 2 and 4 kJ•mol^{-1}, respectively. Berman (1988) based his value for jadeite on reactions involving analbite, and his value for analbite on the difference used by Salje et al. (1985) for the reaction low albite = analbite now shown by Hovis (1988) to be incorrect. Making the appropriate correction (by -2 kJ) shows the calorimetric and phase equilibrium values to be in excellent agreement. The values given by Holland and Powell (1990) for low albite and jadeite are in good agreement, but their value for analbite is significantly different from our value or that given by Berman (1988).

Silicalite as a reference phase for Si

Johnson et al. (1992) have suggested that the reference phase for Si in aqueous HF calorimetry be changed from quartz to silicalite (see Flanigen et al., 1978, for information on the crystal structure). Such a change would result in a significant change in the enthalpy of formation for values based upon aqueous HF calorimetry (such as those discussed above). The change required would be -3.71 kJ•mol^{-1} of Si in the mineral (e.g., -7.42 for jadeite and -11.13 for low albite or microcline) based on the difference between the enthalpies of solution and formation of quartz and silicalite at 298.15 K as reported by Johnson et al. (1987). This effect can be seen from the data listed in Table 5. Reaction 104 represents the dissolution of either quartz (reaction 111) or silicalite (reaction 109). The combination of reactions 105 - 107 represent the determination of the enthalpy of formation of quartz (reaction 112) or silicalite (reaction 110) by fluorine bomb calorimetry. The difference in the sum of reactions 109 plus 110 and 111 plus 112 represents the correction term (refer for example to the reaction scheme for analcime).

Johnson et al. (1992) have suggested that silicalite is the preferred Si reference at 298.15 K because they consider the enthalpy of solution of quartz to be well defined only at temperatures between 348 and 353 K and they considered it to be ill defined at 298.15 K where dissolution takes several hours and the uncertainty is increased by large corrections for heat exchange during the experiment. Silicalite, on the other hand, dissolves rapidly at 298.15 K.

Hemingway et al. (1988) have shown the data for the enthalpy of solution of quartz derived from several concentrations of aqueous HF to be quite consistent at temperatures from 298.15 to 353 K. However, several values reported in the literature do deviate (all in the direction of larger values) from the suggested values. Hemingway et al. (1988) suggest that the larger enthalpies of solution of quartz observed in some studies arise from the enthalpy of stirring during the dissolution period being larger than in the calibration periods because of the transfer of mechanical energy of stirring to abrasion as the quartz sample is stirred. In other cases, a larger enthalpy of solution can be attributed to surface energy effects as the quartz sample was finely ground (Hemingway et al., 1988, and Hemingway and Robie, 1977). For example, Hemingway et al. (1988) show that the enthalpy of solution of quartz increased (by -3.7 kJ•mol^{-1}) when the stirring speed was increased (from 144 to 600 RPM), but all other factors remained constant, and Hemingway and Robie (1977) found that the enthalpy of solution of quartz ground to less than 2μ was larger by -1.4 kJ•mol^{-1} than that for coarser portions of the same sample. The systematic errors suggested here would both produce more negative than appropriate values for the enthalpy of solution of quartz.

Johnson et al. (1987) have calculated what they believe to be the correct value for the enthalpy of solution of quartz in 24.4% HF at 298.15 K. By summing the enthalpies of reaction for reactions 104 and 105 for silicalite and for quartz, one should obtain the same value (as if the SiO_2 phase is removed). The difference (-2.63 kJ•mol^{-1}) observed by Johnson et al. (1987)

was added to the enthalpy of solution of quartz yielding -138.22 ± 1.36 kJ•mol^{-1}. The same calculation can be made using reactions 109 and 110 for silicalite and 111 and 112 for quartz from which the difference is -3.71 kJ•mol^{-1} and the calculated enthalpy of solution of quartz is -139.30 ± 1.36 kJ•mol^{-1}. In the case of either calculation, the estimated value for the enthalpy of solution of quartz is significantly larger than any of the experimental values reported in the literature.

If either of these estimated values is correct, then the values reported in the literature must represent incomplete reaction of quartz in the aqueous HF acid. No authors have noted residual quartz following dissolution reactions. Hemingway and Robie (unpublished data) have varied the reaction time for quartz dissolution at 333 K by about 20% and at 348 K by about 50% and found no significant difference (enthalpy of solution values are listed in Table 3 of Hemingway and Robie, 1977). Therefore, it seems unlikely that incomplete dissolution of quartz is a factor.

