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# Variation of the Enthalpy of Solution of Quartz in Aqueous HF as a Function of Sample Particle Size[1]

By

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## Abstract

Studies of the enthalpy of solution of quartz as a function of particle size support the conclusion reached by Hemingway et al. (1988) that early enthalpy of formation values reported by the U.S. Bureau of Mines and based on the work of King (1951, 1952) need to be corrected by 1.5 kJ·mol$^{-1}$ of $SiO_2$. This value is 0.24 kJ·mol$^{-1}$ larger than the value used by Hemingway and Robie (1977). Quartz, when used as a reference phase in enthalpy of formation reaction schemes, should be 10 micrometers or larger to avoid the effect of excess enthalpy of solution resulting from surface energy contributions.

## Introduction

Hemingway and Robie (1977) have shown that the enthalpy of solution of quartz in aqueous HF varies inversely with the average size of the particles in the sample. Based upon a preliminary set of measurements, they calculated and applied a correction (1.255 kJ per mole of $SiO_2$) to values reported by the U.S. Bureau of Mines for the enthalpy of formation of silicate minerals. This preliminary value needs to be refined.

The effect of particle size on the enthalpy of solution of quartz in aqueous HF has been reported by Savin and Hower (1974) in a progress report. This work was done in cooperation with the study by Hemingway and Robie (1977). Savin and Hower (1974) measured the enthalpy of solution of quartz of 4 size ranges: greater than 36 micrometers, 2 to 5 micrometers, 0.5 to 2 micrometers, and less than 0.5 micrometers, for which the reported values were -140.63, -140.72, -141.21, and -143.67 kJ·mol$^{-1}$, respectively, in 20.1% HF at 75° C. This study showed that the correction applied by Hemingway and Robie (1977) was not excessive, but the separations were not as restrictive as stated in the size fractions listed (Savin, personal communication, 1974). Therefore, some question remained as to the effect of material in the 2 to 5 micron (micrometer) range.

Hemingway et al. (1988) looked at this problem from another perspective. These authors attempted to define the best values for the enthalpy of solution of quartz in 20.1% HF as a function of temperature. Once this function was established, the authors calculated the difference between their recommended value and that used by workers at the U.S. Bureau of Mines (King, 1951 and 1952). Hemingway et al. (1988) suggested that the correction that was needed was 1.49 kJ·mol$^{-1}$ of $SiO_2$ for measurements at 73.7° C.

As part of a planned study for a doctoral thesis, the second author worked in the U.S. Geological Survey Thermodynamics Laboratory measuring the enthalpy of solution of quartz to better define the particle size effect. This work has not previously been published, although, Hemingway et al. (1988) did report some related aspects of this study.

## Sample

The quartz samples used in this study were prepared from MINUSIL, a commercially available quartz flour. The quartz is mined from a deposit located in Berkley Springs, WV. Quartz flour is produced by ball milling the raw quartz using quartz cobbles in the mill. The chemical analysis of MINUSIL indicates greater than 99.7 % pure $SiO_2$, with up to 500 ppm of Al, Fe, Ca, and MG, and traces of Ti and Zr.

The raw MINUSIL sample was sieved to pass a 325 mesh screen and separated into various size fractions with 2 procedures. Material passing the screen was elutriated to remove material less than 10 microns (labeled as 40 micron material). The remaining material (about 2 kg) was dried and then separated using a Donaldson Classifier (air centrifuge) into material <10, <5, <4, <3, ≤2, and ≤1 microns (labeled by the largest nominal particle size). The finest fraction was further separated by elutriation for four days (labeled as 0.5 micron). Material remaining in suspension was concentrated by centrifuging the suspension for four hours. This material was dried at 200°C and stored in a desiccator. The <10 micron fraction was elutriated (in a water/acetone mixture) to remove finer material. Optical examination showed the material to be largely 10 - 12 microns with a small amount as large as 20 microns and as small as 5 - 6 microns. A portion of each sample split was treated with 4*N* HCl to remove Fe and Ca contaminants.

