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A THERMODYNAMIC STUDY OF THE ZEOLITE STILBITE

by

David Adams Howell

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Faculty of The Graduate College
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A THERMODYNAMIC STUDY OF THE ZEOLITE STILBITE

David Adams Howell, M.S.
Western Michigan University, 1987

Stilbite is a calcium-rich zeolite found in low-grade metamorphic and hydrothermally altered environments. In this study, measurements of the enthalpy of formation at 298.15 K, heat capacity from 5 to 350 K, and enthalpy increments from 350 to 500 K were performed on a specimen of stilbite characterized by electron microprobe analysis. The actual formula of the stilbite is: $\text{Ca}_{1.019}\text{Na}_{0.13}\text{K}_{0.006}\text{Al}_{2.180}\text{Si}_{6.820}\text{O}_{18}\cdot 7.33\text{H}_2\text{O}$. Evaluation of the thermodynamic properties for stilbite at $T = 298.15$ K produced the following values: $\Delta_f \text{H}^0_m(T) = -11034.6\pm 6.6 \text{ kJ} \cdot \text{mol}^{-1}$, $C_{p,m}^0(T) = 808.73\pm 1.62 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $S_m^0(T) - S_m^0(0) = 805.54\pm 1.61 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $\Delta_f S_m^0(T) = -2990.44\pm 1.86 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and $\Delta_f G_m^0(T) = -10143.0\pm 6.6 \text{ kJ} \cdot \text{mol}^{-1}$. Comparison of the calorimetrically derived value for the Gibbs free energy of formation, $\Delta_f G_m^0$, of stilbite with that calculated from an estimation method (La Iglesia and Anzar, 1986) shows a difference of 49 kJ·mol⁻¹. An attempt was made to retrieve a consistent Gibbs free energy value for laumontite using available phase equilibria and calorimetric data for heulandite and stilbite.
ACKNOWLEDGEMENTS

I owe many thanks to those who helped make this research successful. I am indebted to my advisor, John D. Grace, for introducing me to the opportunities that existed through the Department of Educational Programs at Argonne National Laboratory. Special thanks are directed to Argonne researchers Patrick A. G. O'Hare, Gerald K. Johnson, and Ian R. Tasker for their patient instruction, guidance and suggestions during the course of my thesis work. Recognition of Professor William S. Wise from the University of California, Santa Barbara, for his preparation and analysis of the stilbite is also due. I am very grateful for the typing expertise of Kay Shields at Argonne. Most dearly, I wish to express my appreciation of the love and support given to me by my parents, Stephen and Ann Howell.

David A. Howell
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CHAPTER I

INTRODUCTION

Increasing attention has been paid to the chemistry of zeolite formation for a variety of reasons. Most notably, widespread industrial applications (Barrer, 1982; Breck, 1974) have prompted the search for inexpensive natural deposits in place of costly synthetic zeolites. Zeolite precipitation can also interfere with oil recovery and geothermal reservoirs that depend on the hydrofracturing of reservoir rock to enhance permeability or surface area (Hawkins, 1981). Zeolites are among the major secondary phases found in the proposed sites for high-level radioactive waste disposal. Lastly, zeolites are petrologically significant in that their occurrence defines the boundary of sedimentary diagenesis and the lowest grade of metamorphism (Winkler, 1979).

The study of zeolite genesis and paragenesis is complicated by the fact that the formation of zeolites takes place at low temperatures and pressures in a variety of geologic environments. Reactions involving zeolites can often form metastable phases which can complicate phase equilibrium studies employing the usual hydrothermal techniques (Dibble & Tiller, 1981). Attempts to derive consistent free energies for individual zeolites are plagued by the problem of compositional variability. The very nature of the open Si-Al tetrahedral framework in zeolites allows variations in the number and positions of similarly sized cations necessary to maintain the electrical neutrality of the crystal. There is also a significant variation in the Si-Al ratio of some individual zeolite phases. In addition to the presence of exchangeable cations, most zeolites incorporate varying amounts
of interstitial water which can display a varying degree of bonding strength to the lattice (Van Reeuwijk, 1974). Calorimetric measurements of the thermodynamic properties of zeolites have only recently been made on a limited number of natural, well-characterized, pure specimens (Johnson, Flotow, O'Hare, & Wise, 1982; Johnson, Flotow, O'Hare, & Wise, 1983; Johnson, Flotow, O'Hare, & Wise, 1985). Earlier thermodynamic data on naturally occurring zeolites had been based on solubility studies, reactions with feldspar, or phase equilibrium studies between coexisting zeolites (Helgeson, Delany, Nesbitt, & Bird, 1978). The uncertainty of the effect of zeolitic water also complicates attempts to derive the thermodynamic properties of zeolites on the basis of known values for their component oxides (Chen, 1975; La Iglesia & Aznar, 1986). As shown by the recent calorimetric studies, errors of the order of 0.5 to 1.0 per cent result from the assumption that equivalent entropy contributions can be attributed to zeolitic water on both sides of the dehydration reaction (Johnson et al., 1985). The thermodynamic properties of zeolites are also affected by a contribution to the third law entropy as a result of Si-Al disorder in the framework (Ulbrich & Waldbaum, 1976).

This study is concerned with the determination of the thermodynamic properties of stilbite, a calcium-rich zeolite. In order to accomplish this, three separate types of measurement were necessary. Heat-capacity measurements from 5 to 350 K were made using an aneroid-type adiabatic cryostat (Westrum, Furukawa, & McCullough, 1968). From this data, the standard entropy and the entropy of formation of stilbite were calculated. The enthalpy of formation of stilbite at 298.15 K was derived from the measured enthalpy of reaction of stilbite and related compounds in 24.4 mass per cent HF using an LKB Productor model.
LKB-8700 precision calorimeter. This information, coupled with enthalpy increment measurements made in a drop calorimeter (Fredrickson, Barnes, Chasnov, Nutall, Kleb, & Hubbard, 1969), extended the Gibbs free energy of formation of stilbite to 500 K with an accuracy of ±0.1 per cent. The symbols used to represent these thermochemical properties and various physical parameters are listed in Appendix A.

This study provides previously unavailable thermodynamic data on a well-characterized sample of stilbite. The experimental determination of the thermodynamic properties of stilbite allowed a comparison of the calorimetrically derived Gibbs free energy of formation with that calculated by an estimation method. It also allowed the calculation of a Gibbs free energy of formation of another important zeolite, laumontite, based on calorimetric and phase equilibrium data for the mineral assemblage stilbite–heulandite–laumontite.

Stilbite Mineralogy

Stilbite (obsolete synonyms: desmine, foresite) is a calcium-rich zeolite belonging to the heulandite group (Breck, 1974). The true symmetry of stilbite is monoclinic with space group C2/m (Gottardi & Galli, 1985). However, because the [102] direction is almost normal to a, stilbite has been described as pseudo-orthorhombic with $\beta \sim 90^\circ$. Passaglia, Galli, Leoni, and Rossi (1978) reported the following range of lattice constants based on a face-centered orthorhombic cell from x-ray diffraction measurements on 65 different stilbite samples: $a = 13.595$ to $13.647$ Å, $b = 18.197$ to $18.309$ Å, $c = 17.775$ to $17.842$ Å, and $\beta = 90.06$ to $90.91^\circ$. From the analysis of the samples he deduced the generalized formula of
stilbite to be: \((Na, K)_{x}(Ca, Mg)_{4+y}Al_{x+4+y}Si_{28-x-2y}O_{72} \cdot 28H_2O\), where \(x < 4.89\) and \(-2.22 < y < 0.33\).

Using the conventional structure units of zeolites (Breck, 1974) the silicate framework of stilbite can be described as consisting of polyhedra constructed of four- and five-membered rings of silicon tetrahedra. This configuration forms a large channel parallel to the \(a\) axis and a smaller channel parallel to the pseudo-orthorhombic \(c\) axis. The exchangeable cations and water molecules occur within the cavities formed by the intersection of these channels (Galli & Gottardi, 1966). There exist five \(Na\) or \(Mg\) cation sites that form bonds with one or two water molecules as well as the framework oxygen atoms (Slaughter, 1970). Both Galli (1971) and Slaughter (1970) have noted that the \(Ca^{2+}\) ion in stilbite is surrounded by eight water molecules thus forming a sphere of hydration which prevents any contact with the framework oxygen atoms.

The order-disorder of the \(Si\)-\(Al\) atoms occupying the five tetrahedral sites in the framework is not yet fully understood. Galli (1971) attributes the problem to the \((Si, Al)\)-O bond distances that differ by an amount considered equal within experimental error of the x-ray structural refinement. Galli (1971) made refinements on a different symmetry model (C2). He varied the placement of aluminum atoms in two or three sites based on the Lowenstein avoidance principle. On the basis of similarities in the ten possible models he proposed the following probabilities for the occupancy of each tetrahedral site \((T)\): \(T_1 = Si(0.50), Al(0.50)\); \(T_2 = Si(1.0)\); \(T_3 = Si(0.50), Al(0.50)\); \(T_4 = Si(1.0)\); \(T_5 = Si(0.50), Al(0.50)\).

**Stilbite Occurrence and Experimental Phase Equilibria**

Stilbite typically forms as a result of the hydrothermal alteration of volcanic
units. Stratigraphic zonations of zeolites in thick volcanic rocks include stilbite or heulandite at the top of the section, a number of possible zeolite phases in the intermediate zone, and laumontite at the bottom (Kristmannsdóttir & Tómasson, 1978; Sukheswala, Avasia, & Gangopadhyay, 1974). The occurrence of the zeolites in the amygdules and the veins of these volcanic units is a function of temperature and the composition of solution from which the zeolites precipitate. Coombs, Ellis, Fyfe, and Taylor (1959) suggested that the availability of free silica strongly determines which zeolites will form. Thus, an observed sequence of cavity fillings can depend on variations in the composition of depositing solutions, changing pressure-temperature conditions, or both.

The formation of stilbite has also been attributed to the low-grade metamorphism of greywackes and other volcanogenic sediments (Coombs et al., 1959; Seki, Oki, Masuda, Mikami, & Okumura, 1969). Some of these occurrences of stilbite in metamorphic rocks appear to be related to magmatic intrusions. Stilbite is often associated with the chemically equivalent but less hydrous zeolite, heulandite. Heulandite and stilbite are considered to be the first calcium rich zeolites formed in the progressive sequence of diagenesis to zeolite facies metamorphism (Liou, 1983). Heulandite, analcime and laumontite together with quartz comprise the assemblage which denotes the onset of zeolite facies metamorphism (Winkler, 1979). Hydrothermal experiments by Liou (1971a) and Cho, Maruyama, and Liou (1986) have established reversible equilibrium between stilbite-laumontite and heulandite-laumontite, respectively. Based on assumed end-member compositions of the minerals the following reactions were investigated:
CaAl$_2$Si$_7$O$_{18} \cdot 7$H$_2$O $\rightarrow$ CaAl$_2$Si$_4$O$_{12} \cdot 4$H$_2$O $+$ 3SiO$_2$ $+$ 3H$_2$O

Stilbite $\rightarrow$ Laumontite $+$ Quartz $+$ Water

CaAl$_2$Si$_7$O$_{18} \cdot 6$H$_2$O $\rightarrow$ CaAl$_2$Si$_4$O$_{12} \cdot 4$H$_2$O $+$ 3SiO$_2$ $+$ 2H$_2$O

Heulandite $\rightarrow$ Laumontite $+$ Quartz $+$ Water

In the system CaAl$_2$Si$_2$O$_8$ $-$ SiO$_2$ $-$ H$_2$O, the three minerals, with excess SiO$_2$ and H$_2$O, define an invariant point at 600 bar and 413 K. From this point three univariant lines radiate as shown in Figure 1. The interpretation by Cho et al. (1986) is that the stability field of heulandite forms a transition zone between stilbite and laumontite. Accordingly, any reaction of stilbite directly to laumontite would occur at pressures lower than the invariant point.
Figure 1. Phase Diagram for the Assemblage Stilbite-Heulandite-Laumontite (Modified From Cho et al., 1986).