Alternatively, there may be a systematic error in one or more of the reactions involving silicalite. Hemingway et al. (1988) have suggested that silicalite, because of channels in the structure and a 33% porosity, may have a higher surface energy contribution to the dissolution reaction than other silicate minerals, except perhaps some zeolites. For quartz, Savin and Hower (1974) found an increase of about -3 kJ for the difference between finely and coarse ground quartz. In support of the use of silicalite, Johnson et al. (1992) suggest that surface energy contributions cancel out in the reaction scheme, that is, the summation of reactions 104 - 106. It is not clear that the effect measured in gaseous fluorine (reaction 105) and aqueous HF (reaction 104) will cancel, especially if the effect is related to differences in the heat of wetting of silicalite versus that for other silicate minerals.

Finally, if silicalite is used as the reference for analcime in place of quartz in the study reported by Johnson et al. (1982), the reactions and calculations discussed above would yield a value of -3315.0 to -3317.2 kJ•mol^{-1} for the enthalpy of formation of analcime depending on which correction value was used. Either of these values is considerably more negative than the value derived from the aqueous HF calorimetry reaction scheme where quartz was dissolved in the temperature range that Johnson et al. (1987) labelled as well constrained (reaction 1). Also, the enthalpy of formation of low albite calculated from the data of Hovis (1988) and using the enthalpy of solution of quartz recommended by Hemingway et al. (1988) agrees well with the value calculated from the molten-salt work reported by Navrotsky et al. (1980).

Taken together, the data listed above argue against a change from quartz to silicalite as the reference phase for Si in aqueous HF calorimetry. However, silicalite would represent a far more convenient reference phase for HF solution calorimetry if the discrepancy listed above could be resolved.

$KAlSi_3O_8$ glass

The enthalpy of formation of $KAlSi_3O_8$ glass is based upon the enthalpy of formation of sanidine and the difference in the enthalpies of solution of sanidine and the glass in aqueous HF (Waldbaum and Robie, 1971) of 44.8 kJ. The revised value for the enthalpy of formation of the glass is -3920.8 ± 4.2 $kJ\bullet mol^{-1}$.

Conclusion

An analysis of the calorimetric data for muscovite does not support a correction of -6.69 kJ in the enthalpy of formation of K-bearing silicate phases as suggested by Sverjensky et al. (1991). Hemingway and Robie (1977) were unable to resolve the discrepancy between reactions based on gibbsite and those based on aluminum chloride hexahydrate, and averaged values derived from each reaction scheme to obtain values for the enthalpy of formation of microcline and sanidine. Based on the discussion above, the enthalpy of solution of aluminum chloride hexahydrate appears to be in error. Thus the recommended value for the enthalpy of formation of microcline (and consequently sanidine) is based on the gibbsite reaction scheme and is more negative than that given by Hemingway and Robie (1977).

Good agreement is found amongst values calculated for the enthalpy of formation of low albite and based on several calorimetric approaches. The data do not support a shift of -6.80 kJ in the enthalpy of formation of Na-bearing silicate phases as suggested by Sverjensky et al. (1991).

This study does not support a change from quartz to silicalite as recommended by Johnson et al. (1992) for the Si reference phase for aqueous HF calorimetric reaction schemes. However, if the problems discussed above could be resolved, we agree with Johnson et al. (1992) that silicalite would be an attractive reference phase.

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Table 1. Reaction scheme for microcline, sanidine and muscovite.

