SOME NATURAL ZEOLITES: RECENT THERMODYNAMIC RESULTS, THEIR APPLICATION, AND THE ESTIMATION OF MISSING THERMODYNAMIC QUANTITIES*  

by  

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ABSTRACT

This paper reports new calorimetric measurements on the following minerals: analcime, dehydrated analcime, natrolite, scolecite, mesolite, and heulandite. The thermodynamic quantities determined include the standard enthalpy of formation, $\Delta H_f(298 \text{ K})$, the high- and low-temperature enthalpy increments, $H^\circ(T) - H^\circ(298 \text{ K})$, the low-temperature (5-350 K) heat capacity, $C_p^\circ(T)$, the standard entropy, $S^\circ(T)$, and the Gibbs energy of formation, $\Delta G_f(T)$. The application of calorimetric data to equilibria of geologic interest is demonstrated. A part of the paper also deals with the estimation of missing thermodynamic quantities.

INTRODUCTION

The majority of reactions that involve zeolites take place at temperatures in the vicinity of 450-500 K and are accompanied by small changes of both entropy and volume. These factors, along with the possibility that some zeolites may be metastable phases, render difficult the study by the traditional hydrothermal techniques of equilibria involving these minerals. An alternative approach is the determination by calorimetric means of the thermodynamic quantities (i.e., $\Delta H_f$, $S^\circ$) that lead to the Gibbs energy of formation, $\Delta G_f$, and thence, by calculation, to equilibrium constants and activities.

This paper, accordingly, describes new calorimetric measurements on the following minerals: analcime, dehydrated analcime, natrolite, scolecite, mesolite, and heulandite. The thermodynamic quantities determined include the standard enthalpy of formation, $\Delta H_f(298 \text{ K})$, the high- and low-temperature enthalpy increments, $H^\circ(T) - H^\circ(298 \text{ K})$, the low-temperature (5-350 K) heat capacity, $C_p^\circ(T)$, the standard entropy, $S^\circ(T)$, and the Gibbs energy of formation, $\Delta G_f(T)$.

Inasmuch as analcime occurs both as a low-temperature, diagenetic phase in sediments and cavities of basaltic rocks and as a feldspathoid in igneous rocks, it has attracted a great deal of mineralogic interest. Because of its relatively simple composition, it is commonly encountered in studies of sodium aluminum silicates. Both scolecite and mesolite are found at
relatively shallow depths in many geothermal areas and heulandite is among the more prominent zeolites found in sedimentary rocks. The zeolites we have chosen for study are thus of considerable geologic interest and, in addition, their relatively simple chemical compositions make them attractive candidates for initial studies in a planned systematic investigation.

EXPERIMENTAL

The experimental results are given in Table I. The enthalpies of formation are based upon solution calorimetric measurements in HF·3.44H₂O, and the heat capacities have been determined by low-temperature adiabatic calorimetry.

ESTIMATION OF HEAT CAPACITY AND ENTROPY OF MESOLITE

The heat capacity of mesolite at 298.15 K has been estimated in the following way. The as-analyzed formula for mesolite is Na₀.₆₇₆Ca₀.₆₅₇Al₁.₉₉S₁₃.₀₁₀₁₂.₆₄₇H₂O. Division by 0.₃₃ of the stoichiometric coefficients gives the rounded-off formula: Na₂Ca₂Al₆S₁₉O₃₀·₈H₂O. For the following equilibrium at 298.15 K:

\[
2\text{CaAl}_2\text{Si}_3\text{O}_{₁₀}·₃\text{H}_₂\text{O} + \text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{₁₀}·₂\text{H}_₂\text{O} \rightleftharpoons \text{Na}_2\text{Ca}_2\text{Al}_₆\text{Si}_₉\text{O}_{₃₀}·₈\text{H}_₂\text{O} \tag{1}
\]

we assume \( \Delta C_p = 0 \). This assumption has proven to be valid for a number of silicate systems (1). We take the \( C_p(298 \text{ K}) \) values for scolecite and natrolite given in Table I and obtain

\[
C_p(\text{Na}_2\text{Ca}_2\text{Al}_₆\text{Si}_₉\text{O}_{₃₀}·₈\text{H}_₂\text{O}, c, 298.15 \text{ K}) = 1125 \text{ JK}^{-1} \text{ mol}^{-1}.
\]