St = Stilbite  Lw = Lawsonite
Hu = Heulandite  Yu = Yugawaraite
Lm = Laumontite  Wk = Wairakite

Open boxes represent the uncertainty ranges in the equilibrium reaction of Cho (1986). Brackets indicate the experimental brackets of the equilibrium reaction of Liou (1971a).
CHAPTER II

ENTHALPY OF FORMATION OF STILBITE AT 298.15 K

The purpose of the measurements to be described was to derive the enthalpy of formation ($\Delta_f H_m^\circ$) of stilbite. Stilbite reacted with hydrofluoric acid as follows:

$$\text{Ca}_{1.019}\text{Na}_{0.136}\text{K}_{0.006}\text{Al}_{2.180}\text{Si}_{6.820}\text{O}_{18} \cdot 7.33\text{H}_2\text{O}(\text{cr}) + 49.64\text{HF}(\text{aq}) = 1.019\text{CaF}_2(\text{cr}) + 0.136\text{NaF} \cdot 0.006\text{KF} \cdot 2.180\text{AlF}_3 \cdot 6.820\text{H}_3\text{SiF}_6 \cdot 25.33\text{H}_2\text{O}(\text{aq}) \text{.}$$

In this study the enthalpy of formation of stilbite was based as follows on the compounds, $\text{SiO}_2$, $\text{Al(OH)}_3$, $\text{NaF}$, $\text{KF}$, $\text{CaF}_2$, $\text{H}_2\text{O}$, and $\text{HF(aq)}$, whose enthalpies of formation are well known:

$$6.820\text{SiO}_2(\text{cr}) + 2.180\text{Al(OH)}_3(\text{cr}) + 0.136\text{NaF}(\text{cr}) + 0.006\text{KF} + 1.019\text{CaF}_2(\text{cr}) + 5.15\text{H}_2\text{O}(\ell) = \text{Ca}_{1.019}\text{Na}_{0.136}\text{K}_{0.006}\text{Al}_{2.180}\text{Si}_{6.820}\text{O}_{18} \cdot 7.33\text{H}_2\text{O}(\text{cr}) + 2.180\text{HF(aq)} \text{.}$$

By appropriate combination of the enthalpies of reaction of the base compounds in $\text{HF(aq)}$ and their reported enthalpies of formation, the standard enthalpy of formation of stilbite can be calculated from the reaction:

$$1.019\text{Ca}(\text{cr}) + 0.006\text{K}(\text{cr}) + 0.136\text{Na}(\text{cr}) + 2.180\text{Al}(\text{cr}) + 6.820\text{Si}(\text{cr}) + 7.33\text{H}_2(\ell) + 12.665\text{O}_2(\ell) = \text{Ca}_{1.019}\text{K}_{0.006}\text{Na}_{0.136}\text{Al}_{2.180}\text{Si}_{6.820}\text{O}_{18} \cdot 7.33\text{H}_2\text{O}(\text{cr}) \text{.}$$

Apparatus

The reaction calorimeter used was a commercial LKB-8700 precision solution calorimeter. This instrument could be used to measure the energy evolved (exothermic) or absorbed (endothermic) by a chemical reaction with a specific
stoichiometry. A block diagram in Figure 2 illustrates the various components of the calorimetric equipment.

The calorimeter assembly consists of a thermostated bath, thermostat control, reaction vessel, calorimeter shell, stirrer, ampoule holder, and a Hewlett-Packard Model 2804-1A quartz-crystal thermometer connected to a Hewlett-Packard 9028 mini-computer. The thermostated bath contains approximately 18 dm$^3$ of water that is circulated in an upwelling pattern by a magnetically coupled stirrer positioned at the bottom. The bath is maintained at a constant temperature to 0.001 K by a proportional controller that can provide a range of temperature from 273 to 313 K. The controller uses a heater with a resistance of 70 ohms that can provide a maximum heating capacity of 40 watts. The bath temperature is monitored by the second channel of the quartz-crystal thermometer precise to 0.0001 K. Careful control of the bath isolates the shell from temperature variations in the laboratory, thus minimizing erratic thermal leaks in or out of the reaction vessel.

The shell is constructed of chromium-plated brass (Figure 3). The two-piece construction consists of a 125-mm-diameter, 150-mm-high can, and a lid that is connected by removable clamps. A rubber O-ring provides a water-tight seal. The interior of the can is polished to diminish radiative heat losses. The reaction vessel is connected to the lid of the outer vessel by a threaded ring around the neck of the reaction vessel. The calibration heater of the reaction vessel is connected by gold-plated pins which feed through the lid. The reaction vessel is constructed of 18-carat gold and has two re-entrant wells which separately house a heater and the probe of the quartz-crystal thermometer. The internal volume of the vessel is 100 cm$^3$. The ampoule holder is also constructed of 18-carat gold and is
Figure 2. Block Diagram of Reaction Calorimeter
Figure 3. Shell, Reaction Vessel, and Stirring Mechanism of Reaction Calorimeter.
attached to a stainless-steel spindle which freely rotates upon stainless-steel ball bearings. The spindle is spring-loaded to allow for the vertical movement of the ampoule onto the spike located at the bottom of the reaction vessel. The spindle is connected to the stirrer drive by means of a flexible cable. The synchronous motor of the drive rotates the ampoule holder at constant rate of 125, 250, or 500 rpm at 50 Hz; the speed of rotation is chosen depending on the reactivity of the compound under investigation, e.g., high speed for low reactivity.

The electronic assembly consists of a power supply, timer, standard resistor, null detector, and D.C. potentiometer. The heater inside the re-entrant well of the reaction vessel is connected to the electronic assembly. This calibration heater is used to liberate a precise quantity of electrical energy into the calorimeter. The energy released is calculated from the current through the heater, the heater resistance, and the length of time the current flows. The amount of calibration energy desired is that which closely corresponded to the amount of energy released by the chemical reaction under investigation. The duration of the calibration heating period also should match the estimated time of the reaction. The calculation of these parameters is described in Appendix B, sec. 1.

Material Preparation

Stilbite

The sample of stilbite used in this study was from the Skookumchuck Dam area in the state of Washington. The material was separated from coexisting phases and crushed to 0.5 mm size grains. The opaque and matrix minerals were separated from the sample by examining the stock of stilbite grains underneath
a microscope. An analysis of approximately 25 grains using an ARL microprobe was done to determine an average composition for the stilbite. A defocused beam with an accelerating voltage of 15 kV and a sample current of 10 nA was used to detect for Na, Si, Al, K, Ca, Mg, Fe, Sr, and Ba. Only the first five elements were found. Standards for analysis were albite, microcline, sanbornite, celestite, and andesine. A sample of stilbite was equilibrated with a 50 per cent relative humidity atmosphere and then heated to 900 K for 24 h to determine the weight loss due to dehydration. This value was used as the reference water content of the stilbite, since this zeolite readily loses, or gains, moisture from the atmosphere. Table 1 contains the analytical results for the stilbite sample.

Gibbsite

The gibbsite, Al(OH)$_3$, used in this study, was Fisher Reagent Al$_2$O$_3$·3H$_2$O. It had previously been heated at 423 K for 6 h and then stored in a desiccator containing drierite. The source of the material and the method of preparation were identical to that of Hemingway and Robie (1977) for their determination of the $\Delta_f H_m^0$ of Al(OH)$_3$.

Hydrofluoric Acid

A 24.4 mass per cent solution of hydrofluoric acid (HF) was obtained by diluting Baker analyzed reagent grade hydrofluoric acid with distilled water.
Table 1
Analysis, Cell Contents, and Structural Parameters for Stilbite From Skookumchuck Dam, Washington

<table>
<thead>
<tr>
<th>Sample Composition (mass per cent)</th>
<th>Cell Contents (number of atoms)*</th>
<th>Cell Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>57.34</td>
<td>Si 27.280 6.820</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>15.55</td>
<td>Al 8.720 2.180</td>
</tr>
<tr>
<td>CaO</td>
<td>8.00</td>
<td>Ca 4.076 1.019</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.59</td>
<td>Na 0.544 0.136</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.04</td>
<td>K 0.024 0.006</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>18.48</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O 29.320 7.33</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

*A - Cell contents based on 72 framework oxygens.
B - Idealized composition (18 framework oxygens) used for calculation of molar thermodynamic properties.
Sample Preparation

A portion of the crushed and analyzed stilbite was stored overnight in a wide-based Petri dish inside a desiccator containing a Mg(NO\textsubscript{3})\textsubscript{2} saturated solution which created a constant 50 per cent relative humidity atmosphere. This was done to ensure equilibrium of the material with the designated working water content for previously investigated zeolites (Johnson et al., 1985). Thus, throughout this study the standard sample of stilbite was that equilibrated with a 50 per cent relative humidity atmosphere. For each experiment an accurately weighed sample of stilbite contained in an air- and water-tight ampoule was required. The ampoules were constructed of 1 cm pieces of 10 mm outer-diameter Teflon tubing with end windows of split-Teflon discs attached with wax. This design isolated the sample from HF reactant until the measurement of the heat capacity of the system (i.e., HF reactant, reaction vessel, ampoule + sample) was made. The preparation procedure was as follows:

1. Five to six ampoules were prefabricated with bottom windows and their respective weights were recorded.

2. Each ampoule was then filled with the desired amount of sample. (see Appendix B, sec. 2). The material and ampoule were then weighed. The actual mass of the sample was the difference of the empty and filled ampoule with a correction for the buoyancy of the materials in air.

3. The unsealed ampoules containing the stilbite were returned to the desiccator and stored overnight in a 50 per cent relative humidity atmosphere.

4. The ampoules and material were reweighed to check for any significant mass gains or losses. Top windows were then placed on the ampoules and they
were quickly sealed with wax.

Experimental Procedure

The calorimeter was first calibrated, then the enthalpy change brought about by reaction of the stilbite was measured and, finally, the calorimeter was calibrated once again. In preparation for the measurement of a compound's enthalpy of reaction, the first adjustment made was to the temperature of the bath. The desired starting temperature was calculated from temperature increments of previously measured zeolites. The calibration heating time and voltage were also estimated from past zeolite experiments (see Appendix B, sec. 1). After these parameters were fixed, the reaction vessel was filled with 100 cm$^3$ of a 24.4 mass per cent HF solution for measurements on stilbite. For gibbsite, the solution used was that which resulted when 0.1g of SiO$_2$ was reacted with 0.1dm$^3$ of 24.4 mass per cent HF. The ampoule containing the stilbite or gibbsite was placed in the stirrer holder. The temperature of the reaction vessel was checked on the first channel of the quartz-crystal thermometer. If its temperature was too far below the optimal starting temperature, then heat was applied by means of a hot-air gun. The stirring mechanism was then screwed into the reaction vessel and the cable drive was attached. The high stirring rate of 500 rpm was used for both the stilbite and gibbsite to ensure complete reaction. The outer vessel was then clamped in position and the whole apparatus placed in the bath.

After a short equilibration period, the temperature of the reaction vessel began to drift towards the temperature of the bath. At this point, a computer program designed to record the temperature at 10 s intervals was invoked on the mini-computer. When a steady foredrift was reached, thus indicating that
equilibrium had been established, the first calibration was begun. This procedure involved the introduction of a known amount of electrical energy, via the heater, into the system, and recording the temperature rise. As mentioned before, this temperature rise should have approximated that from the chemical reaction under investigation. Following the temperature increase, the onset of an afterdrift was observed. Once the afterdrift had reached a stable rate, indicating that equilibrium had been reached once again, the initial calibration was terminated. The apparatus was removed from the thermostated bath and the shell was opened to expose the reaction vessel. The reaction vessel was allowed to cool down to the starting temperature. The shell was then reattached and the apparatus was once more placed in the bath. As before, an equilibrium foredrift was established and recorded. To initiate the chemical reaction, the spring-loaded stirrer was pushed down. This brought the ampoule windows into contact with the spike located in the bottom of the reaction vessel and released the material to react with the HF. Again, the temperature rise (this time due to the chemical reaction) was recorded as well as the equilibrium afterdrift. The last step was to conduct a final electrical calibration. This procedure was a repeat of the initial calibration.

