Key Values for the Thermodynamic Properties of Geologic Materials: 
I. The Enthalpy of Solution of Quartz in Hydrofluoric Acid, 
a Preliminary Evaluation

by

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Abstract

Enthalpy data for the dissolution of quartz in hydrofluoric acid have been collected from the literature and evaluated. Corrections have been applied for differences in the enthalpy of dilution from that in 20.1 weight percent HF. Data sets from eight calorimetric systems were fit with an average deviation of 0.26 kJ/mol by the equation,

$$\Delta H_{\text{soln}} = -140.20 + 0.16017 (73.7 - t) \text{ kJ/mol},$$

that represents the enthalpy of solution of 0.7893 g of quartz in 1000 g of 20.1 percent HF as a function of temperature with t in °C.

The results are based upon a model for the enthalpy of dilution of hydrofluoric acid at temperatures greater than 25 °C and at concentrations other than 20.1 percent HF that requires confirmation. The model predicts a linear decrease in the enthalpy of dilution of HF between 25 °C and 80 °C with the value at 80 °C about 18.2 percent of the value at 25 °C.

Heat contributed from abrasion of the calorimeter by quartz particles during the dissolution period is shown to be a potential systematic error. The effect of abrasion has been studied for changes in stirring speed and for changes in stirring fin surface area at a constant stirring speed.

The dissolution of quartz particles < 2 μ in size is shown to contribute a significant excess enthalpy. Such particles, in small quantities, may increase the scatter of enthalpy of solution data or, in larger quantities, may lead to systematic errors in derived thermodynamic properties.

The results reported in this study support the correction of the enthalpy of formation values for silicates reported by Hemingway and Robie (1977) based upon suggested systematic errors in the values for the enthalpy of solution of quartz (King 1951, 1952) used in calorimetric reference reactions.

Introduction

The mineral quartz has been used as a reference phase for silicon in aqueous hydrofluoric acid and molten salt reaction calorimetric determinations of the enthalpy of formation of silicate minerals. Quartz has also been used as a reactant in many phase equilibria and solubility studies of mineral stabilities. Therefore, it is important to identify those factors that may alter the thermochemical or thermophysical data for quartz and result in systematic errors in experimentally derived thermodynamic values.

Numerous discordant values for the enthalpy of solution of quartz appear in the literature (e.g., Hemingway and Robie, 1977). Many of the values for the enthalpy of formation of silicates are referenced to the enthalpy of solution of quartz reported by King (1951, 1952). Hemingway and Robie (1977) considered King's (1951, 1952) results to be systematically in error and applied a correction of -1.255 kJ/mol of SiO₂ to the enthalpy of formation values calculated from that reference data. The enthalpies of solution of quartz reported by Hemingway and Robie (1977) were systematically different from data reported by Kilday and Prosen (1973). Thus the validity of the corrections made by Hemingway and Robie (1977) may be questioned.
CODATA (Committee on Data for Science and Technology, International Council of Scientific Unions) has organized a Task Group on Geothermodynamic Data whose task shall be the evaluation and recommendation of key values for the thermodynamic properties of geologic materials. The subcommittee on the Thermodynamic Properties of Minerals has selected the enthalpy of solution of quartz in hydrofluoric acid as a key value that should be evaluated. Several articles published since the study of Hemingway and Robie (1977) combined with some unpublished results of Savin and others (1974), Nitkiewicz and others (1983), and Donahoe and Hemingway (1983) provide related information that will allow a preliminary evaluation of the problems related to the determination of the temperature and concentration dependence of the enthalpy of solution of quartz.

**Enthalpy of solution of quartz in hydrofluoric acid**

The enthalpy of solution of quartz has been measured at more than one temperature by King (1951, 1952), Kilday and Prosen (1973), Hemingway and Robie (1977), and Donahoe and Hemingway (1983). Hummel and Schwiete (1959) and Kilday and Prosen (1973) have measured the enthalpy of solution at different concentrations of hydrofluoric acid. The enthalpy of solution at a single temperature and composition of acid also has been measured by Wietzel (1921), Roth and Troitzsch (1932), Troitzsch (1936), Torgeson and Sahama (1948), Kracek and others (1951), Sahama and Neuvonen (1951), Jeffes and others (1954), Stevens and Turkdogan (1955), Weeks (1956), Waldbaum (1970), Hovis (1971), Savin and others (1974), Hovis (1982), Johnson and others (1982), Bennington and Brown (1983), and Nitkiewicz and others (1983).

