

## Thermodynamic studies of zeolites: heulandite<sup>1</sup>

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### Abstract

Calorimetric measurements have been carried out on a natural sample of heulandite (from Gunnadah, Australia) having the composition  $(\text{Ba}_{0.065}\text{Sr}_{0.175}\text{Ca}_{0.585}\text{K}_{0.132}\text{Na}_{0.383})\text{Al}_{2.165}\text{Si}_{6.835}\text{O}_{18} \cdot 6.00\text{H}_2\text{O}$ . Low-temperature heat capacities and enthalpy increments to 475 K were measured by the techniques of adiabatic and drop-calorimetry. The standard enthalpy of formation of heulandite at 298.15 K was determined by solution calorimetry. The following values have been obtained for heulandite at  $T = 298.15$  K and a pressure of 1 bar;  $\Delta H_f^\circ(T) = -10491.0 \pm 10.2$  kJ/mol,  $C_p^\circ(T) = 781.03 \pm 0.78$  J/(mol · K),  $S^\circ(T) - S^\circ(0) = 767.18 \pm 0.77$  J/(mol · K),  $\Delta S_f^\circ(T) = -2734.9 \pm 1.2$  J/(mol · K) and  $\Delta G_f^\circ(T) = -9675.6 \pm 10.2$  kJ/mol.

### Introduction

The thermodynamic properties of the zeolite minerals can be approximated by the addition in the proper proportions of numerical values for the appropriate properties (e.g., heat capacity) of other tectosilicates such as the feldspars, nepheline, and quartz. However, such procedures frequently lead to errors of the order of 0.5 to 1.0% which appear to result mostly from assigning the wrong values to the contribution of zeolitic water (Johnson et al., 1983, p. 1143). Earlier papers in this series focused on zeolites with low Si-to-Al framework compositions (Johnson et al., 1982 and 1983). Heulandite not only represents high-silica zeolites, but is a common zeolite, occurring worldwide and in a variety of environments. Accurate thermodynamic properties for this zeolite will assist in the interpretation of many of these occurrences.

### Materials

#### Heulandite

The heulandite sample used in this study is from Gunnadah, N.S.W., Australia, where it occurs as faintly orange,  $\approx 1$  cm-crystals on a drusy quartz matrix. A stock of about 15 gm was prepared by handpicking the largest and cleanest crystals and crushing them to about 0.5 mm size. Several large cleavage flakes

of the heulandite were analyzed with an ARL electron microprobe to determine the average composition and compositional range. For all elements, an accelerating voltage of 15 kV was used with a sample current of 9 nA and a defocused beam. The elements commonly found in zeolites—Na, Al, Si, K, Ca, Mg, Fe, Sr, Ba—were sought, and all but Mg and Fe were found in amounts large enough to determine. Standards used were albite, microcline, sanbornite, celestite, and andesine. Water content was determined by heating a sample that had been equilibrated with air of 50% relative humidity to 873 K for 24 h and measuring the weight loss. Analytical results along with the cell dimensions are given in Table 1.

*Because heulandite readily loses water, even at room temperature, our measurements were made on, and refer to, heulandite equilibrated with air of 50% relative humidity.*

#### Gibbsite

The gibbsite,  $\text{Al}(\text{OH})_3$ , was Fisher Reagent  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  which had been heated for approximately 6 h at 423 K before use. The source of the gibbsite and its thermal treatment were, therefore, identical to those reported by Hemingway and Robie (1977) for their determination of  $\Delta H_f^\circ[\text{Al}(\text{OH})_3]$ .

#### Sodium, potassium, and barium fluorides

The sodium and potassium fluorides (Ultrapure grades) were obtained from Alfa Inorganics (Danvers, MA). The samples were heated to 475 K for approximately 8 h and were then transferred to a helium-atmosphere glovebox where they were stored. The barium fluoride (Puratronic grade) was obtained from Johnson Matthey Chemicals Limited. This material, which was shipped under argon, was also stored in a helium-atmosphere glovebox and used as received.

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Table 1. Analysis, cell contents, and structural parameters for heulandite from Gunnadah, N. S. W., Australia

Sample composition (mass per cent)		Cell contents (number of atoms)*		Cell dimensions	
		A	B		
SiO <sub>2</sub>	58.37	Si	27.345	6.835	a 17.71(1) Å
Al <sub>2</sub> O <sub>3</sub>	15.68	Al	8.658	2.165	b 17.94(1) Å
BaO	1.40	Ba	0.256	0.065	c 7.24(1) Å
SrO	2.55	Sr	0.692	0.175	β 116° 30(4)'
CaO	4.67	Ca	2.345	0.585	
K <sub>2</sub> O	0.89	K	0.529	0.132	
Na <sub>2</sub> O	1.68	Na	1.526	0.383	
H <sub>2</sub> O	15.35	H <sub>2</sub> O	23.98	6.00	
Total	100.59				

\*A - cell contents based on 72 framework oxygen atoms;

B - idealized composition (18 framework oxygen atoms);

used for calculations of molar thermodynamic properties.