Data Analysis and Results

The information collected by the mini-computer was printed out and stored at the end of each experiment. A typical graph of the recorded temperature against time data is shown in Figure 4 as an example. After the experiment had started the calorimeter temperature began to drift upwards. Once a steady drift was established, a thermal event, representing either the introduction of calibration energy or the release of the sample into the reactant, caused a sharp tem-
Figure 4. Temperature Drift in Calorimeter.
perature increase. The calorimeter temperature then drifted toward the jacket temperature. The experiment was terminated once a steady afterdrift had been recorded. The foredrift and afterdrift were extrapolated by the computer program to a midpoint temperature. The difference between the two extrapolated drifts was the calculated temperature rise ($\Delta \theta_c$). The heat capacity of the system (capsule, sample, HF reactant, and reaction vessel), which was the mean of the initial and final calibration and denoted by $c_{\text{calor}}$, was multiplied by the calculated temperature rise to yield the enthalpy of reaction $c_{\text{calor}} \times (-\Delta \theta_c)$.

A correction for the enthalpy of vaporization of $\text{H}_2\text{O}$ into the free volume of the ampoule ($-0.01 \text{ J}$) and the breaking of the ampoule ($0.09 \text{ J}$) were combined to give a total correction of $0.08 \text{ J}$ to the enthalpy of the reaction. Division by the mass of sample gave the specific enthalpy of reaction, $\Delta_rH_m/M$. The average of a statistically significant number of experiments yielded the values for the specific enthalpies of reaction of stilbite and gibbsite (Table 2).

To derive the enthalpy of formation of stilbite, a set of balanced equations was formulated. This thermochemical or Hess cycle was keyed to the value for the enthalpy of reaction for 0.1 g of silicalite with 100 cm$^3$ of 24.4 mass percent HF (Johnson et al., 1987). Table 3 shows the reactions and their enthalpy values used in the present work. The molar enthalpies of reactions 2 and 6 are based on the mean specific enthalpies in Table 2. For this conversion the molar masses of stilbite and gibbsite were taken to be 714.605 and 78.0034 g·mol$^{-1}$, respectively, based on the 1979 atomic weights (Holden, 1980). Using Hess’ law the enthalpy of formation ($\Delta_rH_m^0$) was derived as shown in Table 3, equation 15. The uncertainty of the ($\Delta_rH_m^0$) value reported for stilbite was the square root of the sum of the squared uncertainties for each reaction.
<table>
<thead>
<tr>
<th>M/s</th>
<th>$\varepsilon$(calor)/(J K$^{-1}$)</th>
<th>$\Delta Q_0/\Delta_0$</th>
<th>$\varepsilon$(calor)/(−$\Delta Q_0$)</th>
<th>$\Delta H_{expt}$/J</th>
<th>$\Delta H_{m}/M$/J g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17503</td>
<td>403.76</td>
<td>0.86535</td>
<td>−349.39</td>
<td>0.08</td>
<td>−1995.7</td>
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<td>0.17462</td>
<td>403.36</td>
<td>0.86481</td>
<td>−348.83</td>
<td>0.08</td>
<td>−1997.2</td>
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<td>0.17463</td>
<td>403.32</td>
<td>0.86359</td>
<td>−348.30</td>
<td>0.08</td>
<td>−1994.0</td>
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<tr>
<td>0.17462</td>
<td>403.46</td>
<td>0.86474</td>
<td>−348.89</td>
<td>0.08</td>
<td>−1997.5</td>
</tr>
<tr>
<td>0.17437</td>
<td>403.03</td>
<td>0.86479</td>
<td>−348.54</td>
<td>0.08</td>
<td>−1998.4</td>
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<tr>
<td>0.17452</td>
<td>401.67</td>
<td>0.86715</td>
<td>−348.31</td>
<td>0.08</td>
<td>−1995.3</td>
</tr>
<tr>
<td>0.17423</td>
<td>401.29</td>
<td>0.86848</td>
<td>−348.51</td>
<td>0.08</td>
<td>−1999.8</td>
</tr>
</tbody>
</table>

Average $\Delta_r H_m/M = -1996.8 \pm 0.7$ J g$^{-1}$

Stilbite, $\text{Ca}_{1.019}\text{Na}_{0.116}\text{K}_{0.006}\text{Al}_{2.180}\text{Si}_{6.820}\text{O}_{18} \cdot 7.33\text{H}_2\text{O}$

Gibbsite, $\text{Al(OH)}_3$

<table>
<thead>
<tr>
<th>M/s</th>
<th>$\varepsilon$(calor)/(J K$^{-1}$)</th>
<th>$\Delta Q_0/\Delta_0$</th>
<th>$\varepsilon$(calor)/(−$\Delta Q_0$)</th>
<th>$\Delta H_{expt}$/J</th>
<th>$\Delta H_{m}/M$/J g$^{-1}$</th>
</tr>
</thead>
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<tr>
<td>0.04138</td>
<td>403.90</td>
<td>0.21927</td>
<td>−88.39</td>
<td>0.07</td>
<td>−2134.0</td>
</tr>
<tr>
<td>0.04172</td>
<td>401.93</td>
<td>0.22184</td>
<td>−89.16</td>
<td>0.07</td>
<td>−2135.3</td>
</tr>
<tr>
<td>0.04168</td>
<td>402.81</td>
<td>0.22076</td>
<td>−88.92</td>
<td>0.07</td>
<td>−2131.6</td>
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<tr>
<td>0.04175</td>
<td>403.07</td>
<td>0.22204</td>
<td>−89.50</td>
<td>0.07</td>
<td>−2141.8</td>
</tr>
<tr>
<td>0.04162</td>
<td>402.46</td>
<td>0.22202</td>
<td>−89.35</td>
<td>0.07</td>
<td>−2145.0</td>
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</tbody>
</table>
Table 2—Continued

<table>
<thead>
<tr>
<th>M</th>
<th>ε(calor)</th>
<th>Δθ_c</th>
<th>ε(calor)(−Δθ_c)</th>
<th>ΔH_corr</th>
<th>ΔrH_m/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>g</td>
<td>J·K⁻¹</td>
<td>K</td>
<td>J</td>
<td>J</td>
<td>J·g⁻¹</td>
</tr>
<tr>
<td>0.04162</td>
<td>403.53</td>
<td>0.22140</td>
<td>−89.34</td>
<td>0.07</td>
<td>−2144.7</td>
</tr>
<tr>
<td>0.04157</td>
<td>403.02</td>
<td>0.22137</td>
<td>−89.22</td>
<td>0.07</td>
<td>−2144.3</td>
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<tr>
<td>0.04158</td>
<td>402.46</td>
<td>0.22038</td>
<td>−88.62</td>
<td>0.07</td>
<td>−2131.2</td>
</tr>
</tbody>
</table>

Average ΔrH_m/M = −2138.5±4.2 J·g⁻¹

* The column headings are M, the mass of the sample reacted; ε(calor), the mean energy equivalent of the calorimetric system before and after the experiment; Δθ_c, the temperature change of the calorimeter corrected for heat exchange with the environment; ΔH_corr, the combined correction for the thermal effects of opening the ampoule and of vaporizing the solvent into the free volume of the ampoule; and ΔrH_m/M, the specific enthalpy of reaction.

† The uncertainty is the standard deviation of the mean.

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## Table 3

**Thermochemical Cycle Used to Derive the Standard Enthalpy of Formation of Stilbite at 298.15 K**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta_H^\circ \text{kJ·mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 6.820 SiO(_2) (silicalite) + 5417.67HF-18640.63 H(_2)O (\rightarrow) ([A])</td>
<td>(-987.54\pm0.68^a)</td>
</tr>
<tr>
<td>2. 2.180 Al(OH)(_3) (cr) + ([A]) (\rightarrow) ([B])</td>
<td>(-363.65\pm0.72^b)</td>
</tr>
<tr>
<td>3. 0.136 NaF(cr) + ([B]) (\rightarrow) ([C])</td>
<td>(-0.66\pm0.05^c)</td>
</tr>
<tr>
<td>4. 0.006 KF(cr) + ([C]) (\rightarrow) ([D])</td>
<td>(-0.17\pm0.01^c)</td>
</tr>
<tr>
<td>5. 1.019 CaF(_2) (cr) + ([D]) (\rightarrow) ([E])</td>
<td>(-0.00\pm0.41)</td>
</tr>
<tr>
<td>6. ([E]) (\rightarrow) Ca(<em>{1.019}) Na(</em>{0.136}) K(<em>{0.006}) Al(</em>{2.180}) Si(<em>{6.820}) O(</em>{18}) · 7.33 H(_2)O + 5419.85HF-18635.48 H(_2)O</td>
<td>(1425.85\pm1.00^b)</td>
</tr>
<tr>
<td>7. 5417.67HF-18627.98H(_2)O + 12.65H(_2)O(l) (\rightarrow) 5417.67HF-18640.63H(_2)O</td>
<td>(-5.26\pm0.03^d)</td>
</tr>
<tr>
<td>8. 2.180HF·7.50H(_2)O (\rightarrow) 1.090H(_2)O(g) + 1.090F(_2) (g) + 7.50H(_2)O(l)</td>
<td>(699.67\pm1.42^d,e)</td>
</tr>
<tr>
<td>9. 5.15H(_2)O(g) + 2.575O(_2) (g) (\rightarrow) 5.15H(_2)O(l)</td>
<td>(-1472.02\pm0.22^e)</td>
</tr>
<tr>
<td>10. 6.820Si(cr) + 6.820O(_2) (g) (\rightarrow) 6.820SiO(_2) (silicalite)</td>
<td>(-6173.46\pm5.73^a)</td>
</tr>
<tr>
<td>11. 2.180Al(cr) + 3.27O(_2) (g) + 3.27H(_2) (g) (\rightarrow) 2.180Al(OH)(_3) (cr)</td>
<td>(-2822.93\pm2.55^f)</td>
</tr>
<tr>
<td>12. 0.136Na(cr) + 0.068F(_2) (g) (\rightarrow) 0.006NaF(cr)</td>
<td>(-78.41\pm0.09^g)</td>
</tr>
<tr>
<td>13. 0.006K(cr) + 0.003F(_2) (g) (\rightarrow) 0.006KF(cr)</td>
<td>(-3.42\pm0.00^g)</td>
</tr>
<tr>
<td>14. 1.019Ca(cr) + 1.019F(_2) (g) (\rightarrow) 1.019CaF(_2) (cr)</td>
<td>(-1252.62\pm0.43^g)</td>
</tr>
<tr>
<td>15. 1.019Ca(cr) + 0.006K(cr) + 0.136Na(cr) + 2.180Al(cr) + 6.820Si(cr) + 7.33H(_2)O(g) + 12.665O(_2) (g) (\rightarrow) Stilbite</td>
<td>(-11034.6\pm6.6^h)</td>
</tr>
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</table>
Table 3—Continued

<table>
<thead>
<tr>
<th>Formula</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A] = 6.820H₂SiF₆·5376.75HF·18654.27 H₂O</td>
<td></td>
</tr>
<tr>
<td>[B] = 6.820H₂SiF₆·2.180AlF₃·5370.21HF·18660.81 H₂O</td>
<td></td>
</tr>
<tr>
<td>[C] = 0.136NaF·6.820H₂SiF₆·AlF₃·5370.21HF·18660.81 H₂O</td>
<td></td>
</tr>
<tr>
<td>[D] = 0.006KF·0.136NaF·6.820H₂SiF₆·AlF₃·5370.21HF·18660.81 H₂O</td>
<td></td>
</tr>
<tr>
<td>[E] = 1.019CaF₂·0.006KF·0.136NaF·6.820H₂SiF₆·AlF₃·5370.21HF·18660.81 H₂O</td>
<td></td>
</tr>
</tbody>
</table>


*bFrom Table 2.*

*cJohnson et al. (1985).*

*dJohnson et al., (1973).*

*eCODATA (1978).*

*fJohnson et al., (unpublished results).*

*gParker et al., (1976).*

*hΔfH°ₘ (stilbite).*
CHAPTER III

HEAT CAPACITIES OF STILBITE FROM 5 TO 350 K

In order to derive the Gibbs free energy of stilbite as a function of tempera­
ture it was necessary to determine its standard entropy as a function of temper­
ature. By accurately measuring the incremental heat capacities from 5 to 350 K
and by using an estimate for \( S^0(5 \text{ K}) - S^0(0) \), the entropy from 0 to 350 K was
derived from the relationship:

\[
S^0(T) - S^0(0) = \int_0^T \frac{C_{p,m}}{T} \, dT
\]

where \( C_{p,m} \) is the molar heat capacity.