Reaction	$\Delta_r H$ kJ
1. $3SiO_2(c,R_1) + 18HF(soln,R_2) = 3H_2SiF_6(soln,R_2)$	-413.463
$+ 6H_2O(soln,R_2)$	±0.200
2. $Al(OH)_3(c,R_1) + 3H^+(soln,R_2) = Al^{3+}(soln,R_2)$	-149.536
$+ 3H_2O(soln,R_2)$	±0.126
3. $KCl(c,R_1) = K^+(soln,R_2) + Cl^-(soln,R_2)$	6.778
	±0.293
4. $11.731H_2O(l,R_1) = 11.731H_2O(soln,R_2)$	42.584
	±1.513
5. $HCl \bullet 12.731H_2O(l,R_1) = H^+(soln,R_2)$	46.614
$+ Cl^-(soln,R_2) + 12.731H_2O(soln,R_2)$	±0.377
6. $KAlSi_3O_8(c,R_1) + 18HF(soln,R_2) + 4H^+(soln,R_2) =$	-599.040
$(K^+ + Al^{3+} + 3H_2SiF_6 + 8H_2O)(soln,R_2)$	±1.339
7. $(3SiO_2 + Al(OH)_3 + KCl)(c,R_1) + 11.731H_2O(l,R_1) =$	38.789
$KAlSi_3O_8(c,R_1) + HCl \bullet 12.731H_2O(l,R_1)$	±2.090
8. $3Si(c) + 3O_2(g) = 3SiO_2(c)$	-2732.100
	±3.000
9. $Al(c) + 3/2H_2O(l) + 3/4O_2(g) = Al(OH)_3(c)$	-864.381
	±1.200
10. $K(c) + 1/2Cl_2(g) = KCl$	-436.470
	±0.140

Table 1. Continued.

Reaction	$\Delta_r H$ kJ
11. $1/2H_2(g) + 1/4O_2(g) = 1/2H_2O(l)$	-142.915 ±0.021
12. $1/2H_2 + 1/2Cl_2(g) + 12.731H_2O(l) = HCl \bullet 12.731H_2O(l)$	-162.440 ±0.210
13. $K(c) + Al(c) + 3Si(c) + 4O_2(g) = KAlSi_3O_8(c)$ (microcline)	-3974.6 ±3.9
14. $KAlSi_3O_8$(microcline) = $KAlSi_3O_8$(sanidine)	9.0 ±1.3
15. $K(c) + Al(c) + 3Si(c) + 4O_2(g) = KAlSi_3O_8(c)$ (sanidine)	-3965.6 ±4.1
16. $KAl_3Si_3O_{10}(OH)_2(c,R_1) + (18HF + 10H^+)(soln,R_2) = (K^+ + 3Al^{3+} + 3H_2SiF_6 + 12H_2O)(soln,R_2)$	-919.794 ±1.088
17. $KAlSi_3O_8(c,R_1) + 2Al(OH)_3(c,R_1) = KAl_3Si_3O_{10}(OH)_2(c,R_1) + 2H_2O(l,R_1)$	14.422 ±1.763
18. $2Al(c) + 3H_2(g) + 3O_2(g) = 2Al(OH)_3(c)$	-2586.256 ±2.384
19. $K(c) + 3Al(c) + 3Si(c) + 6O_2(g) + H_2(g) = KAl_3Si_3O_{10}(OH)_2(c)$ muscovite	-5974.8 ±4.9

R = reference temperature, R_1 = 298.15 K (25° C) and R_2 = 346.85 K (73.7° C).

Table 2. Reaction scheme for microcline utilized by Waldbaum (1968) and Robie and Waldbaum (1968).

Reaction	Δ_rH kJ
20. $KAlSi_3O_8(c,R_1) + 18HF(soln,R_2) + 4H^+(soln,R_2) =$ $(K^+ + Al^{3+} + 3H_2SiF_6 + 8H_2O)(soln,R_2)$	-599.040 ±1.339
21. $4(HCl{\bullet}12.731H_2O)(l,R_1) = 4H^+(soln,R_2)$ $+ 4Cl^-(soln,R_2) + 50.924H_2O(soln,R_2)$	168.398 ±1.508
22. $3SiO_2(c,R_1) + 18HF(soln,R_2) = 3H_2SiF_6(soln,R_2)$ $+ 6H_2O(soln,R_2)$	-417.856 ±2.008
23. $KCl(c,R_1) = K^+(soln,R_2) + Cl^-(soln,R_2)$	6.778 ±0.293
24. $AlCl_3{\bullet}6H_2O(c,R_1) = Al^{3+}(soln,R_2) + 3Cl^-(soln,R_2)$ $+ 6H_2O(soln,R_2)$	-75.396 ±0.335
25. $46.924H_2O(l,R_1) = 46.924H_2O(soln,R_2)$	164.571 ±0.357
26. $(3SiO_2 + AlCl_3{\bullet}6H_2O + KCl)(c,R_1) +$ $46.924H_2O(l,R_1) = KAlSi_3O_8(c,R_1) +$ $4HCl{\bullet}50.924H_2O(l,R_1)$	108.739 ±2.880
27. $3Si(c) + 3O_2(g) = 3SiO_2(c)$	-2731.943 ±5.021
28. $Al(c) + 3HCl{\bullet}38.193H_2O(l) = AlCl_3{\bullet}6H_2O(c)$ $+ 32.193H_2O(l) + 3/2H_2(g)$	-489.528 ±0.544

Table 2. Continued.

