Thermodynamic studies of mordenite, dehydrated mordenite, and gibbsite

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Abstract

Calorimetric measurements have been carried out on a natural sample of mordenite from Goble, Oregon, having the composition $Ca_{0.289}Na_{0.361}Al_{0.940}Si_{5.060}O_{12} \cdot 3.468H_2O$ and also on this same material in the dehydrated form. Low-temperature adiabatic calorimetry, high-temperature drop calorimetry, and solution-reaction calorimetry have been used to derive the thermodynamic properties of mordenite from $T \rightarrow 0$ to 500 K and of dehydrated mordenite from $T \rightarrow 0$ to 900 K. The following values have been obtained at $T = 298.15$ K and $P^0 = 0.1013$ MPa:

	$\Delta H_f^0(T)$ (kJ/mol)	$C_P^0(T)$ [J/(mol·K)]	$S^0(T) - S^0(0)$ [J/(mol·K)]	$\Delta G_f^0(T)$ (kJ/mol)
mordenite	-6756.2 ± 4.5	484.33 ± 0.97	486.54 ± 0.97	-6247.6 ± 4.5
dehydrated mordenite	-5661.8 ± 4.6	295.76 ± 0.59	299.10 ± 0.60	$-5338.6 \pm 4.6.$

The average binding energy and entropy of zeolitic H_2O in mordenite are 29.7 ± 1.8 kJ/mol and 54.05 ± 0.33 J/(mol·K), respectively. The enthalpy of formation of gibbsite, $Al(OH)_3$, which is an important auxiliary value used to derive the enthalpies of formation of aluminosilicates, was determined to be -1294.9 ± 1.2 kJ/mol. Revised enthalpy of formation and Gibbs energy of formation values are tabulated for analcime, dehydrated analcime, natrolite, scolecite, mesolite, and heulandite.

Introduction

Mordenite commonly occurs with stilbite or heulandite (or clinoptilolite) in basalt amygdules, as an authigenic replacement of volcanic glass in tuff deposits, and as a hydrothermal mineral in geothermal areas (Gottardi and Galli, 1985). In the present paper, a thermodynamic investigation of mordenite and dehydrated mordenite is described. This study forms part of a program to determine calorimetrically the thermodynamic properties of naturally occurring zeolites. Earlier results in this series have been published (Johnson et al., 1982, 1983, 1985, 1989; Howell et al., 1990). Mordenite is of interest because it is abundant in nature and is the most siliceous of all zeolites. Unlike many other zeolites, it can be converted to the dehydrated form without collapse of the aluminosilicate framework (Van Reeuwijk, 1974; Breck, 1974); thus, the calorimetric investigations can give insight into the nature of zeolitic H_2O.

Because the standard molar enthalpies of formation

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ΔH_f^0 of mordenite and its anhydride, as well as those of zeolites previously studied at this laboratory (Johnson et al., 1982, 1983, 1985, 1989; Howell et al., 1990), are based in part on the enthalpy of formation of gibbsite, $\Delta H_f^0[Al(OH)_3]$ is a key auxiliary quantity in our studies. We have determined this value from measurements of the enthalpies of reaction of Al and $Al(OH)_3$ with HF(aq) and report these results in the present paper.

Previously, we referred ΔH_f^0 of zeolites to, inter alia, the molar enthalpy of formation of SiO_2 (α quartz) and its enthalpy of reaction with HF(aq) because α quartz has traditionally been used as a base material in silicate thermochemistry. However, from a practical standpoint, it has the serious disadvantage for calorimetric studies conducted at temperatures close to 298.15 K that its reaction with HF(aq) is extremely slow, and as a consequence, the enthalpy of reaction is correspondingly very uncertain.