The heat capacity measurements were made with an aneroid-type adiabatic
calorimeter (Westrum et al., 1968). The term adiabatic refers to the method
of minimizing exchange of heat between the calorimeter and its surroundings.
The precise measurement of the electrical energy \( (Q) \) introduced and resultant
temperature rise \( (\Delta T) \) was used to calculate an apparent heat capacity from the
formula: \( C_{\text{app}} = Q / \Delta T \). Further analysis, described below, allows the derivation
of \( C_{p,m} \).

Apparatus

The equipment involved in a heat capacity measurement addressed the fol­
lowing tasks:
1. Adherence of the calorimeter to adiabatic conditions within experimental precision.

2. Introduction of a precise amount of energy to the calorimeter to produce a temperature rise.

3. Accurate measurement of the temperature rise.

A detailed cross section of the cryostat assembly is shown in Figure 5. The entire internal apparatus hangs by nylon cords and metal fittings from a cover plate which can be hoisted away from the brass vacuum jacket. This configuration allows access to the calorimeter for loading purposes while reducing the number of thermal pathways from the cryostat to the exterior. The calorimeter is suspended by a nylon cord via a spring to a windlass. The cord serves to position the calorimeter. Nylon was chosen to minimize heat transfer to or from the calorimeter. Suspended above the calorimeter are two coolant tanks. The upper tank serves as the bulk coolant of the cryostat and is always filled with liquid nitrogen. The lower tank provides the operating temperature range for the calorimeter. It can be filled with liquid nitrogen for measurements between 80 to 350 K or with liquid helium for measurements from 80 K down to 4 K. The adiabatic shields that surround the calorimeter consists of a resistance-wire-wound hollow copper cylinder with two lids, the bottom of which is removable. Between the lower tank and the calorimeter is a wire coil designated as RING. This coil can be heated and acts to thermally isolate the adiabatic shields from the lower refrigerant can. Access to the calorimeter, after it is withdrawn from the brass vacuum jacket, is accomplished by removing the radiation shields and the bottom adiabatic shield (BASH) and lowering the calorimeter using the windlass.
Figure 5. Cross-Section of Cryostat (Westrum et al., 1968).
The calorimeter itself (Figure 6) is constructed of oxygen-free, high-conductivity copper. The four-piece construction includes a threaded cone unit, gold gasket, sample holder, and end plate. The internal free volume is 5.976 cm$^3$ at 298.15 K. Along the top edge of the sample well is a stainless steel knife edge which presses tightly against the gold gasket when the calorimeter is sealed. The re-entrant well in the sample holder houses a capsule-type platinum resistance thermometer to measure the temperature of the calorimeter; around this is wound a resistance wire which acts as a heater for the calorimeter. The heater coil and resistance thermometer are coated with Apiezon-T grease for increased thermal contact with the calorimeter. A small amount of grease is placed between the cone unit and gold gasket for the same purpose. Attached to the outside of the calorimeter is a Cr(P)/Au(0.07 Fe) thermocouple that is linked with the middle adiabatic shield (MASH). The adiabatic shields and the calorimeter were maintained at the same temperature. Microvolt signals generated from the thermocouples that monitored the temperature variations between the shields and the calorimeter were amplified and sent to a set of controllers. These controllers responded by sending power, regulated by variacs, to the shields thereby negating the temperature gradient between the shield and calorimeter. In this way, the temperature of the shields and calorimeter were kept to within 0.001 K.

All data was originally taken in the form of voltages as a function of time. The calorimeter temperature was measured using a resistance thermometer (RT) calibrated at the National Bureau of Standards. Its temperature is known accurately as a function of resistance. The resistance of the thermometer was calculated using Ohm's law $R_{RT} = V_{RT} / I_{RT}$. The voltage drop across the resistance thermometer ($V_{RT}$) was measured directly by a calibrated voltmeter working through
Figure 8. Cross-Section of Calorimeter.
a multichannel scanner. The current through the resistance thermometer (I_{RT}) was determined, using Ohm's Law, from the voltage drop \( (V_{R_{st}(RT)}) \) across a standard resistance \( R_{st.(RT)} \) in series with the resistance thermometer; \( I_{RT} = \frac{V_{R_{st}(RT)}}{R_{st.(RT)}} \). The power dissipated in the heater was calculated as \( P_{H} = V_{H} \times I_{H} \). In a manner analogous to the thermometer circuit the voltage drop across the heater \( (V_{H}) \) was measured directly and the current passing through the heater \( (I_{H}) \) was determined from the voltage drop \( (V_{R_{st}(H)}) \) across another standard resistance \( R_{st.(H)} \) in series with the heater: \( I_{H} = \frac{V_{R_{st}(H)}}{R_{st.(H)}} \). Thus, the energy introduced into the system equaled the power dissipated by the heater \( (P_{H}) \) multiplied by the duration of the heating \( (t) \) which was accurately controlled by a calibrated Wang Instruments timer.

Sample Preparation

A number of rather complex steps were involved in preparing a sample for heat capacity measurements. The individual components of the calorimeter assembly were cleaned, rinsed with toluene, and then air dried. This procedure was done to remove any residual sample particles or grease from previous experiments. Each component was then weighed to check for any change in mass due to loss of material. Following a series of weighings and grease additions outlined in Appendix C, the calorimeter was ready for loading of the sample. Since the stilbite that was to be measured was referenced to a 50 per cent relative humidity atmosphere, all loading was done in this environment. A quantity of stilbite was taken from the previously prepared stock and placed along with the calorimeter components inside a glovebag containing an atmosphere maintained at 50 per cent relative humidity. The stilbite was packed tightly into the calorimeter to
provide as large a material-to-calorimeter-mass ratio as possible. A gas-tight seal of the calorimeter was crucial so great care was taken to prevent the adherence of any stilbite grains to the knife edge or threaded portion of the sample holder. A fine-haired brush was used to clean the edge of any contaminants. The cone unit plus the attached gold gasket were then carefully screwed into place.

The calorimeter was set in a specially designed jig to hold it upright and stationary. The jig fit snuggly into a stainless-steel box (also in the glovebag) that could be sealed from the outside atmosphere. The lid of the stainless-steel box had a spring-loaded socket-type device that fit into the recessed head of the calorimeter cone unit. The end of the socket protrudes from the interior of the stainless-steel box through a vacuum seal. By attaching a wrench to the end of the socket, the cone unit could be loosened or tightened while the calorimeter was isolated from the laboratory atmosphere. Attached to the side of the stainless-steel box was a threaded port with a needle valve, the purpose of which was to evacuate the air from the calorimeter and introduce helium as an exchange gas. This was accomplished by attachment of the box to a specially-designed manifold. Under normal circumstances the top of the calorimeter would have been cracked open inside the box and the air evacuated. In this study the water that was loosely occluded in the zeolite structure must remain to maintain a reference water content. Application of a vacuum would have easily removed the water at room temperature. To prevent this, the stainless-steel box with the calorimeter inside was placed in a bath of dry ice and acetone, which lowered the temperature to 195 K. After a reasonable equilibration period, it was assumed that any water in the stilbite was present as ice. The sealed calorimeter in the box was then cracked open from outside and the needle valve opened to draw out
the air. Emphasis was placed on doing this operation slowly (>6 h) since a rapid decrease in pressure would have pulled stilbite grains from the sample well and lodged them between the gold gasket and knife edge thus preventing a gas-tight seal. After evacuation was complete, $4.8 \times 10^{-5}$ mol of helium gas was introduced through the manifold into the calorimeter. The cone unit was then tightened with several turns of a torque wrench done at 5-min intervals with increasing amounts of torque. This allowed the gold gasket to flow onto the knife edge and provide a gas-tight seal. When it was clear that no helium gas was escaping, the calorimeter was weighed to determine the sample mass and then loaded into the cryostat.

**Experimental Procedure**

The platinum resistance thermometer/heater assembly was inserted in the re-entrant well of the calorimeter. Apiezon-T grease was used to enhance the thermal contact between the heater/thermometer and the calorimeter. The calorimeter was then suspended inside the shields from the nylon cord. Connections to the electronic equipment were made for the heater/thermometer unit and the thermocouples that measure the shield temperature. The bottom adiabatic shield and the radiation shields were reattached and the rig was lowered into the brass vacuum jacket. Once the rig was secured, a roughing pump and then an oil-diffusion pump were used to evacuate the system.

To start an experiment, the cryostat was first cooled to 80 K by filling the upper and lower coolant tanks with liquid nitrogen. For runs between 5 and 80 K, liquid helium was used in the lower tank. A set of runs was initiated by separating the calorimeter from the shields and lower tank. The calorimeter
temperature drifted upward due to the conduction and the slight non-adiabatic conditions that exist between the shields and the calorimeter. This temperature increase was tracked using a double potentiometer to measure the resistance of the platinum resistance thermometer. The time and voltages were recorded by a data acquisition computer program known as VIDAR which displayed the information and calculated the temperature drift rate.

After a steady foredrift was established, a thermal event was produced by sending an accurately measured quantity of energy to the heater. The current (as a voltage drop across a standard resistance) and voltage drop across the heater were recorded at preset intervals by the on-line computer. At the cessation of the heating period, an afterdrift was tracked and recorded. The foredrift and afterdrift permit corrections for the non-adiabaticity of the calorimeter to be calculated by the extrapolation of the two slopes to determine the midpoint temperature \(< T >\). During both the heat and drift periods, the temperature difference between the adiabatic shields and the calorimeter was no greater than 0.001 K. The afterdrift for the first run was also the foredrift for the second run. In this way the experiment proceeds, with incremental heats separated by drift periods until the temperature range of interest was covered. The heating increments \(\Delta T\) were 2 K for measurements below 20 K, one-tenth of each preceding midpoint temperature \(< T >\) in the range between 20 and 100 K, and 10 K intervals for measurements above 100 K.

Data Analysis and Results

The data file created by the VIDAR program contained the time, voltages, and a set of integers defining the settings on the electronics during the heat and
drift periods. This file was designated as a CPCALC:DAT file and was edited for subsequent calculations. The editing consisted of inspecting the drift rates and denoting the onset of equilibrium drift, rejecting extraneous readings, and including necessary code lines for running the CPCALC:DAT file on the next program. The next program was named CPCALC whose main function was to calculate the apparent heat capacity of the calorimeter and sample (C_{app}) for the average temperature of the heating increments < T > = \frac{1}{2}(T_1 + T_2). The output of the CPCALC program consisted of two files. The first was a CPCALC:OUT file which listed the time, voltage, temperature, and drift rate during each measurement, and the current and voltage drop across the heater during a heating period. The calculations included in the CPCALC:OUT file were: heater resistance, electrical energy input, voltage corrections, initial temperature, final temperature, drift extrapolation, corrected midpoint temperature, and the heat capacity across the temperature increment. This file was used for inspecting experimental data and checking calculations for errors. The CPCALC program could give certain error messages here, e.g., insufficient drift data or deviation of heater resistance from the measured curve. The second output produced by the CPCALC program was called a CPCALC:LIZ file. This file was an abbreviated version of the CPCALC:OUT file. The tabulated information consisted of the run number, electrical energy introduced, initial temperature, final temperature, average temperature, and the average heat capacity. This data was used to make a preliminary plot of the heat capacity curve and contained the electrical energy, initial temperature and final temperature in a format suitable for subsequent computation. For the region above 15 K the values of C_{app} against T were plotted to check for deviations from the usual sigmoidal curve. For measurements
below 15 K, $C_{app}/T^2$ against $T$ was plotted and should have yielded a straight line since $C_{app}$ is a function of $T^3$ in that temperature range.