The enthalpy of solution results cannot be compared until the data have been reduced to a common reference framework. The studies cited above provide values for the enthalpy of solution of quartz at several different temperatures and/or concentrations of H$_2$SiF$_6$ in the final solution. We shall adopt 0.7893 g of SiO$_2$ per 1000 g of 20.1 weight percent HF as the reference concentration because this was the value chosen for the greatest number of studies of the enthalpies of formation of silicate minerals in hydrofluoric acid solution calorimeters (see references in Hemingway and Robie, 1977).

The dissolution of quartz in hydrofluoric acid results in the formation of an aqueous silica species such as H$_2$SiF$_6$ and the dilution of the acid by the water formed. For most of the studies cited above, the largest correction will be that for the dilution of the acid. Because the concentration of H$_2$SiF$_6$ is not equivalent, a correction for the dilution of H$_2$SiF$_6$ should also be made. The data are insufficient to make this correction quantitatively, however, based upon the enthalpy of dilution of several uni-valent electrolytes (Parker, 1965) and the very dilute nature of these solutions, one can estimate that the largest correction should be less than 100 joules.

**Enthalpy of dilution of hydrofluoric acid**

Correction of the enthalpies of solution of quartz to the chosen standard concentration requires knowledge of the enthalpy of dilution of aqueous hydrofluoric acid at the temperatures of the dissolution reactions. We have obtained the data from the studies of Johnson and others (1973), Parker (1965), and
Hemingway and Robie (1977). We have used the data of Kilday and Prosen (1973) and Hummel and Schwiete (1959) in support of these data.

Johnson and others (1973) and Parker (1965) have published smoothed values of the thermodynamic data for aqueous hydrofluoric acid solutions at 298.15 K. Hemingway and Robie (1977) have directly measured the enthalpy of dilution of 20.1 weight percent HF at 303 and 333 K. The enthalpy of dilution of 20.1 weight percent HF at 298.15 K may be calculated from an extrapolation of the data of Hemingway and Robie (1977) and from the difference in the relative apparent molar enthalpies of aqueous HF reported by Johnson and others (1973), from which we obtain -233 ± 9 and -230 J/mol of water, respectively. These results are in excellent agreement.

The enthalpy of dilution of 20.1 weight percent HF at 353 K may be obtained from an extrapolation of the enthalpy of solution data for water given by Hemingway and Robie (1977) under the assumption that the enthalpy of dilution varies linearly with temperature. The resulting value of -42 ± 10 J/mol of water is about one fifth the value at 298.15 K. We may compare this difference with the change in the observed dependence of the enthalpy of solution of quartz between these two temperatures. Kilday and Prosen (1973) obtained an average value of -80 J/(mol·wt. percent HF) at 353 K for the concentration dependence of the enthalpy of solution of quartz. Hummel and Schwiete (1959) obtained a value of about -350 J/(mol·wt. percent HF) for the same process at 298.15 K. The ratio of these values reflects the same order of decrease with temperature as seen in the enthalpy of dilution results suggesting that the major difference in the enthalpies of solution of quartz at any temperature will arise from differences in the extent to which the acid is diluted.