Reaction	$\Delta_r H$ kJ
29. $K(c) + 1/2Cl_2(g) = KCl$	-436.684
	±0.420
30. $2H_2(g) + O_2(g) = 2H_2O(l)$	-571.660
	±0.084
31. $1/2H_2(g) + 1/2Cl_2(g) + 12.731H_2O(l) =$	-162.440
$HCl \bullet 12.731H_2O(l)$	±0.210
32. $K(c) + Al(c) + 3Si(c) + 4O_2(g) = KAlSi_3O_8(c)$	-3958.6
(microcline)	±5.8

R = reference temperature, R_1 = 298.15 K (25° C) and R_2 = 346.85 K (73.7° C).

Table 3. Reaction schemes for analcime. Ancillary data in Tables 1 and 2.

Reaction	$\Delta_r H$ kJ
33. $NaCl(c,R_1) = Na^+(soln,R_2) + Cl^-(soln,R_2)$	-1.004 ±0.209
34. $NaAlSi_2O_6 \bullet H_2O(c,R_1) + 12HF(soln,R_2) + 6H^+(soln,R_2) = (Na^+ + Al^{3+} + 2H_2SiF_6 + 7H_2O)(soln,R_2)$	-481.034 ±0.586
35. $(2SiO_2 + Al(OH)_3 + NaCl)(c,R_1) + 12.731H_2O(l,R_1) = NaAlSi_2O_6 \bullet H_2O(c,R_1) + HCl \bullet 12.731H_2O(l,R_1)$	54.452 ±1.700
36. $Na(c) + 1/2Cl_2(g) = NaCl$	-411.260 ±0.110
37. $Na(c) + Al(c) + 2Si(c) + 3.5O_2(g) + H_2(g) = NaAlSi_2O_8 \bullet H_2O(c)$ (analcime)	-3308.9 ±2.3
38. $(2SiO_2 + AlCl_3 \bullet 6H_2O + NaCl)(c,R_1) + 47.924H_2O(l,R_1) = NaAlSi_2O_6 \bullet H_2O(c,R_1) + 4HCl \bullet 50.924H_2O(l,R_1)$	116.963 ±2.167
39. $Na(c) + Al(c) + 2Si(c) + 3.5O_2(g) + H_2(g) = NaAlSi_2O_8 \bullet H_2O(c)$ (analcime)	-3300.3 ±2.7
40. $2SiO_2(c,R_1) + 12HF(soln,R_1) = 2H_2SiF_6(soln,R_1) + 4H_2O(soln,R_1)$	-271.18 ±0.38
41. $Al(OH)_3(c,R_1) + 3H^+(soln,R_1) = Al^{3+}(soln,R_1) + 3H_2O(soln,R_2)$	-165.18 ±0.25

Table 3. Continued.

Reaction	$\Delta_r H$ kJ
42. $NaF(c,R_1) = Na^+(soln,R_1) + F^-(soln,R_1)$	-4.06 ±0.12
43. $NaAlSi_2O_6 \bullet H_2O(c,R_1) + 12HF(soln,R_1) +$ $6H^+(soln,R_1) = (Na^+ + Al^{3+} + 2H_2SiF_6 + 7H_2O)(soln,R_1)$	-501.84 ±0.92
44. $3.343H_2O(l,R_1) = 3.343H_2O(soln,R_1)$	-1.39 ±0.14
45. $1/2H_2 + 1/2F_2(g) + 3.343H_2O(l) =$ $HF \bullet 3.343H_2O(l)$	321.23 ±0.39
46. $Na(c) + 1/2F_2(g) = NaF(c)$	-576.55 ±0.67
47. $Na(c) + Al(c) + 2Si(c) + 3.5O_2(g) + H_2(g) =$ $NaAlSi_2O_8 \bullet H_2O(c)$ (analcime)	-3309.8 ±3.3

R = reference temperature, R_1 = 298.15 K (25° C) and R_2 = 346.85 K (73.7° C).