#### Hydrofluoric acid

Hydrofluoric acid was Baker "Analyzed Reagent" diluted to the appropriate concentration with distilled water.

#### Apparatus, experimental procedures, and results

Three different types of measurement were performed in this study. Each of the techniques used, along with the results obtained, will be discussed under separate headings.

#### Heat-capacity measurements

A specially modified calorimeter was used for these measurements to permit the heulandite sample to be loaded into the calorimeter and sealed without altering its water content. The calorimeter (laboratory designation C5B) was of the same general design as calorimeter 6-GS-I which was used in our earlier heat-capacity measurements on analcime (Johnson et al., 1982) and of natrolite, mesolite, and scolecite (Johnson et al., 1983). The C5B calorimeter differed from 6-GS-I in that its volume was much larger (36.93 cm<sup>3</sup>) and that it was fitted with a 0.20-cm diameter copper tube which was soldered to the calorimeter cover. The heulandite sample, a loose powder, was poured into the open calorimeter and the cover was attached with 50:50 lead-tin solder. The calorimeter, with the cover soldered in place and with the copper tube open, was placed for 20 h in a 50 per cent relative humidity atmosphere over a saturated solution of Mg(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O at about 298 K. It was established by weighing the calorimeter and sample before and after these operations that the water content of the sample became constant when exposed to a 50% relative humidity atmosphere. Next, the copper tube on the calorimeter was attached to a vacuum line, but closed off from the vacuum by a small valve. The calorimeter was immersed in a (CO<sub>2</sub> + acetone) bath at 195 K to reduce the sample temperature so that its equilibrium water vapor pressure would be of the order of 1 × 10<sup>-6</sup> atm. The air was then pumped from the calorimeter

and 4.8 × 10<sup>-5</sup> mol of helium was added to promote rapid temperature equilibration during the heat capacity measurements. The copper tube was sealed by pinching it closed by means of a special tool. The calorimeter was shown to be sealed by testing it with a helium leak detector. A small amount of heulandite was lost through the copper tube as the air was pumped out, but this loss was accurately determined by subsequently weighing the sealed calorimeter. The final sample mass on which the heat capacities are based was 31.0411 g.

Information relating to the heat-capacity apparatus and measuring techniques have been given previously (Johnson et al., 1983). The adiabatic technique can reproduce heat-capacity values to ±0.05 per cent at any temperature above 25 K. The accuracy of the results is discussed below.

#### Heat-capacity results

Since heulandite has a significant equilibrium water-vapor pressure from about 260 K, and since the calorimeter had a significant free internal volume (23.0 cm<sup>3</sup>), it was necessary to correct our heat-capacity results for the enthalpy effect due to the vaporization of water which occurred during heating. To do this we have used the equation:

$$\log (P/\text{atm}) = 6.773 - 2533(T/K)^{-1} \quad (1)$$

to represent the vapor pressure of water in equilibrium with the sample of heulandite. The results given by van Reeuwijk (1974) were used to develop this equation. The enthalpy of vaporization of this water, 48.5 kJ/mol, was also taken from van Reeuwijk (1974). This vaporization correction increased the measured heat capacities by 0.02% near 250 K, 0.15% near 300 K, 0.63% near 325 K, and 1.3% near 350 K.

The heat capacities corrected for vaporization,  $C_p^{\circ}(T)$ , are given in Table 2 in order of increasing mean temperature  $\langle T \rangle$ . Plots of  $C_p^{\circ}(T)$  against  $\langle T \rangle$  did not reveal any anomalous or unusual features. The temperature increment for each measurement below 20 K was about 2 K, between 20 and 100 K it was 0.1  $\langle T \rangle$ , and above 100 K it was 10 K. Individual values of  $C_p^{\circ}(T)$  in Table 2 are estimated to have a probable error of 5 per cent near 6 K, 1% near 14 K, and 0.2% above 20 K.

#### Thermodynamic functions

The experimental heat capacity values below 40 K were fitted to a polynomial in  $T$  by a weighted least-squares method. A second, overlapping polynomial was used to fit the values from 20 to 350 K. Individual values of  $C_p^{\circ}(T)$  above 15 K, with one exception, deviated from the polynomials by less than 0.1%; one value, at 25 K, deviated by 0.12%. Values of  $C_p^{\circ}(T)$  calculated from these polynomials are given at selected temperatures in Table 3.