This undesirable situation can be greatly improved upon by using instead a polymorph of SiO_2, silicalite. This material reacts spontaneously and very rapidly with HF(aq), and we have recently (Johnson et al., 1987) determined its enthalpy of formation by F_2 combustion calorimetry and its enthalpy of reaction with HF(aq). Although the
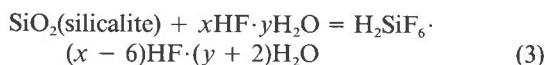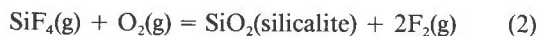
TABLE 1. Analysis, cell contents, and lattice parameters for mordenite and dehydrated mordenite (Goble, Columbia County, Oregon)

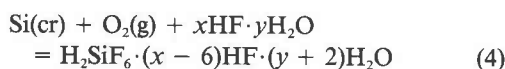| Sample composition (mass percent)			Cell contents (number of atoms)		Lattice parameters	
			A*	B**	Mordenite (nm)	Dehydrated mordenite (nm)
SiO_2	68.62	Si	40.480	5.060	$a = 1.808(5)$	$a = 1.802(4)$
Al_2O_3	10.79	Al	7.520	0.940	$b = 2.043(6)$	$b = 2.040(5)$
CaO	3.83	Ca	2.312	0.289	$c = 0.7506(3)$	$c = 0.7499(2)$
Na_2O	2.64	Na	2.888	0.361		
H_2O	14.12	H_2O	27.744	3.468		

* A = Cell contents based on 96 framework O atoms.
** B = Idealized composition (12 framework O atoms) used for calculation of molar thermodynamic properties.

scientific community has not yet adopted silicalite as a thermochemical reference standard for solution-reaction calorimetry, we feel that, for this purpose, it is superior to α quartz, especially for reactions at or near 298.15 K, and we have used it as such. Surface energy effects in the silicalite are not a concern here as, in the overall Hess cycle used to derive the enthalpy of formation of a silicate by solution calorimetry in HF, the silicalite cancels out. If we consider the three experimental calorimetric reactions:

$$Si(cr) + 2F_2(g) = SiF_4(g) \quad (1)$$

$$SiF_4(g) + O_2(g) = SiO_2(silicalite) + 2F_2(g) \quad (2)$$

$$SiO_2(silicalite) + xHF \cdot yH_2O = H_2SiF_6 \cdot (x - 6)HF \cdot (y + 2)H_2O \quad (3)$$

their sum is given by

$$Si(cr) + O_2(g) + xHF \cdot yH_2O = H_2SiF_6 \cdot (x - 6)HF \cdot (y + 2)H_2O \quad (4)$$

which is independent of silicalite and, thus, surface effects therein. That does not imply that in either Reactions 2 or 3 surface energy may not play a role, rather that, by combining them, such effects should cancel. Accordingly, we have recalculated our earlier results to refer to silicalite as the SiO_2 base.

MATERIALS

Mordenite

The mordenite used in the present study was taken from a small quarry 0.2 km north of Goble, Columbia County, Oregon. It occurred as a mass of needles filling cavities in a basalt breccia. Individual crystals were about 5 mm in length and 0.1 mm in width. A stock of about 12 g was prepared by hand-picking scattered stilbite crystals from the mordenite fibers. A sample of crushed fibers was embedded in epoxy and ground to expose a number of crystals. About 25 grains were analyzed with an ARL

electron microprobe equipped with a Tracor EDS system. For all elements, the accelerating voltage was 15 kV, the sample current was 9 nA, and the beam diameter was defocused to about 20 μm. The elements commonly found in zeolites, namely, Na, Al, Si, K, Ca, Mg, Fe, Sr, and Ba, were sought, but only Na, Ca, Al, and Si were found in amounts over 0.02 mass%. Albite, microcline, and andesine were used as analytical standards. Because the mordenite fibers were so thin, accurate analyses for Na and Ca could not be obtained by the microprobe technique; instead, Na was determined by atomic absorption and Ca by ICP methods. Even so, consistent totals of the elemental components could not be obtained, although the mole ratio of Si to Al was very nearly constant at 5.38 $\pm$ 0.05. The H_2O content was deduced by dehydrating (at 873 K for 24 h) to constant mass a portion of the mordenite that had been equilibrated with an atmosphere at 50% relative humidity. The microprobe analytical results for Al and Si, relatively low because of the fibrous nature of the mordenite, were increased to give a total of 100% for the sum of the oxides. Details of the analyses are given in Table 1.