The enthalpy of dilution correction has been discussed by Taylor and Wells (1938). That procedure will be followed in this study, where possible, to correct the enthalpy of solution results for quartz to the reference concentration specified above (see Table 1). Using the data from Johnson and others (1982) for 24.4 weight percent HF as an example, the calculation is as follows. From the conditions before dissolution we calculate the number of moles of HF per mole of SiO₂ (739) and the concentration of HF (16.2, the moles of HF per 1000 g of H₂O), and similarly for the final solution (733 and 15.98). Next we calculate the difference in the relative apparent molal enthalpy of aqueous HF (109 J/mol from the data of Parker, 1965). The product of the change in concentration, the number of moles of HF involved, and the difference in the relative molal enthalpy yields the enthalpy produced in the dilution of the acid when one mole of SiO₂ is dissolved (-11185 J/mol). Subtracting this value from the value derive for 20.1 weight percent HF (-8165 J) provides the correction to the enthalpy of solution in 24.4 percent HF (+3020 J/mol.) The revised enthalpy of solution for quartz is -135.59 kJ/mol +3.02 kJ/mol = -132.57 kJ/mol. This value is in good agreement with an extrapolation of the data given by Hemingway and Robie (1977).

The enthalpies of solution of quartz at temperatures other than 25 °C and in concentrations other than 20.1 percent HF were corrected based upon the assumption that the dilution term linearly decreases to 80 °C, as shown earlier for 20.1 percent HF, to 18.2 percent of the value calculated at 25 °C. The corrected values are listed in Table 1 and are shown graphically in Figure 1.
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1Values have been corrected to the dissolution process at the given temperature using the heat content for quartz given by Robie and others (1979).

2Values have been corrected for the error in the electrical calibration (see Hovls, 1982).
Figure 1. Corrected experimental values for the enthalpy of solution of quartz (see Table 1). The experimental values are (beginning in the upper right of the figure): square, Kilday and Prosen (1973); large rectangle, Kracek and others (1951); X, King (1951, 1952); large triangle, Sahama and Neuvonen (1951); small triangle, Hemingway and Robie (1977); octagon, Savin and others (1974); vertical bar, Torgeson and Sahama (1948); diamond, Bennington and Brown (1983); opposing triangles, Roth and Troitzsch (1932) and Troitzsch (1936); X over small square, Weeks (1956); plus, Waldbaum (1970) and Hovis (1982, 1971); X over inverted triangle, Donahoe and Hemingway (1983); triangle over vertical bar, Nitkiewicz and others (1984); six pointed star, Hummel and Schwiete (1959); asterisk, Johnson and others (1982); Z, Stevens and Turkdogan (1955); and filled square, Jeffes and others (1954).
A straight line can be fit through the two average values for the enthalpy of solution of quartz in 20.1 percent HF given by Hemingway and Robie (1977) and the single corrected value of Nitkiewicz and others (1983), as shown in Figure 1. The slope of this line is parallel to a line that can be fit through the corrected enthalpy of solution data given by Kilday and Prosen (1973) for temperatures between 75 and 85 °C and the corrected value for solution at 25 °C given by Johnson and others (1982). The difference between these curves is about 0.3 percent and within the expected uncertainty of this type of experiment. The data of Bennington and Brown (1983), Donahoe and Hemingway (1983), Savin and others (1974), Torgeson and Sahama (1948) and Roth and Troitzsch (1932) are consistent with these results. Equation (1) fits the data set with

\[ \Delta H_{\text{soln}} = -140.20 + 0.16017 \times (73.7 - t) \text{ in kJ/mol} \]  

an average deviation of 0.26 kJ/mol, where \( t \) is temperature in °C. The data of Troitzsch (1936), King (1952, 1951), Kracek and others (1951), Weeks (1956), Hovis (1982, 1971), Waldbaum (1970), and the results of Kilday and Prosen (1973) for temperatures between 25 and 51 °C are not consistent with equation (1).

Other fits to the data can be obtained that result in calculated slopes that are somewhat less negative than that selected above. The slope selected above is based upon the results from eight calorimeters. However, because the majority of the data are concentrated in the temperature region of 73 to 80 °C, the slopes are determined primarily by the choice of the values at the lower temperatures, that is, either the results of Kilday and Prosen (1973), Hovis (1982, 1971), and Waldbaum (1970), or the results of Johnson and others (1982), Donahoe and Hemingway (1983), Nitkiewicz and others (1983), and Hemingway and Robie (1977).