A plot of  $C_p^{\circ}(T)/T$  against  $T^2$  was constructed using the results below 13 K in Table 2. A smooth curve through these values and  $C_p^{\circ}(T) = 0$  at  $T \rightarrow 0$  represented the results within expected error limits. Values of  $C_p^{\circ}(T)$  read from this curve at 1 K intervals up to 10 K were used to compute the thermodynamic functions at 10 K given in Table 3. The two polynomials referred to in the preceding paragraph

Table 2. Experimental heat capacities of heulandite

$\langle T \rangle$	$C_p^o(T)$	$\langle T \rangle$	$C_p^o(T)$	$\langle T \rangle$	$C_p^o(T)$
K	J/(mol·K)	K	J/(mol·K)	K	J/(mol·K)
5.60	0.362	32.91	60.44	164.96	488.60
6.58	0.568	33.96	64.04	174.98	515.72
7.29	0.821	36.39	72.57	185.04	542.20
8.58	1.460	40.27	86.24	195.07	567.61
9.22	1.840	44.62	101.74	205.01	591.94
10.58	2.957	49.44	119.05	214.94	615.22
11.10	3.500	53.28	132.74	224.90	637.55
12.09	4.670	58.82	152.48	229.49	648.40
12.59	5.332	64.94	174.03	239.35	669.09
14.07	7.577	71.78	197.94	249.34	690.52
14.68	8.592	79.37	223.94	259.33	709.98
16.07	11.21	87.76	252.39	269.36	729.53
16.74	12.58	95.54	277.92	279.39	747.70
18.07	15.51	97.00	282.53	289.40	765.74
18.75	17.10	104.53	306.85	299.41	783.46
20.07	20.34	114.84	340.11	309.42	799.50
20.78	22.18	124.93	371.88	319.39	815.95
22.07	25.66	135.01	403.02	329.38	830.71
22.94	28.14	145.03	432.55	336.89	841.58
25.31	35.21	154.99	461.08	341.94	848.78
27.91	43.50	155.48	462.03	347.21	856.11
30.76	53.04				

were used to compute the thermodynamic properties at higher temperatures. The uncertainties given for the functions at 298.15 K (Table 3) represent errors from all known sources.

#### Enthalpy of reaction measurements at 298.15 K

An LKB-8700 precision calorimetric system was used for the enthalpy of reaction measurements. The 100-cm<sup>3</sup> reaction vessel and stirrer were both constructed of 18-carat gold. The reaction vessel was modified for quartz-crystal thermometry by the addition of a re-entry well, in which was placed the sensor of a quartz-crystal thermometer (Hewlett-Packard Model 2801 A). The samples were contained in ampoules constructed from Teflon as previously described (Johnson et al., 1983).

The energy equivalent of the calorimetric system was based on electrical calibrations performed before and after each reaction experiment. The calibrations covered the same temperature range as the corresponding enthalpy of reaction measurements, and the mean temperature of all such experiments was 298.15 ± 0.01 K.

Calorimetric measurements were made of the enthalpies of reaction or solution of heulandite, gibbsite, sodium fluoride, potassium fluoride, and barium fluoride in approxi-

mately 24.4 mass % HF(aq). The heulandite was quickly loaded into the ampoules after having been equilibrated with a 50% relative humidity atmosphere. The fluorides were loaded into ampoules in the glovebox. The amount of each sample reacted was determined by the stoichiometry of the heulandite and the base reaction in the cycle—0.0017944 mol of SiO<sub>2</sub> with 100 cm<sup>3</sup> of 24.4% HF(aq). It was assumed that the CaF<sub>2</sub> and SrF<sub>2</sub> produced in the heulandite reaction precipitated quantitatively. In separate experiments, no enthalpy change was detected when pure CaF<sub>2</sub> or SrF<sub>2</sub> were introduced into an HF(aq) solution. The detailed results for the calorimetric reactions are given in Table 4.