Cell dimensions for mordenite and dehydrated mordenite were refined from X-ray powder diffraction data, which were obtained with a Scintag DAD X diffractometer equipped with a heating stage and vacuum system. The data were from a single sample of ground mordenite mixed with Si (NIST Standard Reference Material 6400) as an internal standard. This was first X-rayed under atmospheric conditions, then heated to 773 K at a pressure of 1.3×10^{-3} Pa over a period of 4 h, cooled to room temperature, and X-rayed again while still under vacuum. The results are shown in Table 1.

Because mordenite readily loses H_2O, even at room temperature, all our analytical and thermodynamic results refer to mordenite in equilibrium with an atmosphere of 50% relative humidity.

Dehydrated mordenite

Dehydrated mordenite was prepared by heating a portion of the mordenite sample at 900 K in an He atmosphere glove box for several days; the product was stored in the glove box and exposed only to the dry He following dehydration to constant mass.

Gibbsite

Gibbsite, $Al(OH)_3$, was Fisher reagent $Al_2O_3 \cdot 3H_2O$ which, before use, had been heated for approximately 6 h at 423 K.

Al

The Al was part of a single-crystal bar (Leytess Chemical Co.). Filings taken from this bar in the glove box were subjected to chemical and spectrochemical analysis, and the following impurities (mass fraction $\times 10^{-6}$) were found: 0, 663; C, 40; N, 231; H, 33; Mg, 5; and Mn, 5.

Hydrofluoric acid

Hydrofluoric acid was Fisher reagent HF diluted with distilled H_2O to a concentration of approximately 24.4 mass%.

APPARATUS, EXPERIMENTAL PROCEDURES, AND RESULTS

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

Heat-capacity measurements

Different calorimeters were used for the hydrated and dehydrated mordenite because of the diverse handling requirements of each sample.

For the measurements on dehydrated mordenite, the calorimeter (laboratory designation 6-GS-1) was constructed from high-thermal-conductivity, O-free Cu and had an internal volume of 5.976 cm³ at 298.15 K. It was loaded with 3.2498 g of dehydrated mordenite in a glove box filled with dry He. The calorimeter was evacuated, and 1.84×10^{-5} mol of He was added to promote rapid thermal equilibration during heat-capacity measurements. The calorimeter was sealed by means of an Au gasket and knife edge. For buoyancy corrections and volume calculations, the density of dehydrated mordenite was taken to be 1.83 g/cm³, calculated from the unit-cell dimensions. Further details on calorimeter 6-GS-1 are available in the literature (Osborne et al., 1972; Westrum et al., 1953; Johnson et al., 1982).

A specially modified calorimeter was used for the measurements on mordenite to permit the sample to be loaded into the calorimeter and sealed without altering its H_2O content. The calorimeter (laboratory designation C5-B) was that used in our earlier heat-capacity measurements on heulandite (Johnson et al., 1985) with a modification to prevent sample loss during evacuation of air. C5-B was of the same general design as 6-GS-1 but was much larger (internal volume, 36.93 cm³ at 298.15 K), and its cover had a cylindrical loading port (0.59 cm internal diameter, 0.65 cm high) and an attachment for removing air and sealing the calorimeter. For the measurements on mordenite, the attachment was simply a Cu tube with a diameter of 0.2 cm soldered to the calorimeter with 50:50 (Pb + Sn) solder. This tube permitted removal of air but led to the loss of a minor amount of sample. To prevent this, a small L-shaped Cu fitting with square cross section 0.32 cm wide was drilled out to receive the Cu tube and the small connection port on the lid. Cu-felt disc (0.24 cm diameter and 0.05 cm thick) was placed inside the L-shaped fitting and held firmly against the mouth of the port by a Cu spacer inside the fitting. The calorimeter top, fitting, and tube were attached with 50:50 (Pb + Sn) solder. The calorimeter was loaded with mordenite, the filing port cover attached with the solder, and the entire assembly was placed in a 50% relative humidity atmosphere for 24 h. During that time, the Cu tube was left open and equilibrium was monitored by weighing. Next, the Cu 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 (carbon dioxide + acetone) bath at 195 K to reduce the sample temperature so that its equilibrium H_2O vapor pressure would be very low (of the order of 0.1 Pa or lower). The air was then pumped from the calorimeter, and 4.8×10^{-5} mol of He was added to promote rapid temperature equilibrium during the heat-capacity measurements. The Cu tube was sealed by pinching it closed. The calorimeter was shown to be sealed by testing it with an He-leak detector.