### Intercomparison of Calorimetric Systems

Difference in the enthalpy of solution of quartz can arise from several factors, e.g., systematic errors in energy calibration measurements, systematic errors in corrections for heat exchange, or contributions from fine grained particles. Systematic errors within a calorimetric system can only be detected by comparison of the results of several calorimetric systems. Differences that arise from a distribution of particles sizes can be determined by direct measurements.

The calorimetric systems used by Kilday and Prosen (1973), Hemingway and Robie (1977), Johnson and others (1982), Donahoe and Hemingway (1983), and Nitkiewicz and others (1983) have been compared through the study of the dissolution of Standard Reference Material 724, tris (hydroxymethyl) aminomethane (TRIS) in 0.100 N HCl. The average values from the first three systems differed by no more than 0.08 percent (see Montgomery and others, 1977). Unpublished results (Hemingway, 1984) confirm that the calorimetric system used by Donahoe and Hemingway (1983) and Nitkiewicz and others (1983) yields a value for the enthalpy of solution of TRIS that agrees with the value reported by Montgomery and others (1977) to better than 0.1 percent. The results show that there are no systematic errors in the electrical calibration procedures used in these calorimetric systems. However, TRIS is not an adequate standard for intercomparison in this case. The TRIS reaction is fast at 25 °C (less than 30 min)
compared to the dissolution time required for quartz (6 to 10 hours at 25 °C). Therefore, the TRIS protonation reaction will not test for systematic errors in the evaluation of the heat exchange correction for dissolution reactions of long duration.

We may also intercompare calorimetric systems through the values reported for other compounds. The enthalpy of solution of gibbsite has been measured in hydrofluoric acid by Barany and Kelley (1961) and Koehler and others (1961), Hemingway and Robie (1977), Hemingway and others (1978), Hovis (1982), Johnson and others (1982), and Donahoe and Hemingway (1983). Hemingway and others (1978) have shown that the enthalpies of solution of gibbsite in 20.1 percent HF reported by Barany and Kelley (1961), Koehler and others (1961), and Hemingway and Robie (1977) as well as their own results are in good agreement. Donahoe and Hemingway (1983) have measured the enthalpy of solution of gibbsite in 24.4 percent HF at two temperatures and in the calorimeter used by Nitkiewicz and others (1983). These results can be extrapolated to 25 °C (yielding -164.72 kJ/mol) and compared with the value reported by Johnson and others (1982) for the dissolution of gibbsite in 24.4 percent HF (-165.18 kJ/mol). The difference between these values is 0.3 percent and is identical to the difference noted earlier for the enthalpy of solution of quartz from these calorimetric systems. Hovis (1982) has measured the enthalpy of solution of gibbsite at 49.7 °C in 20.1 percent HF obtaining a value 0.64 percent greater than the value calculated from the data of Hemingway and others (1978). After applying a correction for dilution (+ 430 J/mol) to the data of Hovis (1982), the difference is 0.35 percent.

The calorimetric systems used by Waldbaum (1970) and Hovis (1982, 1971), and by Hemingway and Robie (1977) may be compared through measurements of the enthalpy of dissolution of albite in 20.1 percent HF. Hovis (1982) reported a value of -627.22 kJ/mol for the enthalpy of solution at 49.7 °C. Hemingway and Robie (1977) measured the enthalpy of solution of several low albite samples and reported a value of -628.98 kJ/mol for the average value at 60 °C. The data provided by Hemingway and Robie (1977) suggest that there is little or no temperature dependence for the dissolution reaction at these temperatures. Correcting the value reported by Hovis (1982) for the difference in feldspar dissolved from that used by Hemingway and Robie (1977) yields a value of -629.05 kJ/mol. Waldbaum and Robie (1971) report a value of -627.37 kJ/mol for the dissolution reaction at 49.7 °C. Correcting this value to the concentration used by Hemingway and Robie (1977) yields -627.76 kJ/mol. Waldbaum and Robie (1971) suggest that the enthalpy of solution decreases slightly with temperature. Applying this correction to the data of Hemingway and Robie (1977) yields a value of -628.39 kJ/mol for the dissolution reaction at 49.7 °C.