Provided that the deviations from the curve were acceptable, the data (collected and edited CPCALC:LIZ files) were ready to be run on the POLYFIT program. This program generated a listing of successively higher order (n) polynomials up to $n = 20$ that fit a curve through the apparent heat capacities and the corresponding average temperatures. Representation of experimental heat capacity as a function of temperature was necessary to permit calculation of a curvature correction; it also gave an early indication of rogue data points or anomalies in the heat capacity of the material. Past investigations have shown that if a single polynomial was used, the degree (n) centers around 50. To lessen the amount of computation, two polynomials were employed. One was calculated from data obtained in the region from 5 to 40 K and the other from the region 20 to 350 K, thus providing a 20 K region of overlap. The polynomial used was the one which had the lowest degree with the most reasonable standard deviation term (SIGGU). To avoid the extreme oscillation of the curve near the edge of the domain of measured points, "tie-down" points were calculated by extrapolation of the previously mentioned plots. These points served to restrict the flexing of the curve at its extremities, thus reducing the introduction of significant errors.

At this stage the temperature dependency of the heat capacity of the calorimeter and sample ($C_{app}$) was well represented. In order to extract the heat capacity of the sample alone, the contribution to $C_{app}$ of the calorimeter was subtracted. This information was obtained from a prior set of experiments using the empty calorimeter. All experimental details for this 'blank' run were identical to those mentioned above except that there was no sample in the calorimeter. The pro-
gram that calculated the actual heat capacity of the pure sample was referred to as CPFIT. The input consisted of the same data used in the POLYFIT programs; information on the heat capacity of the empty calorimeter and the molar amount of stilbite. Corrections were made for any deviations from the measured empty calorimeter with respect to the mass of the calorimeter and the amounts of helium, gold and grease used. A correction, \( \left( \frac{d^2C_p,m}{dT^2} \right) (\Delta T)/24 \), was also made for the curvature that resulted from incremental temperature measurements rather than point measurements.

The two output files from the CPFIT program were designated CPFIT:OUT and CPFIT:LIZ. CPFIT:OUT contained details of the calculation performed on the input low- and high-end data. The polyfit of appropriate degree was regenerated; agreement between this and the prior POLYFIT served as a check on the program. The file also contained the tabulated values for: the run number, apparent heat capacity corrected for curvature, the heat capacity contribution of the calorimeter, and the total emendation. The total emendation was the correction for differences in the amount of helium and mass of calorimeter components used in the 'blank' run versus the 'stilbite' run. The net heat capacity and the empty calorimeter contribution to the apparent heat capacity were also reported; the latter serves as another check on the program since the values given here must agree with those of the empty run. Finally, molar heat capacities for the corresponding midpoint temperatures were listed for the pure sample. The CPFIT:LIZ file contained only the temperatures and molar heat capacities for the low and high end data. These were in a format suitable for further computation. Data in the CPFIT:LIZ file were then examined to determine a reasonable point of crossover in the overlap region and hence yield a unique data set. The
resultant molar heat capacities at the individual temperatures are shown in Table 4 and Figure 7.

New "tie-down" points were obtained using the previously mentioned procedure, and the entire data set was split into two regions, the low end containing data in the 5 to 40 K region, and the high end containing data in the 20 to 350 K region. These data sets were separately run on the POLYFIT program. Polynomials of a degree that optimally represent each data set were then chosen. The overlap region (20 - 40 K) was then inspected to ascertain a temperature at which data representation changes from one polynomial to the other. By examining calculated data from the two polynomials we found a temperature at which the calculated molar heat capacity and its second derivative with respect to temperature showed close agreement between the two polynomials. At this stage in the data manipulation, we had the temperature dependency of the molar heat capacity of the sample represented by two polynomials covering the ranges 5 K to \( T_x \) and \( T_x \) to 350 K where \( T_x \) was the temperature at which we cross over from one polynomial to the other. In this study, the cross-over temperature equaled 25.55 K. Appropriate integrations of these polynomials would yield further thermodynamic information about the sample once we have made some estimation of the behavior of \( C_{p,m} \) in the region below 5 K. The following procedure was used. It was assumed that below 5 K a cubic relation holds between \( C_{p,m} \) and \( T \):

\[
C_{p,m} = AT^3.
\]

A value of the molar heat capacity at, for example, 5 K \([C_{p,m}(5 \text{ K})]\) was either read from the graph or calculated from the fit. Then, using standard thermodynamic relations the estimates were calculated as follows:
Table 4

Experimental Molar Heat Capacities of Stilbite

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<th>T°K</th>
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<th>T°K</th>
<th>C°J K⁻¹mol⁻¹</th>
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<th>C°J K⁻¹mol⁻¹</th>
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Figure 7. Plot of Molar Heat Capacities of Stilbite Against Temperature.
\[ S_m^0(5 \text{ K}) - S_m^0(0) = \int_0^5 \frac{C_{p,m}}{T} dT \]
\[ = \int_0^5 \frac{AT^3}{T} dT = \int_0^5 AT^2 dT \]
\[ = \frac{1}{3} [AT^3]^5_0 = \frac{1}{3} [C_{p,m}]^5_0 \]
\[ = \frac{1}{3} C_{p,m}(5 \text{ K}) \]

Similarly,
\[ H_m^0(5 \text{ K}) - H_m^0(0) = \int_0^5 C_{p,m} dT = \int_0^5 AT^2 dT \]
\[ = \frac{1}{4} T \cdot C_{p,m}(5 \text{ K}) \]

Using these estimates, the program THFNS calculated the thermodynamic functions \( S_m^0(T) - S_m^0(0) \), \( H_m^0(T) - H_m^0(0) \) and \( -[G_m^0(T) - H_m^0(0)]/T \) over the whole temperature range. The inputs for THFNS were the data inputs for the second set of POLYFITS, the corresponding order of the polynomials and their crossover temperature, and the ‘seed’ values of \( S_m^0(5 \text{ K}) - S_m^0(0) \) and \( H_m^0(5 \text{ K}) - H_m^0(0) \) described above. The resultant thermodynamic properties at rounded temperatures are listed in Table 5.
Table 5

Low-Temperature Thermodynamic Properties for Stilbite* ($p^o = 101.325$ kPa)

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Table 5—Continued

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*Molar mass of stilbite was taken to be 714.605 g·mol⁻¹.*
CHAPTER IV

ENTHALPY INCREMENTS RELATIVE TO 298.15 K OF STILBITE
FROM 350 TO 500 K

The accurate determination of high-temperature enthalpy increments for stilbite combined with the standard entropy and enthalpy of formation allowed the calculation of the Gibbs free energy as a function of temperature. The method employed in this part of the investigation was drop calorimetry. In a typical experiment, a sample contained in a capsule of known heat capacity was heated to a predetermined temperature and was then dropped into a copper-block calorimeter at approximately 298.15±0.15 K. The resultant rise in temperature of the calorimeter due to the heat transfer from the capsule + sample provided the necessary information to generate a table of enthalpies at incremental temperatures relative to the enthalpy at 298.15 K, \( H_m^o(T) - H_m^o(298.15 \text{ K}) \).

Apparatus

The drop calorimeter (Fredrickson et al., 1969) assembly consists of the drop mechanism, furnace and copper-block calorimeter (Figure 8). The furnace of the drop calorimeter consists of a four-piece cylindrical molybdenum chamber which surrounds the capsule containing the sample. The chamber is heated by tantalum resistance wires sheathed in alumina and wound vertically about the core. A total of nine stainless steel and molybdenum sheet metal cylinders with increasing diameters form passive radiation shields which sit in a coaxial configuration about
Figure 8. Cross-Section of Drop Calorimeter (Fredrickson et al., 1969).
the molybdenum core. Holes drilled into the core house platinum-platinum/10 per cent rhodium thermocouples. The leads to the thermocouples are sheathed in alumina. The furnace assembly is encased in a 1.3 cm thick stainless steel vacuum jacket that is cooled by water flowing through copper tubing wrapped around its exterior.

Attached to the top of the furnace is a long metal tube which supports the drop mechanism. The drop mechanism consists of a windup motor, metal drop tape, a clutch actuator, eddy current brake, metal bob or drop weight, and the tantalum drop wire. The purpose of this part of the apparatus is to allow repeated heating and dropping of the capsule containing the sample while the whole system is under vacuum or low pressure helium atmosphere (≈ 1 kPa). The capsule was hung from a very straight tantalum wire. The top of the drop wire was connected to a metal bob which was connected to the metal drop tape. Before the heating was begun the windup motor was used to wrap the metal tape onto a pulley thus positioning the capsule at the top of the furnace. After the capsule and furnace were at thermal equilibrium, the clutch actuator was tripped allowing the near free-fall of the capsule + wire. As the metal bob passed by the coil the eddy current brake was activated thus decelerating the capsule so that it gently landed in the copper block calorimeter.

The calorimeter assembly located below the furnace consists of a machined copper block surrounded by a water jacket, and it is attached to the furnace by a flanged acrylic tube connected to the jacket with machine screws. The acrylic tube is separated from the furnace by a pneumatic gate which compresses a section of neoprene tubing to prevent heat flow from furnace to calorimeter. Below the gate is a housing for an optical prism with a reflective coating, which
can be inserted into the drop path. This device allows the inspection of the capsule while it was being heated. A shutter system is located between the copper block and the acrylic tube. This shutter can be closed around the drop wire when the capsule is inside the copper-block calorimeter thus minimizing the heat flow to or from the calorimeter.

The capsule which contained the sample was constructed of (platinum + 10 per cent rhodium) alloy. Figure 9 shows the design of the capsule. The sample was loaded into the capsule through the neck which was then crimped, trimmed and welded shut. The capsule was suspended from the drop wire by an angled piece of tantalum wire attached to the fabricated holders on the capsule.

Sample Preparation

Prior to loading, the capsule was heated in a gas flame until it was glowing red. This procedure burned off any impurities or condensates that may have formed inside the capsule during its fabrication. From this point on, the capsule was handled with cotton gloves to prevent any contamination with skin oils. The empty capsule was allowed to cool to the balance temperature and was then weighed. A sample from the stilbite stock was then transferred to the capsule through the loading tube using a stainless steel funnel rinsed with acetone and air dried. The stilbite was packed tightly by tapping the bottom of the capsule. It was loaded to a level just below the top of the capsule. The capsule + material were then returned to the desiccator to equilibrate overnight in a 50 per cent relative humidity atmosphere. Afterwards, the loading tube was cleaned with a pipe brush to remove residual material, weighed (see Appendix D, sec. 1) and then crimped shut using flatnose pliers. The excess tubing was cut along the
Figure 9. Cross-Section of Capsule Used in Drop Calorimeter.
crimped portion with shears to a height that would allow the free movement of the support wire that was later attached to the tabs on the capsule. The capsule and sheared portion were weighed individually. The crimped portion of the tube was then placed in a portable vise that acted as a heat sink to prevent the volatilization of any water while the capsule was being welded shut. The welded seal along the crimped tube was inspected with a binocular microscope. A final weighing was made. The attachment of the tantalum support wire completed the preparation procedure and the capsule + sample were now ready for loading into the drop calorimeter.

Experimental Procedure

To begin an experiment, the acrylic tube between the copper block and the optical viewing port was detached. The copper block calorimeter was then separated from the furnace assembly by lowering the adjustable stand on which it rested. With the wire in the drop position the capsule was placed on a hook formed by the upturned end of the drop wire. It was crucial that the total length of the wire and suspended capsule correspond to a dropped position that would place the capsule exactly inside the well of the calorimeter. This was done to ensure the maximum heat transfer to the calorimeter and protect the drop wire from kinking. The capsule was then raised into the furnace by wrapping the metal drop tape around the pulley connected to the windup motor. In the raised position, the capsule was inside the top of the molybdenum core furnace.