#### Standard enthalpy of formation at 298.15 K

The reactions and enthalpy values necessary to derive the standard enthalpy of formation of heulandite are given in Table 5. The molar enthalpies of reactions 2, 3, 4, 5, and 8 are based on the corresponding mean specific enthalpies of reaction in Table 4. For this conversion, the molar masses of heulandite, Al(OH)<sub>3</sub>, NaF, KF, and BaF<sub>2</sub> were

Table 3. Low-temperature thermodynamic functions of heulandite\*

$T$	$C_p^o(T)$	$S^o(T)$	$H^o(T) - H^o(0)$	$-\{G^o(T) - H^o(0)\}/T$
K	J/(mol·K)	J/(mol·K)	J/mol	J/(mol·K)
10	(2.449)	(0.732)	(5.642)	(0.168)
15	9.181	2.834	32.69	0.655
20	20.15	6.892	104.5	1.667
25	34.27	12.85	239.4	3.274
30	50.47	20.51	450.7	5.487
50	121.04	62.63	2160	19.43
70	191.74	114.65	5291	39.06
100	292.47	200.12	12570	74.42
120	356.44	259.14	19064	100.27
140	417.58	318.72	26809	127.23
160	475.11	378.27	35742	154.88
180	528.99	437.38	45789	183.00
200	579.60	495.76	56880	211.36
220	626.92	553.25	68951	239.84
240	670.78	609.70	81934	268.31
260	711.35	665.02	95760	296.71
280	749.05	719.13	110369	324.96
300	784.17	772.02	125705	353.00
320	816.62	823.68	141718	380.81
340	846.04	874.09	158349	408.36
350	860.08	898.81	166880	422.01
273.15	736.43	700.73	105281	315.30
298.15	781.03	767.18	124257	350.42
	±1.56	±1.53	±249	±0.70

\*Molecular mass of heulandite was taken to be 708.13 g/mol.

Table 4. Enthalpies of reaction (298.15 K) with HF(aq) of heulandite, gibbsite, sodium fluoride, potassium fluoride, and barium fluoride\*

$\frac{m}{g}$	$\epsilon(\text{calor})^{**}$ J/K	$\Delta\theta_c$ K	$\epsilon(\text{calor})(-\Delta\theta_c)$ J	$\Delta H_{\text{corr}}^{\dagger}$ J	$\frac{\Delta H/M}{J/g}$
Heulandite, (Ba <sub>0.065</sub> Sr <sub>0.175</sub> Ca <sub>0.585</sub> K <sub>0.132</sub> Na <sub>0.383</sub> )Al <sub>2.165</sub> Si <sub>16.835</sub> O <sub>18</sub> ·6.00H <sub>2</sub> O					
0.18659	401.06	0.94665	-379.66	0.09	-2034.2
0.18622	400.80	0.94486	-378.70	0.09	-2033.1
0.18667	400.84	0.94685	-379.54	0.09	-2032.7
0.18645	401.34	0.94461	-379.11	0.09	-2032.8
0.18639	400.82	0.94448	-378.57	0.09	-2030.6
0.18665	400.93	0.94527	-378.99	0.09	-2030.0
0.18598	401.12	0.94225	-377.96	0.09	-2031.8
Average $\Delta H/M = -2032.2 \pm 0.6$ J/g <sup>††</sup>					
Gibbsite, Al(OH) <sub>3</sub>					
0.04436	400.68	0.23645	-94.74	0.09	-2133.7
0.04463	401.05	0.23785	-95.39	0.09	-2135.3
0.04443	400.70	0.23707	-94.99	0.09	-2135.9
0.04457	400.44	0.23820	-95.38	0.09	-2138.0
0.04447	400.70	0.23714	-95.02	0.09	-2134.7
Average $\Delta H/M = -2135.5 \pm 0.7$ J/g <sup>††</sup>					
Sodium Fluoride, NaF					
0.00416	400.7	0.00124	-0.50	0.08	-101.0
0.00421	400.7	0.00152	-0.61	0.08	-125.9
0.00429	400.7	0.00158	-0.63	0.08	-128.2
0.00432	400.7	0.00149	-0.60	0.08	-120.4
0.00401	400.7	0.00137	-0.55	0.08	-117.2
0.00421	400.7	0.00135	-0.54	0.08	-109.3
0.00449	400.7	0.00137	-0.55	0.08	-104.7
Average $\Delta H/M = -115.2 \pm 4.0$ J/g <sup>††</sup>					
Potassium Fluoride, KF					
0.00228	400.7	0.00293	-1.17	0.08	-478.1
0.00190	400.7	0.00247	-0.99	0.08	-478.9
0.00204	400.7	0.00243	-0.97	0.08	-436.3
0.00205	400.7	0.00278	-1.11	0.08	-502.4
0.00195	400.7	0.00272	-1.09	0.08	-517.9
0.00197	400.7	0.00283	-1.13	0.08	-533.0
Average $\Delta H/M = -491.1 \pm 14.1$ J/g <sup>††</sup>					
Barium Fluoride, BaF <sub>2</sub>					
0.00289	400.7	0.00079	-0.32	0.08	-83.0
0.00306	400.7	0.00083	-0.33	0.08	-81.7
0.00313	400.7	0.00086	-0.34	0.08	-83.1

Table 4. (cont.)