The intercomparison of the laboratory results discussed above suggest that there is no systematic error in the methods used to evaluate heat exchange or in the electrical calibration procedures used with these calorimetric systems. Differences are shown to exist only for the dissolution of quartz and not for similar reactions involving gibbsite or albite.

**Enthalpy of Abrasion**

We are left with a situation in which it can be shown that each of the calorimetric systems that help determine the slope of the enthalpy of solution
reaction for quartz has produced consistent results using compounds other than quartz. Quartz presents a unique problem because quartz particles can abrade the calorimeter walls. The result of such abrasion would be an apparent increase in the enthalpy of solution. Nitkiewicz and others (1983) have measured the enthalpy of abrasion of quartz on a gold calorimeter by varying the surface area (increasing the area by 57 percent) of the fins used to stir the solvent. With fins that extended to near the calorimeter wall, the apparent enthalpy of solution of quartz (>3 \( \mu \) particles) was -140.70 kJ/mol (average of 7 runs) at 34.8 °C in 24.4 percent HF. Reducing the fins surface area by 1.9 cm\(^2\) or 10.6 percent decreased the enthalpy of solution to -136.55 kJ/mol (average of 4 runs) and a 5 percent reduction in fin area lowered the apparent enthalpy of solution to -137.72 kJ/mol (average of 7 runs). Donahoe and Hemingway (1983) studied the effect of increasing the stirring speed of the smaller surface area fins from 144 rpm to 600 rpm and observed an increase in the apparent enthalpy of solution of quartz at 49.4 °C from -137.63 to -141.30 kJ/mol. The latter results were included by Liou and Donahoe (1984) without interpretation.

The abrasion results are applicable only to the calorimeter in which the measurements were made because the amount of abrasion that occurs in a calorimeter will be a function of stirring speed, solution time, and system geometry. However, the magnitude of the apparent increase in the enthalpy of solution provides a measure of the potential error that can occur in other calorimeters. This effect can easily be overlooked because the small amount of abraded metal is very fine grained and tends to accumulate on exposed organic surfaces, e.g., grease, teflon, or O-rings.

### Enthalpy Difference Associated with Particle Size Effects

It is a well documented fact that the use of very fine grained samples can lead to erroneously large enthalpy of solution values (e.g., Taylor and Wells, 1938, and Natarajan and others 1969). Kilday and Prosen (1973) noted a difference of about 320 J/mol for quartz that was ground to less than 74 \( \mu \) and separated into two batches through an elutritive process. Hemingway and Robie (1977) found a difference of 1200 to 1400 J/mol for material with an average grain size less than 2 \( \mu \) as compared to material with a grain size greater than 37 \( \mu \). Kilday and Prosen (1973) processed the quartz sample with dilute HCl and several washings with distilled water, each of which would tend to remove the finest materials. Kilday and Prosen (1973) provide a brief description of the procedure used to separate the sample into a coarser and finer fraction, but the information is not adequate to allow an estimate to be made of the average particle size and the authors did not provide that information.

More detailed studies of the effect of particle size on the enthalpy of solution of quartz have been completed by Savin and others (1974) and Nitkiewicz and others (1983). Savin and others (1974) separated a crushed quartz sample into material greater than 36 \( \mu \), 2 to 5 \( \mu \), 0.5 to 2 \( \mu \), and less than 0.5 \( \mu \) from which they obtained -140.63, -140.72, -141.21, and -143.67 kJ/mol, respectively, for the enthalpies of solution (75 °C in 20.1 percent HF). Nitkiewicz and others (1983) separated a sample of quartz into batches larger than 3 \( \mu \), less than 2 \( \mu \), and less than 0.5 \( \mu \), and measured enthalpies of solution (34.5 °C in 24.4 percent HF) of -136.32 kJ/mol (average of 18 measurements of sized material
greater than 3 μ and less than 149 μ), -137.05 kJ/mol (average of 8 values), and -139.32 kJ/mol (average of 2 values), respectively.