A test drop was made to ensure that the fall of the capsule was unimpeded. The eddy current brake was turned on and the clutch was tripped. This signalled the actuator to release the pulley and the capsule fell freely. Once the drop was
satisfactory, the capsule was prepared for heating. The capsule was placed in the furnace using the windup motor. The heater current and voltage were set on the current supply and variacs, respectively. The gate to the furnace was closed and the copper block was raised and reconnected. The system was pumped down using a roughing pump and an oil diffusion pump. To facilitate the transfer of heat from the capsule to the copper block, 1.33 kPa of helium gas was leaked into the calorimeter through its vacuum system. After a sufficient heating period (>3 h), the furnace temperature was measured. A Leeds and Northrop null detector in conjunction with a generated ice-point reference and potentiometer were used to read the voltages generated by the three thermocouples inside the furnace. The average reading was used to calculate the temperature and ensure that the capsule and furnace were at equilibrium. During the heating period, the copper block calorimeter was cooled to below 298.15 K. This was done by circulating cold nitrogen around the outside of the copper block. The temperature of the calorimeter drifted upwards and was recorded every 10 s by a quartz-crystal thermometer housed in a re-entrant well of the copper block. After an equilibrium foredrift was established in the calorimeter, the gate and shutter were opened. The clutch was tripped and the capsule fell as the metal tape unwound due to the weight of the metal bob. Once the capsule reached the top of the calorimeter, it was decelerated by the braking motion of the metal bob as it passed through the coil. The gate and shutter were then quickly closed to minimize the heat leak between the furnace and calorimeter. Meanwhile, the mini-computer automatically recorded the rise in temperature of the copper block. After an equilibrium afterdrift was established, the experiment was terminated. The gate and shutter were opened and the capsule was returned to the furnace. The heater current
and voltage were reset for the next temperature. This procedure was repeated in increments of 50 K followed by a 25 K decrease through the range from 350 to 500 K. This pattern of data acquisition checks the lower temperature points. A marked difference from a previously measured point could have indicated a phase change in the material, thermal decomposition, or a leak in the capsule. The experiment was terminated at 500 K because the capsule began to deform due to the high water vapor pressure built up inside it.

Data Analysis and Results

The energy equivalent, \( e(\text{calor}) \), of the calorimeter was established from previous electrical calibrations during past investigations on zeolites (Johnson et al., 1982-85). The temperature rise \((\Delta \theta_c)\) of the calorimeter was calculated using the same procedure for the extrapolation of the fore- and afterdrift as described for the reaction calorimeter in Chapter 2. Thus, the amount of energy released by the capsule and sample into the calorimeter was: \( Q = -e(\text{calor}) \times (\Delta \theta_c) \). The standard enthalpy at \( T \) relative to 298.15 K was determined by subtracting enthalpy contributions of the capsule and the air inside it, and enthalpy of condensation of the water released from the zeolite inside the capsule (see Appendix D, sec. 2) from \( Q \). A correction for the deviation of the copper-block calorimeter temperature from 298.15 K was also made. The results of the nine experimental runs were listed in Table 6.

The enthalpy increments for stilbite, including those between 298.15 K and 350 K from the low temperature study, were fitted over the range from 298.15 to 500 K by the method of least squares. The following equation gave the best fit:
### Table 6

**Drop-Calorimetric Results for Stilbite**

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>( T ) K</th>
<th>( \Delta \theta ) K</th>
<th>( \theta_{(calor)} ) J K(^{-1})</th>
<th>( \theta_{(calor)}(\Delta \theta) ) J</th>
<th>( \Delta H_{(capsule)} ) J</th>
<th>( \Delta H_{(air)} ) J</th>
<th>( \Delta H_{(H_2O)} ) J</th>
<th>( \Delta H_{(final T)} ) J</th>
<th>( H^0(T) - H^0(298.15K) ) J mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>349.85</td>
<td>0.14295</td>
<td>4376.86</td>
<td>625.67</td>
<td>-144.62</td>
<td>-0.13</td>
<td>-1.20</td>
<td>0.17</td>
<td>43466</td>
</tr>
<tr>
<td>2</td>
<td>376.36</td>
<td>0.22008</td>
<td>4376.69</td>
<td>963.24</td>
<td>-219.00</td>
<td>-0.25</td>
<td>-4.01</td>
<td>0.30</td>
<td>67035</td>
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<tr>
<td>3</td>
<td>399.78</td>
<td>0.29081</td>
<td>4376.77</td>
<td>1272.79</td>
<td>-285.01</td>
<td>-0.19</td>
<td>-7.31</td>
<td>0.07</td>
<td>88810</td>
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<tr>
<td>4</td>
<td>400.93</td>
<td>0.29395</td>
<td>4376.60</td>
<td>1286.53</td>
<td>-288.28</td>
<td>-0.31</td>
<td>-7.31</td>
<td>0.00</td>
<td>89724</td>
</tr>
<tr>
<td>5</td>
<td>425.66</td>
<td>0.37160</td>
<td>4376.51</td>
<td>1626.34</td>
<td>-358.44</td>
<td>-0.37</td>
<td>-16.33</td>
<td>0.55</td>
<td>113333</td>
</tr>
<tr>
<td>6</td>
<td>425.82</td>
<td>0.37139</td>
<td>4376.69</td>
<td>1625.43</td>
<td>-358.90</td>
<td>-0.25</td>
<td>-16.33</td>
<td>-0.08</td>
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<tr>
<td>7</td>
<td>450.19</td>
<td>0.44972</td>
<td>4376.64</td>
<td>1968.20</td>
<td>-428.60</td>
<td>-0.43</td>
<td>-28.73</td>
<td>0.37</td>
<td>136863</td>
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<tr>
<td>8</td>
<td>475.55</td>
<td>0.53325</td>
<td>4376.33</td>
<td>2333.73</td>
<td>-501.87</td>
<td>-0.50</td>
<td>-47.16</td>
<td>0.59</td>
<td>161689</td>
</tr>
</tbody>
</table>

*The entries in the table are: \( T \), the temperature of the furnace and sample; \( \Delta \theta \), the change in temperature of the calorimeter corrected for heat exchange with the surroundings; \( \theta_{(calor)} \), energy equivalent of the calorimeter; \( \theta_{(calor)}(\Delta \theta) \), the energy absorbed by the calorimetric system; \( \Delta H_{(capsule)} \), the enthalpy contribution due to the capsule; \( \Delta H_{(air)} \), the correction for the enthalpy of air in the capsule; \( \Delta H_{(H_2O)} \), the correction applied for the condensation of the water vapor in the capsule; \( \Delta H_{(final T)} \), the correction for the difference between the final temperature of the experiment and 298.15 K; and \( H^0(T) - H^0(298.15K) \), the standard enthalpy at temperature \( T \) relative to 298.15 K. Moles of stilbite used was .0110406 mol.
\[ H_m^o(T) - H_m^o(298.15 \text{ K}) = -181021.58 + 442.9607812 \ (T/\text{K}) + 0.308669217 \ (T/\text{K})^2 + 0.001202851867 \ (T/\text{K})^3 - 0.0000013 \ (T/\text{K})^4 \]

The thermodynamic functions for stilbite were calculated in 20 K intervals over the high temperature region investigated (Table 7). The root-mean-square deviation of the results from the above equation was 0.14 per cent.
<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta H^o(T)$, J/mol</th>
<th>$\Delta H^o(T)$, J/mol</th>
<th>$\Delta H^o(T)$, J/mol</th>
<th>$\Delta H^o(T)$, J/mol</th>
<th>$\Delta H^o(T)$, J/mol</th>
<th>$\Delta H^o(T)$, J/mol</th>
<th>$\Delta H^o(T)$, J/mol</th>
<th>$\Delta H^o(T)$, J/mol</th>
<th>$\Delta H^o(T)$, J/mol</th>
<th>$\Delta H^o(T)$, J/mol</th>
<th>$\Delta H^o(T)$, J/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>806.73</td>
<td>806.54</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>300</td>
<td>811.26</td>
<td>805.56</td>
<td>810.55</td>
<td>810.55</td>
<td>810.55</td>
<td>810.55</td>
<td>810.55</td>
<td>810.55</td>
<td>810.55</td>
<td>810.55</td>
<td>810.55</td>
</tr>
<tr>
<td>320</td>
<td>838.09</td>
<td>807.54</td>
<td>863.77</td>
<td>915.36</td>
<td>965.42</td>
<td>1014.05</td>
<td>1061.30</td>
<td>1107.21</td>
<td>1151.79</td>
<td>1195.05</td>
<td>1236.98</td>
</tr>
<tr>
<td>400</td>
<td>931.45</td>
<td>838.92</td>
<td>963.06</td>
<td>1014.05</td>
<td>1061.30</td>
<td>1107.21</td>
<td>1151.79</td>
<td>1195.05</td>
<td>1236.98</td>
<td>1280.61</td>
<td>1325.98</td>
</tr>
<tr>
<td>500</td>
<td>987.88</td>
<td>905.58</td>
<td>1277.57</td>
<td>1859.98</td>
<td>1501.98</td>
<td>1053.98</td>
<td>605.98</td>
<td>1501.98</td>
<td>1859.98</td>
<td>1501.98</td>
<td>1277.57</td>
</tr>
</tbody>
</table>
CHAPTER V

DISCUSSION OF RESULTS AND CONCLUSION

Comparison With Estimation Method

Due to the time-consuming nature of calorimetric measurements several methods (Chen, 1975; La Iglesia & Aznar, 1986; Nriagu, 1975; Tardy & Garrels, 1974) have been devised to estimate the Gibbs free energies of formation ($\Delta_f G_m^0$) of zeolites and layer silicates. La Iglesia and Aznar (1986) have developed a method specifically for zeolites based on the assumption that $\Delta_f G_m^0$ is a function of chemical composition only. Their method estimates the $\Delta_f G_m^0$ of the zeolite from the $\Delta_f G_m^0$ of the constituent oxides. They calculated the $\Delta_f G_m^0$ contribution of each oxide based on previous experimental values reported for zeolites. An estimate of the $\Delta_f G_m^0$ of the stilbite is shown in Table 8. A comparison of the value derived from the calorimetric measurements with the estimate shows a difference of 49 kJ·mol$^{-1}$.

A major concern with this method is the manner in which the Gibbs free energy contribution of the zeolitic water is accounted for. This method uses a single molar value to represent the contribution of water to the overall Gibbs free energy of the mineral. A number of studies (Hemingway & Robie, 1984; Johnson et al., 1985; Knowlton, White, & McKague, 1981) have shown that the thermochemical properties of water vary not only among structurally different zeolites but within the individual zeolite itself. The complex nature of the zeolitic water does not lend itself to the simplification presented in this method as
illustrated by the large deviation of the calculated $\Delta_f G^o_m$ from the experimentally derived value.