$\frac{m}{g}$	$\epsilon(\text{calor})^{**}$ J/K	$\Delta\theta_c$ K	$\epsilon(\text{calor})(-\Delta\theta_c)$ J	$\Delta H_{\text{corr}}^{\dagger}$ J	$\frac{\Delta H/M}{J/g}$
0.00289	400.7	0.00098	-0.39	0.08	-107.3
0.00304	400.7	0.00101	-0.40	0.08	-105.3
0.00302	400.7	0.00083	-0.33	0.08	-82.8
0.00287	400.7	0.00084	-0.34	0.08	-90.6
0.00296	400.7	0.00101	-0.40	0.08	-108.1
Average $\Delta H/M = -92.7 \pm 4.3$ J/g <sup>††</sup>					

\*The column headings are  $m$ , the mass of the sample reacted or dissolved;  $\Delta\theta_c$ , the temperature change of the calorimeter corrected for heat exchange with the environment;  $\epsilon(\text{calor})$ , the mean energy equivalent of the calorimetric system before and after the experiment;  $\Delta H_{\text{corr}}$ , the combined correction for the thermal effects of opening the ampoule and of vaporizing the solvent into the free volume of the ampoule; and  $\Delta H/M$ , the specific enthalpy of reaction or solution.

\*\* $\epsilon(\text{calor})$  was not measured for the experiments with NaF, KF or BaF<sub>2</sub> but was taken to be the average of the values for the Al(OH)<sub>3</sub> experiments.

† $\Delta H_{\text{corr}}$  includes the enthalpy effect of opening the ampoule, which was 0.10 J, as well as a correction for the vaporization of solvent into the free volume of the ampoule.

††The uncertainty is the standard deviation of the mean.

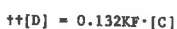
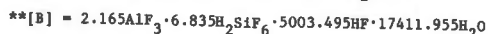
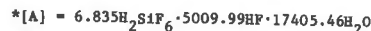
taken to be 708.13, 78.0034, 41.9882, 58.0967, and 175.327 g/mol, respectively, based on the 1979 atomic weights (Holden, 1980). The enthalpy of reaction of  $\alpha$ -quartz with HF(aq), reaction 1, was taken from Johnson et al. (1982). The enthalpy of dilution of HF(aq), reaction 9, is based on an earlier study at this laboratory (Johnson et al., 1973). The enthalpy of formation of HF·3.4432H<sub>2</sub>O is based on the value for  $\Delta H_f^\circ(\text{F}^-, \text{aq})$  selected by CODATA (1978). For reactions 11, 12, and 13 the enthalpies of formation of H<sub>2</sub>O(1) (CODATA, 1978), SiO<sub>2</sub>( $\alpha$ ) (Wise et al., 1963), and Al(OH)<sub>3</sub> (Hemingway and Robie, 1977) were taken from the literature. For reactions 14, 15, 16, 17, and 18 the enthalpies of formation of NaF, KF, BaF<sub>2</sub>, SrF<sub>2</sub>, and CaF<sub>2</sub> were taken from Parker et al. (1976). The standard enthalpy of formation,  $\Delta H_f^\circ(298.15 \text{ K})$ , for heulandite was calculated to be  $-10491.1 \pm 10.2$  kJ/mol.

#### Enthalpy-increment measurements

The drop calorimeter used for the enthalpy increment measurements on heulandite has been described in detail (Fredrickson et al., 1969). The system consisted essentially of a resistance-heated, molybdenum-core furnace and a copper-block calorimeter. Measurements of the furnace temperature were made with platinum-to-(platinum + 10 per cent rhodium) thermocouples. The temperature of the calorimeter was determined with a quartz-crystal thermometer. The energy equivalent of the empty calorimeter was determined by electrical calibrations. For the present experiments, the calorimeter and furnace were filled with helium at a pressure of about 13 mbar, which substantially decreased equilibration times within the furnace and allowed measurements to be conducted at temperatures as low as 350 K. The performance of the calorimetric system was checked (Johnson et al., 1980) by determining the en-

Table 5. Thermochemical cycle used to derive the standard enthalpy of formation of heulandite at 298.15 K