The results of these studies show that the enthalpy of solution of quartz is significantly increased as the average particle size of the sample is decreased below 2 μ as noted earlier by Hemingway and Robie (1977). Furthermore, the presence of small amounts of quartz grains less the 2 μ may lead to a large scatter in the observed enthalpy of solution or, if homogeneously distributed, to a systematic difference from the heat of solution of a macroscopic sample.

Appropriateness of quartz as a reference material for reaction calorimetry

Johnson et al. (1987) have recently reported thermodynamic properties for silicalite (SiO₂) and have proposed the use of this material rather than quartz as the reference material for Si in reaction calorimetry. Johnson et al. (1987) determined the enthalpy of formation of silicalite by fluorine-combustion calorimetry and combined this result with similar data for quartz and with measurements of the enthalpies of solution of quartz and silicalite in aqueous HF to show that the enthalpies of solution of quartz were inconsistent. Based upon the results of their analysis and because the reaction between silicalite and aqueous HF is very fast (5 minutes vs more than 3 hours for quartz), Johnson et al. (1987) have recommended the use of silicalite in place of quartz as the reference phase for Si in aqueous HF reaction calorimetry.

Silicalite is a polymorph of SiO₂ that has a molecular sieve structure. As such, silicalite has a very large surface area to aqueous HF. The mean diameter of the crystals in the silicalite sample was 0.004 mm. Consequently, the reaction of silicalite with aqueous HF should show a significant surface energy contribution. Unfortunately, we have insufficient data to accurately predict the magnitude of this enthalpy contribution or the dependence of the surface energy contribution with changes in acid concentration. Based upon an analogy with fine-grained quartz, we may estimate that the enthalpy of solution of silicalite could show an excess enthalpy as large as -3 kJ/mol. Furthermore, the surface energy contribution to the solution enthalpy should be largely a heat of wetting effect and should be proportional to the activity of water. Thus one may reason that the enthalpy contribution should increase as the acid concentration is decreased and the observed difference between the enthalpy of solution of silicalite in acids of varying concentration should be smaller than that observed for quartz.

The observations cited above are consistent with the observations of Johnson et al. (1987) and represent an alternative explanation of their results. Johnson et al. (1987) predicted that the enthalpy of solution of quartz should be significantly more negative than those reported in the literature. If the enthalpy of solution of silicalite contains a surface energy contribution, the procedure followed by Johnson et al. (1987) to calculate the enthalpy of solution of quartz would necessarily carry forward that contribution to the enthalpy of solution of quartz. The magnitude and direction of the change proposed by Johnson et al. (1987) is consistent with a surface energy contribution to the enthalpy of solution of silicalite. Johnson et al. (1987) observed a significantly smaller difference in the enthalpy of solution of silicalite with acid
concentration than that observed for quartz by Kilday and Prosen (1973) and Hummel and Schwiete (1959). As noted above, the expected effect of surface wetting would tend to compensate for the change in the enthalpy of solution with concentration. Therefore, the observations of Johnson et al. (1987) may be interpreted as representing systematic problems that would argue against the use of silicalite as a reference for Si in aqueous HF reaction calorimetry.

Although resolution of the questions posed by Johnson et al. (1987) and within this paper is an important matter, the majority of enthalpy of formation values referenced to quartz utilize a value for the reaction at 73.7 °C that is consistent with the value recommended in this paper. Few enthalpies of formation of minerals (e.g., analcime, Johnson et al., 1982, and albite, Hemingway and Robie, 1977) depend upon the enthalpy of solution of quartz at other temperatures. Haas et al. (1981) and Robinson et al. (1982) have performed simultaneous evaluation of data from numerous experimental techniques (e.g., gas reduction, phase equilibria, and molten salt calorimetry) and have derived enthalpies of formation for several phases that have also been determined by aqueous HF calorimetry. With few exceptions (e.g., gehlenite where the sample preparation probably resulted in hydration of the sample), the results of the HF calorimetry are consistent with the analysis of Haas et al. (1981) and Robinson et al. (1982). This observation suggests that the enthalpy of solution of quartz in aqueous HF cannot be greatly in error at the higher temperatures. In addition, Navrotsky et al. (1980) have confirmed the enthalpy of formation of albite reported by Hemingway and Robie (1977) through molten salt calorimetry (see Hemingway et al., 1981) which suggests that the enthalpy of solution of quartz in aqueous HF at 30 °C is also not significantly in error. Thus an error of the order of -3 kJ/mol of SiO₂ in the enthalpy of solution of quartz as suggested by Johnson et al. (1987) is not supported by the foregoing analysis.