Each enthalpy of solution measurement was made in a fresh batch of 24.4 weight percent HF at about 34.7° C. The nominal sample size was 0.5 g and the solvent was 477.0 g.

## Experimental data

Experimental data are listed in Table 1. The mean values and associated uncertainties are shown in Figure 1 as a function of particle size of the sample together with a smoothed curve representing the assumed model for this process. No effect was observed for pretreatment with HCl.

## Discussion

The cluster of values representing the results of dissolution of material of 2 to 5 microns in size represent material that is easily prepared and likely to represent the finest material that was used by King (1951, 1952). King (1951) stated that his quartz sample was ground to pass a 325 mesh sieve, then it was elutriated for 3 hours and dried at 180° C. Using the average of these values, -137.4 $kJ\cdot mol^{-1}$, the limit of difference that could be expected to be seen in the data of King (1951, 1952) for dissolution of fine grained quartz is about 2.1 ± 0.5 kJ. The difference of 1.5 kJ calculated by Hemingway et al. (1988) for 73.7° C is therefore a reasonable value.

## References


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Table 1. Values for the enthalpy of solution of quartz in 24.4% HF as a function of the sample particle size.

| Size | Mass | Temperature | $\Delta_{soln}H$ * | Mean |
|---|---|---|---|---|
| 305-360** | 0.5007 | 34.4999 | -135.11 | |
| 325-400 | 1.0003 | 34.6435 | -134.77 | |
| 325-400 | 0.5001 | 34.6846 | -135.30 | |
| 325-400 | 0.5004 | 35.0667 | -136.05 | |
| 325-400 | 0.5005 | 35.0598 | -134.71 | |
| 325-400 | 0.5014 | 35.0674 | -134.36 | |
| 325-400 | 0.5012 | 34.2854 | -136.84 | |
| 325-400 | 0.4990 | 34.2618 | -136.60 | |
| 325-400 | 0.5019 | 34.2264 | -134.27 | -135.33 ± 0.32 |
| <10 | 0.4999 | 34.5789 | -135.72 | -135.72 ± 0.10 |
| <5 | 0.5004 | 34.5759 | -136.67 | |
| <5 | 0.5009 | 34.5729 | -138.31 | |
| <5 | 0.2501 | 35.0052 | -137.12 | |
| <5 | 0.4998 | 34.2946 | -137.62 | |
| <5 | 0.4993 | 34.3317 | -138.01 | -137.55 ± 0.30 |
| <4 | 0.5013 | 34.5391 | -137.00 | |
| <4 | 0.5007 | 34.5410 | -136.56 | |
| <4 | 0.5025 | 34.3227 | -136.39 | |
| <4 | 0.5035 | 34.3052 | -136.68 | -136.66 ± 0.13 |
| <3 | 0.5003 | 34.5716 | -137.74 | |
| <3 | 0.5008 | 34.8139 | -139.10 | |
| <3 | 0.5012 | 34.7847 | -137.80 | |
| <3 | 0.4999 | 34.6284 | -137.93 | |
| <3 | 0.5014 | 34.3995 | -137.39 | -137.99 ± 0.29 |
| <2 | 0.5001 | 34.5871 | -138.59 | |
| <2 | 0.5002 | 34.5231 | -137.15 | |
| <2 | 0.5005 | 34.7841 | -137.76 | |
| <2 | 0.5014 | 35.1078 | -137.80 | |
| <2 | 0.5003 | 35.1900 | -137.96 | -137.85 ± 0.23 |
| <1 | 0.4997 | 34.3279 | -139.02 | |
| <1 | 0.5003 | 34.3251 | -138.36 | |
| <1 | 0.5015 | 34.2874 | -139.00 | -138.79 ± 0.22 |
| <0.5 | 0.4757 | 34.4901 | -139.47 | |
| <0.5 | 0.4763 | 34.4949 | -139.17 | -139.32 ± 0.15 |

* Average of two measured values.
** Sample label is 40 micrometers for this set of values.