**Retrieval of Gibbs Free Energy of Formation of Laumontite**

The presence of laumontite is often taken to indicate low-grade metamorphic conditions; thus, its lower stability limit is of interest (Boles, 1977). In nature, laumontite is associated with stilbite and heulandite. Reversible equilibrium experiments have shown laumontite forming from stilbite (Liou, 1971a) and from heulandite (Cho, 1986) as follows:

$$\text{CaAl}_2\text{Si}_7\text{O}_{18} \cdot 7\text{H}_2\text{O} \rightarrow \text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O} + 3\text{SiO}_2 + 3\text{H}_2\text{O}$$

Stilbite $\rightarrow$ Laumontite $+$ Quartz $+$ Water

$$\text{CaAl}_2\text{Si}_7\text{O}_{18} \cdot 6\text{H}_2\text{O} \rightarrow \text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O} + 3\text{SiO}_2 + 2\text{H}_2\text{O}$$

Heulandite $\rightarrow$ Laumontite $+$ Quartz $+$ Water

In these experiments end-member compositions were assumed. Since thermodynamic data now exists for well-characterized samples of stilbite and heulandite (Johnson et al., 1985) it is possible to calculate values of the $\Delta_f G^o_m$ of laumontite on the basis of the above equations. The method of Helgeson et al. (1978) allows the retrieval of the $\Delta_f G^o_m$ from experimental phase equilibria data. If the above equations are written with the calorimetrically studied compositions of stilbite and heulandite the resulting laumontites would have different compositions because of the variation in the cation content of the initial phases. However, if the Gibbs free energy contributions of the individual cations are approximated by the suggested values of La Iglesia and Aznar (1986) then the laumontite can be
Table 8
Estimated Gibbs Free Energy of Formation of Stilbite*

<table>
<thead>
<tr>
<th>Component</th>
<th>Gibbs Free Energy</th>
<th>% Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO · Al₂O₃</td>
<td>(1.019)(-2312.68)</td>
<td>-2356.6</td>
</tr>
<tr>
<td>Na₂O · Al₂O₃</td>
<td>(0.068)(-2273.06)</td>
<td>-154.6</td>
</tr>
<tr>
<td>K₂O · Al₂O₃</td>
<td>(0.003)(-2331.82)</td>
<td>-6.7</td>
</tr>
<tr>
<td>SiO₂</td>
<td>(6.820)(-855.94)</td>
<td>-5837.5</td>
</tr>
<tr>
<td>H₂O</td>
<td>(7.33)(-237.17)</td>
<td>-1738.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>-10,094</strong></td>
</tr>
</tbody>
</table>

\[
\Delta r G_m^{\circ} (\text{exp.}) \quad \quad \Delta r G_m^{\circ} (\text{calc.}) \quad \% \text{ Deviation}
\]

-10,143.0 ± 6.6 -10,094 ± 25 0.48

adjusted to a single composition. The auxiliary thermodynamic data for quartz and water were taken from Robie, Hemingway, and Fisher (1978) and Helgeson and Kirkham (1974) respectively. The derived values of $\Delta_r G_m^0$ of laumontite were $-6778.93 \text{ kJ} \cdot \text{mol}^{-1}$ for the reaction with stilbite and $-6667.74 \text{ kJ} \cdot \text{mol}^{-1}$ for the reaction with heulandite. The latter value is closer to the value of $-6682.03 \text{ kJ} \cdot \text{mol}^{-1}$ retrieved by Helgeson et al. (1978) based on the phase equilibria reported by Liou (1971b).

There are several factors which could account for the wide discrepancy. Helgeson's retrieval equations work on the assumption that $(\partial \Delta V_r^0/\partial P)_T = (\partial V_{H_{2}O}^0/\partial P)_T$ and $(\partial \Delta V_r^0/\partial T)_P = (\partial V_{H_{2}O}^0/\partial T)_P$, where $V_r^0$ and $V_{H_{2}O}^0$ denote the standard molar volume of reaction and the standard molar volume of water, respectively. This may not adequately represent the thermodynamic behavior of zeolites as a function of pressure since the zeolitic water is less bound by structural constraints and might exhibit abnormally large expansibilities and compressibilities (Helgeson et al., 1978). Another possible cause for the discordant values is the uncertainty of the true compositions of reactants and products in the equilibrium experiments of Liou (1971b) and Cho et al. (1986). The initial composition of the minerals, and the fluid chemistry can drastically alter the equilibrium phase boundaries (Boles & Coombs, 1977). Finally, the effect of Si-Al disorder on the calorimetrically derived third-law entropies has not been calculated. This is due to the lack of Si-Al site occupancy data for the particular samples used in the present study. A rough indication of how much this contribution could be is to use the estimated site occupancies of a less-silicic (Si/Al = 2.50) stilbite (Galli, 1971). Based on these occupancies Ulbrich and Waldbaum (1975) calculated that an additional 38.16 J\cdot K^{-1}\cdot \text{mol}^{-1}$ would need to be incorporated into the
third law entropy for the stilbite investigated by Galli (1971). This value is based on a molecular formula adjusted to 18 framework oxygens.

Conclusion

The calorimetric measurements conducted on this specimen of stilbite have allowed the derivation of its thermodynamic properties up to 500 K. This study provides the first available thermochemical information for a well-characterized sample of stilbite. These derived results are internally consistent with the previously reported thermodynamic values for the zeolites listed in Table 9.

The availability of precise thermodynamic information on well-characterized phases is valuable to those concerned with mineral formation in either low-grade metamorphic, hydrothermally altered, or diagenetic environments. The mechanism by which zeolite formation takes place is still being debated. Recent studies (Dibble & Tiller, 1981; Donahoe & Liou, 1985; Hawkins, 1981) have focused on the kinetic aspects of zeolite growth, especially those phases which are prevalent in diagenetic environments. Parameters which control the formation of zeolites in these environments are believed to be a function of the pH of the solutions from which the zeolites precipitate and the rate of crystal growth. It has been suggested that the Gibbs free energy differences of some zeolite phases are so slight that a number of phases can form from the same solution (Dibble & Tiller, 1981). Investigations into the hydrothermal formation of zeolites have attributed strong influences to $P_{\text{CO}_2}$ and $P_{\text{fluid}}/P_{\text{total}}$ of the system as well as to the $\text{SiO}_2(\text{aq})$ in the fluid (Bird, Schiffman, Elders, Williams, & McDowell, 1984; Giggenbach, 1981). In both of these environments the formation of some zeolites are believed
<table>
<thead>
<tr>
<th>Zeolite</th>
<th>$\Delta_f H_m^O$ / kJ · mol$^{-1}$</th>
<th>$\Delta_f G_m^O$ / kJ · mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stilbite, Ca$<em>{1.019}$Na$</em>{0.135}$K$<em>{0.006}$Al$</em>{2.180}$Si$<em>{6.820}$O$</em>{18}$ · 7.33H$_2$O</td>
<td>-11034.6 ± 6.6$^a$</td>
<td>-10143.0 ± 6.6$^a$</td>
</tr>
<tr>
<td>Analcime, Na$<em>{0.96}$Al$</em>{0.96}$Si$<em>{2.04}$O$</em>{6}$ · H$_2$O</td>
<td>-3305.8 ± 3.3$^b$</td>
<td>-3086.1 ± 3.3$^b$</td>
</tr>
<tr>
<td>Dehydrated Analcime, Na$<em>{0.96}$Al$</em>{0.96}$Si$<em>{2.04}$O$</em>{6}$</td>
<td>-2979.1 ± 3.5$^b$</td>
<td>-2812.6 ± 3.5$^b$</td>
</tr>
<tr>
<td>Natrolite, Na$_2$Al$_2$Si$<em>3$O$</em>{10}$ · 2H$_2$O</td>
<td>-5732.7 ± 5.0$^c$</td>
<td>-5330.7 ± 5.0$^c$</td>
</tr>
<tr>
<td>Scolecite, CaAl$_2$Si$<em>3$O$</em>{10}$ · 3H$_2$O</td>
<td>-6063.1 ± 5.0$^c$</td>
<td>-5612.0 ± 5.0$^c$</td>
</tr>
<tr>
<td>Mesolite, Na$<em>{0.676}$Ca$</em>{0.657}$Al$<em>{1.990}$Si$</em>{3.01}$O$_{10}$ · 2.647H$_2$O</td>
<td>-5961.2 ± 5.4$^c$</td>
<td>-5527.3 ± 5.4$^c$</td>
</tr>
<tr>
<td>Heulandite, Ba$<em>{0.065}$Sr$</em>{0.175}$Ca$<em>{0.585}$K$</em>{0.132}$Na$<em>{0.383}$Al$</em>{2.165}$Si$<em>{6.835}$O$</em>{18}$ · 6.00H$_2$O</td>
<td>-10518.9 ± 10.2$^d$</td>
<td>-9703.5 ± 10.2$^d$</td>
</tr>
<tr>
<td>Mordenite, Ca$<em>{0.289}$Na$</em>{0.361}$Al$<em>{0.940}$Si$</em>{5.060}$O$_{12}$ · 3.468H$_2$O</td>
<td>-6756.2 ± 4.5$^c$</td>
<td>-6247.6 ± 4.5$^c$</td>
</tr>
<tr>
<td>Dehydrated Mordenite, Ca$<em>{0.289}$Na$</em>{0.361}$Al$<em>{0.940}$Si$</em>{5.060}$O$_{12}$</td>
<td>-5661.8 ± 4.6$^c$</td>
<td>-5338.6 ± 4.6$^c$</td>
</tr>
</tbody>
</table>

$^a$ This study.

$^b$ Johnson et al. (1982).

$^c$ Johnson et al. (1983).

$^d$ Johnson et al. (1985).

to represent metastable intermediate phases resulting from favorable growth kinetics over the more stable phases. The reaction scheme follows the Ostwald step rule which states that the stability of the chemical system is attained through a series of irreversible reactions progressing toward a more thermodynamically stable state.

Many of the mineral assemblages found in active geothermal areas are similar to phases reported in low grade metamorphic and contact metamorphic rocks. The implications of these previously mentioned studies and how they pertain to zeolite formation in metamorphic rocks is hampered by the lack of reliable thermodynamic data for the phases present in these environments. The delineation of petrogenetic grids in these low P-T regimes depends on the ability to differentiate between metastable phases and those which comprise equilibrium assemblages. The determination of the thermodynamic properties of the phases involved affords this information.

As illustrated in the previous sections reliance on estimation methods and phase equilibria data can lead to inconsistent thermochemical information. However, problems remain in the application of calorimetrically derived data. A number of important zeolite phases remain to be investigated (e.g. laumontite, chabazite, wairakite). More importantly, a better understanding of the effects of variations in zeolitic water, cation content, and Si-Al disorder on the thermodynamic properties of zeolites is necessary in order to correct for the variable compositions which can occur in zeolites. Thermodynamic studies of synthetic zeolites with systematic variations in Si-Al ratios and cations are ideally suited for such an investigation.
APPENDIX A

DEFINITION OF SYMBOLS

Å  A unit of length equal $10^{-10}$ meters.
T  Temperature in kelvins.
K  Kelvin, the unit of temperature.
J  Joule, the unit of energy.
mol Amount of a substance of a system that contains as many elementary entities as there are atoms in 0.012 kilograms of carbon 12.
° Superscript indicates that the substance is in its standard state.
po The standard pressure which is equal to 101325 pascals.
cc Substance in crystalline state.
aq Substance in aqueous state.
l Substance in liquid state.
$\Delta_r H_m^0$ Molar enthalpy of formation from the elements in their standard state.
$\Delta_r H_m$ Molar enthalpy of reaction.
$S^o(T) - S^o(0)$ Entropy at temperature $T$ relative to 0 K.
$S^o(T) - S^o(298.15)$ Entropy at temperature $T$ relative to 298.15 K.
$C_{p,m}^0$ Molar heat capacity at constant pressure.
$C_{app}$ Apparent heat capacity.
\[ H_m^o(T) - H_m^o(0) \] Enthalpy at temperature \( T \) relative to 0 K.

\[ H_m^o(T) - H_m^o(298.15) \] Enthalpy at temperature \( T \) relative to 298.15 K.

\[-\frac{\{G_m^o(T) - H_m^o(0)\}}{T} \] Gibbs energy function.

\[ \Delta_f G_m^o \] Gibbs free energy of formation from the elements in their standard states.
APPENDIX B

CALCULATIONS PERTAINING TO ENTHALPY OF REACTION MEASUREMENTS FOR STILBITE AND GIBBSITE

1. Estimation of calibration starting temperature, bath temperature, and heating time.

The recent investigation of heulandite (Johnson et al., 1985) reported an enthalpy of reaction ($\Delta H/M$) of $2032.2 \pm 0.6$ J·g$^{-1}$. Since stilbite is structurally similar, $\Delta H/M$ is expected to deviate only slightly from that of heulandite. Based on this information, the amount of energy released from the reaction of $\sim 0.174$ g of stilbite in 24.4 mass per cent HF was estimated to be:

$$(0.174 \text{ g})(2032.2 \text{ J} \cdot \text{g}^{-1}) = 353.6 \text{ J}$$

The energy equivalent of the reaction vessel was approximately 401.0 J·K$^{-1}$ so the expected temperature rise for the reaction was:

$$\frac{353.6 \text{ J}}{401.0 \text{ J} \cdot \text{K}^{-1}} = 0.885 \text{ K}$$

Since there was a drift in the temperature of the reaction vessel, it was necessary to cool the reaction vessel below the desired 298.15 K mean temperature. The starting temperature was calculated as:

$$298.15 \text{ K} - \frac{1}{2}(\text{expected temperature rise})$$

$$\therefore \text{starting temperature} = 298.15 \text{ K} - 0.44 \text{ K} = 297.71 \text{ K}$$
The bath temperature was set so that it approximated the reaction vessel temperature at the end of an experiment. This was simply calculated as:

\[
298.15 \text{ K} + \frac{1}{2}(\text{expected temperature rise})
\]

\[
\therefore \text{bath temperature} = 298.15 \text{ K} + 0.44 \text{ K} = 298.59 \text{ K}
\]

To calculate the duration of the calibration heating period, the following formula was used:

\[
t = \frac{\Delta H_{\text{elec}}}{(I^2)(R_{\text{std}} \times V_h - \frac{1}{2}(R_l))}
\]

where \( t = \) time

\( \Delta H_{\text{elec}} = \) calibration energy

\( I = \) current

\( R_{\text{std}} = \) standard resistance

\( V_h = \) voltage drop across heater

\( R_l = \) resistance of heater leads

So in our example:

\[
t = \frac{353.6 \text{ J}}{(0.1 \text{ A})^2[(50.0 \text{ }\Omega \times 1.006201) - \frac{1}{2}(0.0165 \text{ }\Omega)]}
\]

\[
t = 703 \text{ s}
\]

and the calorimeter calibration heater was run for 700 s.