Reaction	$\frac{\Delta H}{\text{(kJ/mol)}}$
1. $6.835\text{SiO}_2(\text{a}) + 5051.00\text{HF} \cdot 17391.79\text{H}_2\text{O} \rightarrow [\text{A}]^*$	$-926.76 \pm 1.23$
2. $2.165\text{Al}(\text{OH})_3(\text{c}) + [\text{A}]^* \rightarrow [\text{B}]^{**}$	$-360.65 \pm 0.24$
3. $0.383\text{NaF}(\text{c}) + [\text{B}]^{**} \rightarrow [\text{C}]^\dagger$	$-1.85 \pm 0.13$
4. $0.132\text{KF}(\text{c}) + [\text{C}]^\dagger \rightarrow [\text{D}]^{\dagger\dagger}$	$-3.77 \pm 0.22$
5. $0.065\text{BaF}_2(\text{c}) + [\text{D}]^{\dagger\dagger} \rightarrow [\text{E}]^{\dagger\dagger\dagger}$	$-1.06 \pm 0.10$
6. $0.175\text{SrF}_2(\text{c}) + [\text{E}]^{\dagger\dagger\dagger} \rightarrow [\text{F}]^\ddagger$	$0 \pm 0.20$
7. $0.585\text{CaF}_2(\text{c}) + [\text{F}]^\ddagger \rightarrow [\text{G}]^\ddagger\ddagger$	$0 \pm 0.20$
8. $[\text{G}] \rightarrow (\text{Ba}_{0.065}\text{Sr}_{0.175}\text{Ca}_{0.585}\text{K}_{0.132}\text{Na}_{0.383})$ $\text{Al}_{2.165}\text{Si}_{6.835}\text{O}_{18} \cdot 6\text{H}_2\text{O}(\text{c})$ $+ 5053.165\text{HF} \cdot 17387.955\text{H}_2\text{O}$	$1439.06 \pm 0.85$
9. $5053.165\text{HF} \cdot 17387.955\text{H}_2\text{O} + 11.290\text{H}_2\text{O}(\text{l}) \rightarrow$ $5053.165\text{HF} \cdot 17399.245\text{H}_2\text{O}$	$-4.58 \pm 0.25$
10. $2.165(\text{HF} \cdot 3.4432\text{H}_2\text{O}) \rightarrow 1.0825\text{H}_2(\text{g})$ $+ 1.0825\text{F}_2(\text{g}) + 7.455\text{H}_2\text{O}(\text{l})$	$694.86 \pm 1.45$
11. $3.835\text{H}_2(\text{g}) + 1.9175\text{O}_2(\text{g}) + 3.835\text{H}_2\text{O}(\text{l})$	$-992.61 \pm 0.15$
12. $6.835\text{Si}(\text{c}) + 6.835\text{O}_2(\text{g}) \rightarrow 6.835\text{SiO}_2(\text{a})$	$-6226.00 \pm 9.57$
13. $2.165\text{Al}(\text{c}) + 3.2475\text{H}_2(\text{g}) + 3.2475\text{O}_2(\text{g})$ $\rightarrow 2.165[\text{Al}(\text{OH})_3]$	$-2799.56 \pm 2.60$
14. $0.383\text{Na}(\text{c}) + 0.1915\text{F}_2(\text{g}) \rightarrow 0.383\text{NaF}(\text{c})$	$-220.82 \pm 0.26$
15. $0.132\text{K}(\text{c}) + 0.066\text{F}_2(\text{g}) \rightarrow 0.132\text{KF}(\text{c})$	$-75.21 \pm 0.09$
16. $0.065\text{Ba}(\text{c}) + 0.065\text{F}_2(\text{g}) \rightarrow 0.065\text{BaF}_2(\text{c})$	$-79.01 \pm 0.27$
17. $0.175\text{Sr}(\text{c}) + 0.175\text{F}_2(\text{g}) \rightarrow 0.175\text{SrF}_2(\text{c})$	$-214.02 \pm 0.74$
18. $0.585\text{Ca}(\text{c}) + 0.585\text{F}_2(\text{g}) \rightarrow 0.585\text{CaF}_2(\text{c})$	$-719.12 \pm 0.25$
19. $0.065\text{Ba}(\text{c}) + 0.175\text{Sr}(\text{c}) + 0.585\text{Ca}(\text{c})$ $+ 0.132\text{K}(\text{c}) + 0.383\text{Na}(\text{c}) + 2.165\text{Al}(\text{c})$ $+ 6.835\text{Si}(\text{c}) + 120_2(\text{g}) + 6\text{H}_2(\text{g}) \rightarrow \text{Heulandite}$	$\Delta H_f^\circ = -10491.1 \pm 10.2 \text{ kJ mol}^{-1}$



### Enthalpy-increment results

The results of the drop-calorimetric experiments are given in Table 6 in order of increasing temperature.