Table 4. Reaction schemes for sodium aluminate, albite, analbite and jadeite. Ancillary data in Tables 1, 2 and 3.

Reaction	$\Delta_r H$ kJ
Reactions in 4.360*m* HCl	
48. $Al(c,R_3) + 3H^+(soln,R3) = Al^{3+}(soln,R_3) +$	-531.577
$3/2H_2(g,R_3)$	±0.500
49. $NaCl(c,R_3) = (Na^+ + Cl^-)(soln,R_3)$	8.033
	±0.042
50. $14.731H_2O(l,R_3) = 14.731H_2O(soln,R_3)$	-5.021
	±0.084
51. $NaAlO_2(c,R_3) + 4H^+(soln,R_3) =$	-214.304
$(Na^+ + Al^{3+} + 2H_2O)(sonl,R_3)$	±0.084
52. $HCl \bullet 12.731H_2O(l,R_3) = HCl \bullet 12.731H_2O(soln,R_3)$	-0.029
	±0.029
53. $Al(c,R_3) + NaCl(c,R_3) + 14.731H_2O(l,R_3) =$	-314.232
$NaAlO_2(c,R_3) + HCl \bullet 12.731H_2O(l,R_3)$	±0.544
54. $Al(c,R_1) + NaCl(c,R_1) + 14.731H_2O(l,R_1) =$	-313.310
$NaAlO_2(c,R_1) + HCl \bullet 12.731H_2O(l,R_1)$	±0.544
55. $Na(c,R_1) + Al(c,R_1) + O_2(g,R_1) = NaAlO_2(c,R_1)$	-1133.73
(sodium aluminate)	±0.60

Table 4. Continued.

Reaction	$\Delta_r H$ kJ
Reactions in 20.1% HF	
56. $Al(c,R_3) + 3H^+(soln,R3) = Al^{3+}(soln,R_3) + 3/2H_2(g,R_3)$	-594.725 ±1.200
57. $NaCl(c,R_3) = (Na^+ + Cl^-)(soln,R_3)$	-3.578 ±0.180
58. $14.731H_2O(l,R_3) = 14.731H_2O(soln,R_3)$	-3.138 ±0.080
59. $NaAlO_2(c,R_3) + 4H^+(soln,R_3) = (Na^+ + Al^{3+} + 2H_2O)(sonl,R_3)$	-287.417 ±0.610
60. $HCl{\bullet}12.731H_2O(l,R_3) = HCl{\bullet}12.731H_2O(soln,R_3)$	2.119 ±0.013
61. $Al(c,R_3) + NaCl(c,R_3) + 14.731H_2O(l,R_3) = NaAlO_2(c,R_3) + HCl{\bullet}12.731H_2O(l,R_3)$	-316.143 ±1.360
62. $Al(c,R_1) + NaCl(c,R_1) + 14.731H_2O(l,R_1) = NaAlO_2(c,R_1) + HCl{\bullet}12.731H_2O(l,R_1)$	-315.222 ±1.360
63. $Na(c,R_1) + Al(c,R_1) + O_2(g,R_1) = NaAlO_2(c,R_1)$ (sodium aluminate)	-1135.64 ±1.40
64. $NaAlSi_3O_8(c,R_4) + (18HF + 4H^+)(soln,R_4) = (Na^+ + Al^{3+} + 3H_2SiF_6 + 8H_2O)(soln,R_4)$	-621.271 ±0.850

Table 4. Continued.