For the as-analyzed composition:

\[
C_p(\text{Na}_₀.₆₇₆\text{Ca}_₀.₆₅₇\text{Al}_₁.₉₉\text{S}_₁₃.₀₁₀₁₂.₆₄₇\text{H}_₂\text{O}) = 371 \text{ JK}^{-1} \text{ mol}^{-1}.
\]

The standard entropy \( S^\circ \) of mesolite at 298.15 K has been estimated, also based on equilibrium (1), by means of the equation:

\[
S^\circ(\text{mesolite}) = A[B + V^\circ(\text{mesolite})]/2B \tag{2}
\]

where

\[
A = 2S^\circ(\text{scolecite}) + S^\circ(\text{natrolite}) \quad \text{and}
B = 2V^\circ(\text{scolecite}) + V^\circ(\text{natrolite}).
\]

In the above equations, \( V^\circ \) denotes molar volume at 298.15 K \( (P = 1 \text{ bar}) \). The molar volumes are calculated from the molecular masses and the densities and the requisite entropies are taken from Table I. Thus, we estimate

\[
S^\circ(\text{Na}_2\text{Ca}_2\text{Al}_₆\text{Si}_₉\text{O}_{₃₀}·₈\text{H}_₂\text{O}, c, 298.15 \text{ K}) = 1094 \text{ JK}^{-1} \text{ mol}^{-1}
\]

and, for the as-analyzed composition,

\[
S^\circ(\text{Na}_₀.₆₇₆\text{Ca}_₀.₆₅₇\text{Al}_₁.₉₉\text{S}_₁₃.₀₁₀₁₂.₆₄₇\text{H}_₂\text{O}) = 361 \text{ JK}^{-1} \text{ mol}^{-1}.
\]
It is interesting to compare the experimental results for $S^\circ$ (natrolite) (Table I) with a recent estimate (1) based on the equilibrium:

$$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O} + \text{SiO}_2 \rightleftharpoons 2\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$$

Using a formula similar to equation (2) and our result for $S^\circ$ (analcime), the estimate (1) for $S^\circ$ (natrolite) is recalculated to be 409 JK$^{-1}$ mol$^{-1}$. The published estimate is 425 JK$^{-1}$ mol$^{-1}$; but both values differ significantly from the experimental result, 360.2 JK$^{-1}$ mol$^{-1}$. Of course, one implicit assumption in this estimation procedure is that the entropy contributions from the zeolitic water on both sides of the equation are the same. Such an assumption is not valid. Indeed, if a correction of $2(55-32) = 46$ JK$^{-1}$ mol$^{-1}$ is made for the difference in the entropies of the zeolitic water in analcime and scolecite (2), then the calculated $S^\circ$ (natrolite) is 409-46 = 363 JK$^{-1}$ mol$^{-1}$, in good agreement with experiment.

There are several topics of interest in the geochemistry of zeolites to which the results of the present study are applicable. Such topics include, for example, various (feldspar + zeolite) equilibria at high pressures, the state of order/disorder of zeolitic water, and the influence of cation substitution and Al/Si ratio on thermodynamic stabilities. Because of space limitations, however, we are able to briefly discuss only one such item and that has to do with the following equilibrium:

$$\text{low albite} + \text{H}_2\text{O}(l) \rightleftharpoons \text{analcime} + \text{SiO}_2(aq)$$

The equilibrium concentration, [$\text{SiO}_2$, aq], has been directly determined by Hemley (3) as a function of temperature at $P = 1$ kbar. We have used thermodynamic data to derive the same results and, in Table II, two sets of calculated log[$\text{SiO}_2$, aq] values are given. One set is based upon $\Delta H_f$(low albite) determined calorimetrically by Hemingway and Robie (4) and the other is based upon a somewhat different value which Helgeson et al. (1) deduced from a consideration of various equilibria involving low albite. Clearly, the agreement between the calculated [$\text{SiO}_2$, aq)] and the experimental result is much better when the $\Delta H_f$(low albite) suggested by Helgeson et al. is used and this indicates that this value should be redetermined experimentally. We plan to carry out such a study on a specimen of highly-ordered low albite that is being prepared at the present time.