2. Calculation of the amount of stilbite and gibbsite used.

Since the thermochemical cycle was based on the enthalpy of reaction for 0.1 g silicalite \((\text{SiO}_2)\) in 24.4 mass per cent HF, the amount of stilbite desired was
that which contained 0.1 g SiO$_2$ or 0.046743 g Si. The formula for the sample of stilbite is:

$$\text{Ca}_{1.019}\text{Na}_{0.136}\text{K}_{0.008}\text{Al}_{2.180}\text{Si}_{6.820}\text{O}_{18} \cdot 7.33\text{H}_2\text{O}$$

$$\text{MW} = 714.605 \text{ g \cdot mol}^{-1}$$

From the formula it was calculated that the stilbite contained 26.8243 per cent Si per unit formula. To find the desired amount ($x$):

$$(.268243)(x) = 0.46743$$

$$x = .17426 \text{ g stilbite or } 2.44034 \times 10^{-4} \text{ mol}$$

Aluminum also exists in significant amounts in the formula. The amount of gibbsite needed was:

$$(2.180)(2.44034 \times 10^{-4}\text{ mol}) = 5.3199 \times 10^{-4}\text{ mol} \text{ gibbsite}$$

$$\text{MW gibbsite} = 78.0034 \text{ g \cdot mol}^{-1}$$

$$\text{Gram amount} = (5.3199 \times 10^{-4}\text{ mol})(78.0034 \text{ g \cdot mol}^{-1})$$

$$= 0.0415 \text{ g of gibbsite}$$
APPENDIX C

WEIGHINGS AND CORRECTIONS FOR
LOW-TEMPERATURE CALORIMETER

The following series of measurements were necessary to correctly calculate
the heat capacity contribution of the empty calorimeter:

• Before unloading:
  — Weight of sealed calorimeter + previous sample + thermometer grease
  — Weight of sealed calorimeter + previous sample

• After unloading calorimeter in glovebox and cleaning:
  — Weight of calorimeter without cone unit
  — Weight of cone
  — Weight of gold gasket
  — Weight of gold gasket with grease
  — Weight of cone + gold gasket with grease
  — Weight of cone assembly with graphite brushed on threads

• After loading calorimeter in glovebox:
  — Weight of sealed calorimeter
  — Weight of sealed calorimeter + thermometer grease

The following procedure was followed for the aforementioned measurements.
The determination of the mass of the empty calorimeter is provided as an exam­
ple.
1. At various times during weighing (e.g., each half hour), note:
   a. Atmospheric pressure
   b. Balance temperature
   c. Dry-bulb temperature
   d. Wet-bulb temperature

   Example

   \[
   \begin{align*}
   11:01 \text{ a.m.} & : \\
   & \text{zero} \quad 0.0000 \\
   & \text{wt. cal.} \quad 16.2190 \text{ g} \\
   & \text{zero} \quad 0.0000 \\
   \\
   11:14 \text{ a.m.} & : \\
   & \text{zero} \quad 0.0000 \\
   & \text{wt. cal.} \quad 16.2190 \text{ g} \\
   & \text{zero} \quad 0.0000 \\
   \end{align*}
   \]

   \[T_{\text{bal}} = 23.85^\circ C\]
   \[T_{\text{wet}} = 55.8^\circ F\]
   \[T_{\text{dry}} = 75.0^\circ F\]
   \[P = 744.0 \text{ mm Hg}\]

2. Make zero corrections:
   In this case zero correction = 0.0000
   \[\therefore \text{ apparent weight of calorimeter} = 16.2190 \text{ g}\]

3. Make balance corrections:
   Weights: \[10.0 \text{ g} \quad 6.0 \text{ g} \quad 0.2 \text{ g}\]
   NBS calibrated weight correction: \[-0.0001 \quad 0.0000 \quad -0.0001\]
   \[\therefore \text{ total balance weight correction} = -0.0002 \text{ g}\]
   \[\therefore \text{ air weight of calorimeter} = 16.2188 \text{ g}\]
4. Calculate the density of moist air (Weast, 1972):

\[ D_T = D_O \times \frac{T}{T_o} \times \frac{P}{P_o} \]

- \( D_T \) = density at experimental temperature \( T \) and pressure \( P \)
- \( D_O \) = known density at \( T_O \times P_O \)
- \( P_{corr} \) = corrected pressure from experimental \( P \) to allow for moisture

\[ P_{corr} = P - [0.3783 \times (\text{relative humidity}) \times (\text{vapor pressure } H_2O \text{ at } P, T)] \]

To calculate relative humidity from wet-bulb depression (CRC Handbook, p. E-39)

Wet bulb depression = 75.0 - 55.8 = 19.2°F

\[ \text{Relative humidity} = 0.25 \]

For vapor pressure of \( H_2O \) (CRC Handbook, p. D-148)

At 23.85°C, vapor pressure of \( H_2O = 22.177 \text{ mm Hg} \)

\[ P_{corr} = -(0.3783 \times 0.25 \times 22.18) + 744.0 \]

\[ = 744.0 - 2.1 \]

\[ = 741.9 \text{ mmHg} \]

\[ \text{Density of air} = 1.2929 \times 10^{-3} \left( \frac{T_41.9}{760.0} \times \frac{273.15}{297.06} \right) \text{ g/cc} \]

\[ = 1.1608 \times 10^{-3} \text{ g/cc} \]

5. Make buoyancy corrections:

Correction to apparent mass (\( \Delta \)) is

\[ \Delta = d_{air} \times (V_{sample} - V_{weights}) \]

\[ = d_{air} \times \frac{m}{d_{sample}} - \frac{m}{d_{weights}} \]

- Assume calorimeter copper \( \therefore \) \( d_{sample} = 8.92 \text{ g/cc} \)
- Assume weights have stated density = 8.00 g/cc
\[
\Delta = 1.1608 \times 10^{-3} \times 16.2188 \times (8.92^{-1} - 8.00^{-1}) \\
= -0.0002 \text{ g}
\]

\[
\therefore \text{ The mass of the calorimeter } = 16.2188 - 0.0002 \\
= 16.2186 \text{ g}
\]
APPENDIX D

CALCULATIONS PERTAINING TO THE ENTHALPY INCREMENTS OF STILBITE

1. Weight corrections due to the buoyancy in air for empty and loaded capsule.

Weight original capsule = 20.43270 g
Weight removed stub = 0.76881 g
Weight of empty capsule = 19.66389 g

Buoyancy correction for empty capsule:

\[1 + \left(\frac{1}{\rho_{\text{capsule}}} - \frac{1}{\rho_{\text{weights}}}\right)\rho_{\text{air}}\] \times \text{mass of capsule in air} = \text{mass of capsule in vacuum}

\[1 + \left(\frac{1}{20.0} - \frac{1}{8.4}\right)(.00117) = .999919\]

\[\therefore \text{corrected mass of empty capsule} = (19.66398)(.999919)\]

\[= 19.66239 \text{ g}\]

Weight stilbite = 7.88648 g

Buoyancy correction for stilbite:

\[1 + \left(\frac{1}{\rho_{\text{stilbite}}} - \frac{1}{\rho_{\text{weights}}}\right)\rho_{\text{air}}\] \times \text{mass of stilbite} = \text{mass of stilbite in vacuum}

\[1 + \left(\frac{1}{2.16} - \frac{1}{8.4}\right)(.00117) = 1.000402\]

\[\therefore \text{corrected mass of stilbite} = (7.88648)(1.000402)\]

\[= 7.88965 \text{ g}\]
To calculate mass of air in capsule:

- stilbite molecular weight = 714.605 g • mol\(^{-1}\)
- moles of stilbite = 0.011041 mol
- density of stilbite = 2.16 g • cm\(^{-3}\)
- volume of stilbite = 3.653 cm\(^{-3}\)
- internal volume of capsule = 6.42 cm\(^{-3}\)
- free volume in capsule = 2.767 cm\(^{-3}\)
- moles of air = 0.0001131 mol
- molecular weight of air = 28.8 g • mol\(^{-1}\)

\[\therefore \text{ mass of air} = 0.00326 \text{ g}\]

Total mass of unsealed capsule + stilbite:

- mass of air = 0.00326 g
- mass of capsule = 19.66239 g
- mass of stilbite = 7.88965 g

\[27.55530 \text{ g}\]

Mass of capsule after welding = 27.55012 g

External volume of capsule = 7.4 cm\(^{-3}\)

Density of capsule = 3.72 g • cm\(^{-3}\)

Buoyancy correction of sealed capsule:

\[1 + \left(\frac{1}{\rho_{\text{ capsule}}} - \frac{1}{\rho_{\text{ weights}}}\right)\left(\rho_{\text{ air}}\right)\]

\[1 + (1/3.72 - 1/8.4)(0.00117) = 1.00018\]

\[\therefore \text{ Final mass of sealed capsule and contents} = (27.55012)(1.00018) = 27.55495 \text{ g}\]
2. Vapor correction for \( \text{H}_2\text{O} \) over stilbite.

Below 373.15 K

\[
\log P = \frac{-49.100}{19.15} \frac{1}{T} + \frac{(188.7 - 58.6)}{19.15} \]

\[
= \frac{2564}{T} + 6.7937
\]

\( T = 350 \text{ K} \quad \log P = -0.5320 \quad P = 0.294 \text{ atm} \)

Above 373.15 K, \( P_{\text{stilbite}} = P_{\text{H}_2\text{O}(l)} \)

<table>
<thead>
<tr>
<th>( T )</th>
<th>( P )</th>
<th>Vol</th>
<th>( n_{\text{H}_2\text{O}} )</th>
<th>( \Delta E_{\text{evap}} )</th>
<th>( \text{Corr} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>0.294</td>
<td>( 0.002767 )</td>
<td>( 0.0000289 )</td>
<td>41,538</td>
<td>1.20</td>
</tr>
<tr>
<td>375</td>
<td>1.073</td>
<td>( 0.002767 )</td>
<td>( 0.0000965 )</td>
<td>41,538</td>
<td>4.01</td>
</tr>
<tr>
<td>400</td>
<td>2.087</td>
<td>( 0.002767 )</td>
<td>( 0.001760 )</td>
<td>41,538</td>
<td>7.31</td>
</tr>
<tr>
<td>425</td>
<td>4.956</td>
<td>( 0.002767 )</td>
<td>( 0.003931 )</td>
<td>41,538</td>
<td>16.33</td>
</tr>
<tr>
<td>450</td>
<td>15.994</td>
<td>( 0.002767 )</td>
<td>( 0.011353 )</td>
<td>41,538</td>
<td>47.16</td>
</tr>
<tr>
<td>500</td>
<td>26.117</td>
<td>( 0.002767 )</td>
<td>( 0.017615 )</td>
<td>41,538</td>
<td>73.17</td>
</tr>
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</table>
BIBLIOGRAPHY