Descriptions of the cryostat, peripheral equipment, and calorimetric procedure are available in the literature (Osborne et al., 1972; Westrum et al., 1953; Johnson et al., 1982). Experimental temperatures were measured with a calibrated Pt-resistance thermometer, a calibrated double potentiometer, and a photogalvanometer. The temperature scale used agrees with the thermodynamic scale (IPTS-68) to ±0.1 K from 5 to 14 K, to ±0.03 K from 14 to 90 K, and to ±0.05 K from 90 to 350 K. Temperature differences are reliable to ±0.01 K at 4.2 K, to ±0.0008 K at 14 K, to ±0.0001 K from 25 to 58 K, and to ±0.001 K above 58 K. A preset timer calibrated against NIST station WWV was used to fix the heating time with an uncertainty of less than ±0.01%. All standards of mass, resistance, and voltage are traceable to the National Institute of Standards and Technology. The only significant difference between the equipment used in this work and that described in the literature is that the thermocouple linking the calorimeter with the middle adiabatic shield is now made of chromel P and Au + 7 mass% of Fe.

Heat-capacity results

Since mordenite has a significant equilibrium H_2O-vapor pressure above 273 K and the calorimeter had a considerable free internal volume (30.4 cm³), it was necessary to correct the measured heat capacities for the enthalpy effect due to the vaporization of H_2O that occurred during heating. To do this, we have employed the equation ($P^0 = 0.1013$ MPa)

$$\lg(P/P^0) = 15.458 - 5785/T \qquad (5)$$

where T is expressed in kelvins, to represent the vapor pressure of H_2O in equilibrium with mordenite. The results given by Van Reeuwijk (1974) were used to develop this equation. The enthalpy of vaporization of the zeolitic H_2O, 48.1 kJ/mol, was also taken from Van Reeuwijk (1974). The vaporization correction decreased the measured heat capacities by 0.03% near 300 K and by 0.44% near 350 K. For both mordenite and dehydrated mordenite, the experimental molar heat capacities were calculated as the difference between the results obtained with the loaded calorimeter and those previously obtained for the empty calorimeter. Minor corrections were made for differences in the amounts of He, Apiezon-T grease, Cu,

TABLE 2. Experimental molar heat capacities of mordenite (P^0 = 0.1013 MPa)

$\langle T \rangle$ (K)	$C_P^0(T)$ [J/(mol·K)]	T (K)	$C_P^0(T)$ [J/(mol·K)]
7.04	0.953	85.72	153.08
7.82	1.235	87.29	156.54
8.75	1.615	94.21	170.56
9.90	2.197	103.00	187.80
10.94	2.891	112.60	207.04
11.99	3.773	122.49	226.37
13.14	4.943	132.42	245.85
13.99	5.934	142.45	264.81
15.29	7.645	152.58	283.45
16.06	8.717	162.75	301.63
17.49	10.90	172.87	320.67
18.14	11.95	182.78	339.08
19.67	14.49	192.57	356.92
20.27	15.53	202.36	373.64
22.63	19.80	212.21	388.74
23.47	21.42	222.15	404.11
25.74	25.86	232.16	417.51
28.52	31.58	242.09	430.16
31.50	37.90	252.18	441.99
34.76	44.84	262.25	451.97
38.41	52.67	272.28	462.34
42.50	61.51	282.27	471.32
47.15	71.53	292.24	479.81
52.22	82.60	302.21	487.18
52.51	83.30	312.16	495.02
58.05	95.37	322.05	501.26
64.23	108.59	331.66	507.14
71.02	122.82	341.00	512.58
78.74	138.61	347.93	515.42

TABLE 4. Low-temperature thermodynamic functions of mordenite (P^0 = 0.1013 MPa)