REFERENCES

2. P. A. G. O'Hare, unpublished results.
Table I. Selected Thermodynamic Properties at $T = 298.15$ K

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>$\Delta G_f^\circ(T)/$kJ mol$^{-1}$</th>
<th>$C_p(T)/$JK$^{-1}$mol$^{-1}$</th>
<th>$S(T)/$JK$^{-1}$mol$^{-1}$</th>
<th>$\Delta G_f^\circ(T)/$kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>analcime</td>
<td>$Na_0.96Al_0.96Si_2.04O_6*H_2O$</td>
<td>$-3296.9 \pm 3.3$</td>
<td>$211.53 \pm 0.21$</td>
<td>$226.75 \pm 0.23$</td>
<td>$-3077.2 \pm 3.3$</td>
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<tr>
<td>dehydrated</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>analcime</td>
<td>$Na_0.96Al_0.96Si_2.04O_6$</td>
<td>$-2970.2 \pm 3.5$</td>
<td>$163.49 \pm 0.16$</td>
<td>$171.71 \pm 0.17$</td>
<td>$-2803.7 \pm 3.5$</td>
</tr>
<tr>
<td>natrolite</td>
<td>$Na_2Al_2Si_3O_10*2H_2O$</td>
<td>$-5718.6 \pm 5.0$</td>
<td>$359.57 \pm 0.35$</td>
<td>$360.15 \pm 0.35$</td>
<td>$-5316.8 \pm 5.1$</td>
</tr>
<tr>
<td>scolecite</td>
<td>$CaAl_2Si_3O_10*3H_2O$</td>
<td>$-6049.0 \pm 5.0$</td>
<td>$382.81 \pm 0.37$</td>
<td>$367.42 \pm 0.36$</td>
<td>$-5597.9 \pm 5.1$</td>
</tr>
<tr>
<td>mesolite</td>
<td>$Na_0.676Ca_0.657Al_1.99Si_3.01O_10^{*}$</td>
<td>$-5947.1 \pm 5.4$</td>
<td>$371 \pm 5^*$</td>
<td>$361 \pm 5^*$</td>
<td>$-5513.9 \pm 5.5$</td>
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<tr>
<td>heulandite</td>
<td>$CaAl_2Si_17O_{18}*6H_2O$</td>
<td></td>
<td>$758.4^+$</td>
<td>$744.1^+$</td>
<td></td>
</tr>
</tbody>
</table>

*Estimated (see text)  
+Preliminary

Table II. Values at $P = 1$ kbar for $\log(SiO_2, aq)$ in the equilibrium:

$0.96NaAlSi_3O_8 + H_2O(1) = Na_0.96Al_0.96Si_2.04O_6*H_2O + 0.84SiO_2(aq)$  
(low albite)  
(analcime)

<table>
<thead>
<tr>
<th>T/K</th>
<th>373.15</th>
<th>473.15</th>
<th>573.15</th>
<th>673.15</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>-2.45</td>
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<tr>
<td>B</td>
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<td>-2.77</td>
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<tr>
<td>C</td>
<td>-3.21</td>
<td>-2.78</td>
<td>-2.57</td>
<td>-2.46</td>
</tr>
</tbody>
</table>

A. Experimental results of Hemley (U.S. Geological Survey), private communication.  
B. Based on $\Delta H_f$ (low albite) from Hemingway and Robie (4).  
C. Based on $\Delta H_f$ (low albite) from Helgeson et al. (1).
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