The energy equivalent of the calorimeter,  $\epsilon(\text{calor})$ , varies slightly as a function of  $\Delta\theta_c$ , from 4379.46 J/K for  $\Delta\theta_c \approx 0.5$  K to 4378.68 J/K for  $\Delta\theta_c \approx 1.5$  K. The enthalpy contribution of the capsule was determined in a separate series of experiments with an empty (platinum + 10% rhodium) capsule with dimensions and mass similar to that used for the present experiments. The measured enthalpy was corrected for the enthalpy of the air in the capsule, for the difference (usually less than 0.01 K) of the final calorimetric temperature from 298.15 K, and for the water vapor produced by thermal dehydration of the zeolite. Below 373 K the vapor pressure of water over heulandite was calculated from equation (1). Above 373 K, this equation was not used because the calculated equilibrium pressures were greater than those over pure water. Hence, for temperatures greater than 373 K it was assumed that the water vapor pressure over heulandite was the same as that over pure water. Experiments were not extended beyond 475 K because the capsule began to deform, presumably due to the water-vapor pressure.

The enthalpy increments for heulandite, including those between 298.15 and 350 K from the low-temperature study, were fitted as a function of  $T$  over the range 298.15 to 475 K by the method of least squares. The following equation adequately represented the results:

$$H^\circ(T) - H^\circ(298.15 \text{ K}) = 14108349.5 T^{-1} - 298553.8 + 745.55 T - 0.325666 T^2 (\text{J/mol}). \quad (2)$$

Table 6. Drop-calorimetric results for heulandite\*

Expt. No.	$\frac{T}{\text{K}}$	$\frac{\Delta\theta_c}{\text{K}}$	$\frac{\epsilon(\text{calor})(\Delta\theta_c)}{\text{J}}$	$\frac{\Delta H(\text{capsule})}{\text{J}}$	$\frac{\Delta H(\text{H}_2\text{O})}{\text{J}}$	$\frac{H^\circ(T) - H^\circ(298.15)^{**}}{\text{J/mol}}$
3	350.65	0.11192	488.54	-142.20	-1.46	42968
1	351.41	0.11319	494.09	-144.28	-1.46	43397
2	375.80	0.16841	735.12	-211.25	-4.16	64738
5	376.09	0.16928	738.92	-212.05	-4.16	65122
4	399.52	0.22445	979.72	-276.82	-8.52	86501
7	399.94	0.22562	984.83	-277.98	-8.52	87001
6	424.44	0.28487	1243.44	-346.10	-16.22	109755
9	424.51	0.28519	1244.83	-346.30	-16.22	109918
11	450.07	0.34962	1525.17	-417.73	-29.07	134321
8	450.18	0.34974	1526.57	-418.04	-29.07	134470
10	475.40	0.41563	1814.13	-488.84	-47.93	159124

\*The entries in the table are:  $T$ , the temperature of the furnace and sample;  $\Delta\theta_c$ , the change in temperature of the calorimeter corrected for heat exchange with the surroundings;  $\epsilon(\text{calor})(\Delta\theta_c)$ , the energy absorbed by the calorimetric system;  $\Delta H(\text{capsule})$ , the enthalpy contribution due to the capsule;  $\Delta H(\text{H}_2\text{O})$ , the correction applied for the condensation of the water vapor in the capsule; and  $H^\circ(T) - H^\circ(298.15 \text{ K})$ , the standard enthalpy at temperature  $T$  relative to 298.15 K.

\*\*Includes corrections for the enthalpy of the air in the capsule, and for the difference between the final temperature of the experiment and 298.15 K.

enthalpy of synthetic sapphire (National Bureau of Standards Standard Reference Material 720) over the temperature range from 374 to 836 K.

The sample of heulandite (mass, 5.6834 g) was contained in a welded (platinum + 10% rhodium) capsule (1.2 cm diameter, 4.8 cm long, 5.35 cm<sup>3</sup> internal volume, and 19.1243 g mass) which also included  $1.14 \times 10^{-4}$  mol of air.

This fit was constrained to give, at  $T = 298.15$  K,  $H^\circ(T) - H^\circ(298.15 \text{ K}) = 0$  and  $C_p^\circ(T) = 781.0 \text{ J}/(\text{mol} \cdot \text{K})$ . The root-mean-square deviation on the results from equation (2) is 0.28%.