Conclusion

The agreement between the results produced by eight calorimetric systems (see figure 1) provides strong support for the slope chosen. Deviations from the data chosen for this set may arise from excess heat produced by abrasion of the calorimeter (e.g., the results of Waldbaum, 1970, Hovis, 1971, 1982, and the lower temperature results of Kilday and Prosen, 1973) or from the contribution of fine particles (e.g., the results of King, 1951, 1952, and Kracek and others, 1952), however, the information provided in these studies is not adequate to verify these hypotheses.

The average value for the enthalpy of solution of quartz (-140.20 kJ/mol) in 20.1 percent HF at 73.7 °C (for a concentration of about 0.7893 g of SiO₂ in 1000 g of acid) was calculated from the equally weighted average values at each temperature from the eight consistent calorimetric systems and extrapolated to 73.7 °C using the slope suggested in Figure 1. Equation (1) represents the data from this set of results with an average deviation of 0.26 kJ/mol, and including the uncertainty in the average experimental values used in the fit, the uncertainty in the adopted value is 0.33 kJ/mol.

The value selected at 73.7 °C may be compared with the value given by King (1951) of -141.69 kJ/mol. The difference of 1.49 kJ/mol is slightly larger than the value of 1.255 kJ/mol selected by Hemingway and Robie (1977) for the
correction they applied to enthalpies of formation of silicate minerals that were based upon the data of King (1951, 1952) for the enthalpy of solution of quartz at 73.7 °C. At 50 and 60 °C the difference is about 2.10 kJ/mol. Also, Bennington and Brown (1983), whose result agrees with those of Hemingway and Robie (1977), used carefully sized (greater than 37 μ) quartz and dissolved the material in the calorimeter used by King (1951, 1952). These results support the correction procedure used by Hemingway and Robie (1977) and suggest that the correction required may actually be somewhat greater. However, before additional revisions are made in the enthalpies of formation of silicate minerals referenced to the enthalpy of solution of quartz reported by King (1951, 1952), the enthalpy of dilution of hydrofluoric acid must be determined for several concentration and temperature conditions to check the assumptions made in this study.

The value calculated from equation (1) for 73.7 °C is in excellent agreement with the results of Bennington and coworkers (1978, 1982, and 1984) who have dissolved quartz in a solution containing 0.63 g of K2Cr2O7 per 1000 g of 20.1 percent HF. This would suggest that the enthalpy of solution of quartz is independent of the oxidant K2Cr2O7 in these dilute quantities.

Finally, Haas et al. (1981) and Robinson et al. (1982) have provided tables of thermodynamic data for compounds in the chemical systems CaO-Al2O3-SiO2-H2O-CO2, MgO-SiO2-H2O-CO2, and Fe-FeO-Fe2O3-SiO2 that were obtained by the simultaneous evaluation of experimental data based upon numerous experimental techniques. The enthalpies of formation (from the elements at 298.15 K and 1 bar) for kaolinite, dickite, halloysite, calcium, olivine, larnite, fayalite, and forsterite are consistent with corrected values given by Hemingway and Robie (1976). The corrected values given by Hemingway and Robie (1976) are based upon corrections described earlier in this paper and are consistent with the standard enthalpy of solution of quartz in aqueous HF recommended in this paper. Thus, although somewhat equivocal, these results strongly support the recommended reaction and suggest that silicalite is not an appropriate reference material for Si for most minerals. Good agreement is seen between enthalpies of formation derived by aqueous HF calorimetry and from enthalpies derived from other experimental techniques such as phase equilibria, molten salt calorimetry, HNO3 solution calorimetry, and gas reduction.

References


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