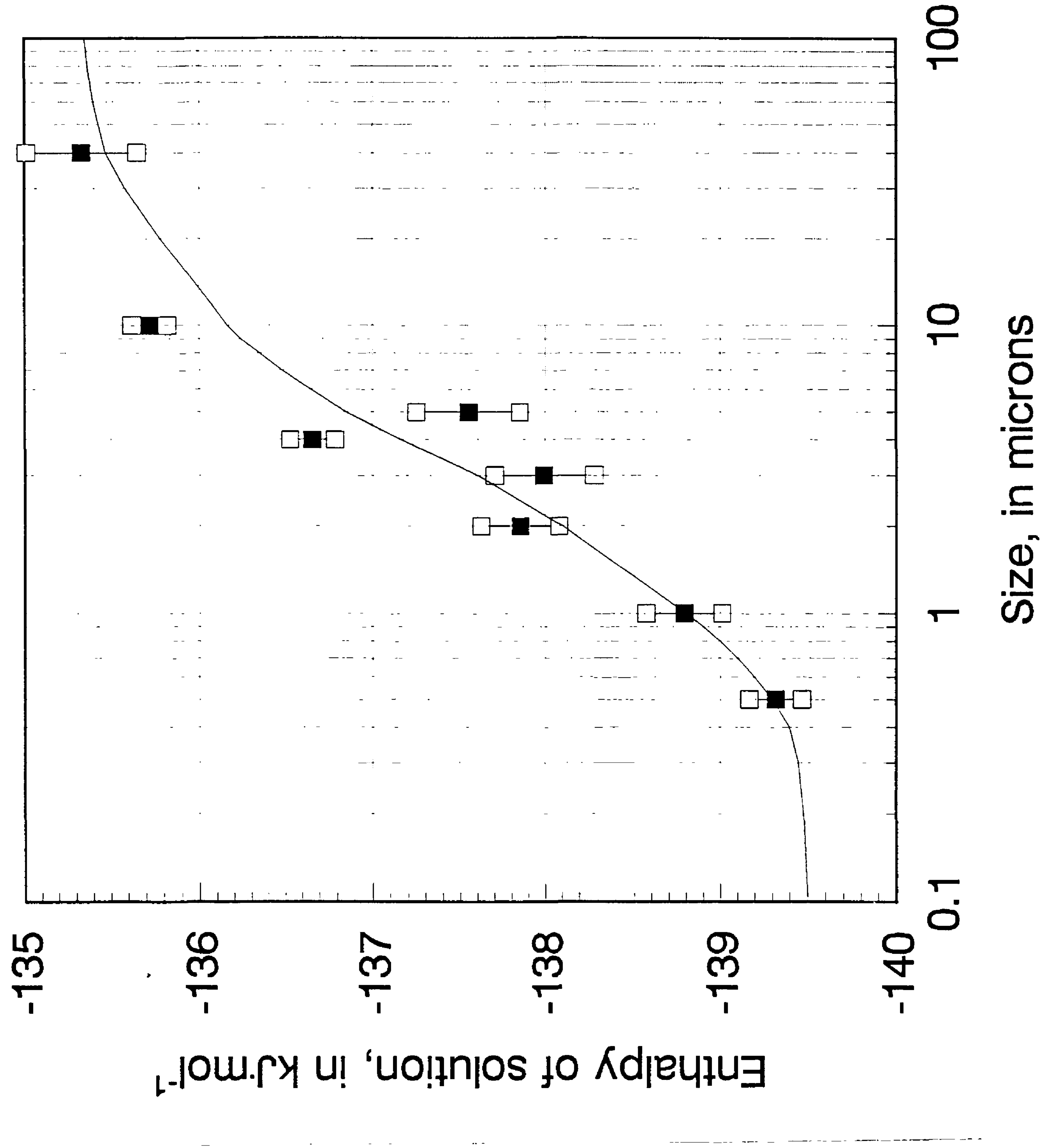


Figure 1. Variation of the enthalpy of solution of quartz in 24.4% HF as a function of particle size (microns = micrometers). The filled squares represent the mean values listed in Table 1, the open squares the uncertainty of the mean, and the smooth curve represents the model behavior.