Reaction	$\Delta_r H$ kJ
65. $Na(c) + 3Al(c) + 3Si(c) + 6O_2(g) + H_2(g) =$ $NaAl_3Si_3O_{10}(OH)_2(c)$ (low albite)	-3935.0 ±3.7
66. $3SiO_2(c,R_5) + 18HF(soln,R_5) =$ $3H_2SiF_6(soln,R_5) + 6H_2O(soln,R_5)$	-408.111 ±0.780
67. $Al(OH)_3(c,R_5) + 3H^+(soln,R_5) =$ $(Al^{3+} + 3H_2O)(soln,R_5)$	-156.955 ±0.115
68. $NaCl(c,R_5) = (Na^+ + Cl^-)(soln,R_5)$	-3.201 ±0.180
69. $HCl{\bullet}12.731H_2O(l,R_5) =$ $(H^+ + Cl^- + 12.731H_2O)(soln,R_5)$	2.799 ±0.013
70. $NaAlSi_3O_8(c,R_5) + (18HF + 4H^+)(soln,R_5) =$ $(Na^+ + Al^{3+} + 3H_2SiF_6 + 8H_2O)(soln,R_5)$	-627.596 ±1.000
71. $11.731H_2O(l,R_5) = 11.731H_2O(soln,R_5)$	-0.135 ±0.064
72. $(3SiO_2 + Al(OH)_3 + NaCl)(c,R_5) + 11.731H_2O(l,R_5) =$ $NaAlSi_3O_8(c,R_5) + HCl{\bullet}12.731H_2O(l,R_5)$	56.159 ±1.288

Table 4. Continued.

Reaction	Δ_rH kJ
73. $(3SiO_2 + Al(OH)_3 + NaCl)(c,R_1) + 11.731H_2O(l,R_1) =$	54.259
$NaAlSi_3O_8(c,R_1) + HCl \bullet 12.731H_2O(l,R_1)$	±1.290
74. $Na(c) + 3Al(c) + 3Si(c) + 6O_2(g) + H_2(g) =$	-3933.96
$NaAl_3Si_3O_{10}(OH)_2(c)$ (low albite)	±2.50
------------------------------------	
75. $3SiO_2(c,R_6) + 18HF(soln,R_6) = 3H_2SiF_6(soln,R_6)$	-413.205
	±0.780
76. $NaAlO_2(c,R_6) + 4H^+(soln,R_6) =$	-282.894
$(Na^+ + Al^{3+} + 2H_2O)(soln,R_6)$	±0.610
77. $NaAlSi_3O_8(c,R_6) + (18HF + 4H^+)(soln,R_6) =$	-628.701
$(Na^+ + Al^{3+} + 3H_2SiF_6 + 8H_2O)(soln,R_6)$	±1.000
78. $(3SiO_2 + NaAlO_2)(c,R_6) = NaAlSi_3O_8(c,R_6)$	-67.398
	±1.407
79. $(3SiO_2 + NaAlO_2)(c,R_1) = NaAlSi_3O_8(c,R_1)$	-67.315
	±1.410
80. $Na(c) + Al(c) + 3Si(c) + 4O_2(g) =$	-3935.06
$NaAlSi_3O_8(c)$ (low albite)	±2.60

Table 4. Continued.

Reaction	$\Delta_r H$ kJ
Reactions in $2PbO \bullet B_2O_3$ at 985 K	
81. $3SiO_2(c,R_7) = 3SiO_2(soln,R_7)$	-10.016
	±0.345
82. $NaAlO_2(c,R_7) = NaAlO_2(soln,R_7)$	16.359
	±0.088
83. $NaAlSi_3O_8(c,R_7) = NaAlSi_3O_8(soln,R_7)$	81.651
	±0.824
84. $(3SiO_2 + NaAlO_2)(c,R_7) = NaAlSi_3O_8(c,R_7)$	-75.308
	±1.022
85. $(3SiO_2 + NaAlO_2)(c,R_1) = NaAlSi_3O_8(c,R_1)$	-66.252
	±1.025
86. $Na(c) + Al(c) + 3Si(c) + 4O_2(g) =$	-3933.99
$NaAlSi_3O_8(c)$ (low albite)	±2.20
------------------------------------	
87. $NaAlSi_2O_6(c,R_7) = NaAlSi_2O_6(soln,R_7)$	88.303
	±0.348
88. $(2SiO_2 + NaAlO_2)(c,R_7) = NaAlSi_2O_6(c,R_7)$	-78.621
	±0.445
89. $(2SiO_2 + NaAlO_2)(c,R_1) = NaAlSi_2O_6(c,R_1)$	-72.362
	±0.450

Table 4. Continued.