The first derivative of equation (2) yielded the following expression for the heat capacity of heulandite above 298.15 K:

$$C_p^\circ(T) = -14108349.5 T^{-2} + 745.55 + 0.65133 T \text{ J}/(\text{mol} \cdot \text{K}) \quad (3)$$

### Thermodynamic functions of heulandite

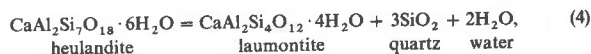
Table 7 gives the thermodynamic functions for heulandite at 20 K intervals and also at 298.15 K. The heat capacities and enthalpies up to 340 K have been taken from the low-temperature study. For the calculation of  $\Delta H_f^\circ(T)$  and  $\Delta G_f^\circ(T)$ , we used the heat capacities and entropies of Ba, Sr, Ca, K, Na, Al, Si, O<sub>2</sub> and H<sub>2</sub> from the compilation of Robie et al. (1978). At 298.15 K the standard entropy of formation,  $\Delta S_f^\circ$  and Gibbs energy of formation,  $\Delta G_f^\circ$ , are  $-2734.9 \pm 1.7 \text{ J}/(\text{mol} \cdot \text{K})$  and  $-9675.6 \pm 10.2 \text{ kJ}/\text{mol}$  respectively.

### Discussion

It is instructive to compare the entropy contribution at 298.15 K of the zeolitic water molecules in heulandite with that in the other zeolites that have been studied. The entropy of anhydrous heulandite was calculated by summing the entropies of 0.065 moles of BaO, 0.175 moles of SrO, (0.065 + 0.175) moles of corundum,  $\{(0.065 + 0.175) \times 2 + 4.670\}$  moles of quartz, 0.585 moles of anorthite, 0.132 moles of microcline, and 0.383 moles of albite. This sum, 464.4 J/(mol · K), is subtracted from the measured 767.2 J/(mol · K) to obtain 302.8 J/(mol · K) as the total contribution for the 6 H<sub>2</sub>O molecules, or 50.5 J/(mol · K) per molecule.

Johnson et al. (1983) showed that the water tightly bonded in such zeolites as natrolite and scolecite contributes only 32 J/(mol · K) at 298.15 K. However, in analcime the entropy contribution is 55 J/(mol · K) (Johnson et al., 1982) and in clinoptilolite it is 57 J/(mol · K) as calculated from data in Hemingway and Robie (1984), both values closer to that of liquid water, 70 J/(mol · K), than to that of ice, 38 J/(mol · K).

The Gibbs free energy of formation of heulandite obtained by calorimetry,  $-9675.6 \pm 10.2 \text{ kJ}/\text{mol}$ , can be compared with a value which can be extracted from the experimental work by Maruyama et al. (1983). They observed that heulandite and laumontite coexisted in equilibrium at  $463 \pm 5 \text{ K}$  at 1.5 kbar and  $478 \pm 5 \text{ K}$  and 2.0 kbar. If the reaction is written:



then the extracted value for  $\Delta G_f^\circ(298.15 \text{ K})$  is  $-9722.2 \text{ kJ}/\text{mol}$  based on the procedures outlined in Helgeson et al. (1978). The auxiliary data for laumontite and quartz were taken from Helgeson et al. (1978), for water from Helgeson and Kirkham (1974) and for heulandite from this study. We realize that the actual compositions of heulandite and laumontite that coexist in equilibrium might differ significantly from the idealized compositions shown in reaction (4) and this could significantly change the derived  $\Delta G_f^\circ$ . However, as Maruyama et al. do not give any analytical data for the equilibrium compositions, we cannot extract meaningful  $\Delta G_f^\circ$  values for heulandite from their work.

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Table 7. Thermodynamic properties of heulandite

$T$ K	$C_p^\circ(T)$ J/(mol K)	$[H^\circ(T) - H^\circ(298 \text{ K})]/T$ J/(mol K)	$-[G^\circ(T) - H^\circ(298 \text{ K})]/T$ J/(mol K)	$S^\circ(T) - S^\circ(0)$ J/(mol K)	$H^\circ(T) - H^\circ(298 \text{ K})$ J/mol	$\Delta H_f^\circ(T)$ kJ/mol	$\Delta G_f^\circ(T)$ kJ/mol
298.15	781.03	0	767.18	767.18	0	-10491.1	-9675.7
300	784.17	4.83	767.19	772.02	1448	-10491.0	-9670.6
320	816.62	54.57	769.11	823.68	17461	-10490.1	-9615.9
340	846.04	100.27	773.82	874.09	34092	-10489.0	-9561.4
360	871.16	142.33	780.75	923.08	51239	-10487.2	-9506.8
380	895.35	181.33	789.50	970.84	68907	-10486.0	-9452.4
400	917.90	217.60	799.74	1017.34	87042	-10483.5	-9398.1
420	939.13	251.46	811.18	1062.65	105614	-10480.6	-9343.8
440	959.26	283.18	823.62	1106.80	124600	-10477.5	-9289.9
460	978.48	313.00	836.87	1149.87	143979	-10474.0	-9235.9
480	996.95	341.11	850.80	1191.91	163734	-10470.2	-9182.1

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