Reaction	$\Delta_r H$ kJ
90. $Na(c) + Al(c) + 2Si(c) + 3O_2(g) =$ $NaAlSi_2O_6(c)$ (jadeite)	-3029.40 ±2.10

Reactions in 20% HF	
91. $NaAlSi_2O_6(c,R_4) + (12HF + 4H^+)(soln,R_4) =$ $(Na^+ + Al^{3+} + 2H_2SiF_6 + 6H_2O)(soln,R_4)$	-478.44 ±0.38
92. $(2SiO_2 + Al(OH)_3 + NaCl)(c,R_1) + 11.731H_2O(l,R_1) =$ $NaAlSi_2O_6(c,R_1) + HCl \bullet 12.731H_2O(l,R_1)$	48.40 ±1.58
93. $Na(c) + Al(c) + 2Si(c) + 3O_2(g) =$ $NaAlSi_2O_6(c)$ (jadeite)	-3029.12 ±2.45
------------------------------------	
94. $NaAlSi_2O_6(c,R_4) + (12HF + 4H^+)(soln,R_4) =$ $(Na^+ + Al^{3+} + 2H_2SiF_6 + 6H_2O)(soln,R_4)$	-480.99 ±2.50
95. $Na(c) + Al(c) + 2Si(c) + 3O_2(g) =$ $NaAlSi_2O_6(c)$ (jadeite)	-3026.56 ±3.50

Reactions in $2PbO \bullet B_2O_3$ at 964 K	
96. $SiO_2(c,R_8) = SiO_2(soln,R_8)$	-4.27 ±0.21

Table 4. Continued.

Reaction	$\Delta_r H$ kJ
97. $NaAlSi_3O_8(c,R_8)$ = $NaAlSi_3O_8(soln,R_8)$	84.22
	±1.34
98. $NaAlSi_2O_6(c,R_8)$ = $NaAlSi_2O_6(soln,R_8)$	86.11
	±0.59
99. $SiO_2(c,R_8)$ + $NaAlSi_2O_6(c,R_8)$ =	-1.13
$NaAlSi_3O_8(c,R_8)$	±1.48
100. $SiO_2(c,R_1)$ + $NaAlSi_2O_6(c,R_1)$ =	1.67
$NaAlSi_3O_8(c,R_1)$	±1.50
101. Na(c) + Al(c) + 2Si(c) + $3O_2(g)$ =	-3026.0
$NaAlSi_2O_6(c)$ (jadeite)	±3.1
Reactions in 20.1% HF	
102. $NaAlSi_3O_8(c,R_5)$ = $NaAlSi_3O_8(soln,R_5)$	11.45
	±0.21
103. Na(c) + Al(c) + 3Si(c) + $4O_2(g)$ =	-3923.61
$NaAlSi_3O_8(c)$ (analbite)	±2.61

R = reference temperature, R_1 = 298.15 K (25° C), R_2 = 346.85 K (73.7° C), R_3 = 303.15 K (30° C), R_4 = 347.85 (74.7° C), R_5 = 322.85 K (49.7° C), R_6 = 333.15 K (60° C), R_7 = 985 K, and R_8 = 964 K.

Table 5. Reaction schemes for silicalite.

Reaction	$\Delta_r H$ kJ
104. $SiO_2(c) + xHF \bullet yH_2O(soln) =$ $[H_2SiF_6 + (x-6)HF \bullet (y+2)H_2O](soln)$	
105. $SiF_4(g) + O_2(g) = SiO_2(c) + 2F_2(g)$	
106. $Si(c) + 2F_2(g) = SiF_4(g)$	
107. $Si(c) + O_2(g) = SiO_2(c)$	
108. $Si(c) + O_2(g) + xHF \bullet yH_2O(soln) =$ $[H_2SiF_6 + (x-6)HF \bullet (y+2)H_2O](soln)$	
Silicalite	
109. $SiO_2(c,R_1) + xHF \bullet yH_2O(soln,R_1) =$ $[H_2SiF_6 + (x-6)HF \bullet (y+2)H_2O](soln,R_1)$	-144.80 ±0.10
110. $Si(c) + O_2(g) = SiO_2(c)$	-905.20 ±0.84
Quartz	
111. $SiO_2(c,R_1) + xHF \bullet yH_2O(soln,R_1) =$ $[H_2SiF_6 + (x-6)HF \bullet (y+2)H_2O](soln,R_1)$	-135.59 ±0.18
112. $Si(c) + O_2(g) = SiO_2(c)$	-910.70 ±1.00

R = reference temperature, R_1 = 298.15 K (25° C)