T (K)	$C_P^0(T)$ [J/(mol·K)]	$S^0(T) - S^0(0)$ [J/(mol·K)]	$H^0(T) - H^0(0)$ (J/mol)	$-[G^0(T) - H^0(0)]/T$ [J/(mol·K)]
5	0.310	0.0526	0.195	0.014
10	2.262	0.787	6.030	0.184
15	7.235	2.514	28.16	0.637
20	15.06	5.624	83.14	1.467
25	24.38	9.961	181.20	2.713
30	34.69	15.31	328.7	4.354
35	45.33	21.45	528.6	6.350
40	56.10	28.21	782.2	8.655
45	66.94	35.44	1090	11.23
50	77.82	43.06	1452	14.02
60	99.48	59.16	2338	20.19
70	120.73	76.10	3440	26.96
80	141.46	93.58	4751	34.19
90	161.81	111.42	6268	41.78
100	181.96	129.51	7987	49.65
120	221.70	166.22	12025	66.01
140	259.98	203.29	16845	82.97
160	297.04	240.43	22416	100.33
180	333.88	277.54	28725	117.96
200	369.43	314.59	35763	135.77
220	401.00	351.32	43475	153.70
240	427.48	387.38	51768	171.68
260	450.01	422.51	60548	189.63
280	469.39	456.58	69748	207.48
300	485.74	489.54	79303	225.20
320	500.06	521.36	89164	242.72
340	511.80	552.04	99289	260.02
350	516.45	566.95	104 430	268.57
273.15	463.11	445.03	66554	201.38
298.15	484.33	486.54	78406	223.57

TABLE 3. Experimental molar heat capacities of dehydrated mordenite (P^0 = 0.1013 MPa)

$\langle T \rangle$ (K)	$C_P^0(T)$ [J/(mol·K)]	T (K)	$C_P^0(T)$ [J/(mol·K)]
6.65	0.532	85.32	95.07
8.24	1.028	89.47	101.44
10.29	1.945	93.82	107.10
11.94	3.000	96.69	110.09
12.51	3.426	103.11	117.78
13.42	4.158	112.63	129.38
14.35	4.873	122.37	141.38
14.96	5.416	132.24	152.30
16.13	6.381	142.29	163.86
16.64	6.962	152.28	174.75
17.84	8.014	162.25	185.05
18.42	8.724	172.25	195.37
19.62	9.910	182.20	204.44
20.29	10.75	192.61	214.85
24.12	14.97	203.11	223.60
26.05	17.32	213.41	232.43
27.94	19.78	223.54	240.62
29.92	22.34	233.65	248.28
32.27	25.42	243.76	257.51
34.98	29.04	254.01	265.21
37.98	33.09	264.41	272.98
41.29	37.42	274.82	280.86
44.86	42.04	284.82	286.10
48.80	47.29	295.02	293.93
53.09	52.82	305.24	300.20
57.77	59.02	315.49	308.26
63.06	65.74	325.78	316.38
68.98	73.34	335.90	321.65
75.51	82.13	345.87	327.40
82.48	90.98		

solder, and Au between the two sets of experiments. A small curvature correction, $-(d^2C_P^0/dT^2)(\Delta T)^2/24$, was applied to each heat-capacity determination. At 5 K, the sample accounted for about 47% of the total heat capacity for mordenite and 15% for dehydrated mordenite; at 20 K, the corresponding values were 52% and 21%; at 100 K, 33% and 11%; and from 200 to 350 K, approximately 44% and 17%. The results are given in Tables 2 and 3 and are estimated to be uncertain by ±5% near 6 K, ±1% near 14 K, and ±0.2% above 20 K. For each set of results in Tables 2 and 3, C_P^0 values were fitted by means of a weighted least-squares routine to two polynomials in $\langle T \rangle$, one for the region below 40 K, the other for the region above 20 K. For mordenite, the polynomials merged smoothly at 27.8 K and the standard deviations of the experimental from the calculated results in each region were ±0.14% and ±0.10%. For dehydrated mordenite, the polynomials merged smoothly at 26.05 K with their standard deviations being ±0.38% and ±0.27%. Heat capacities below 11 K were plotted as C_P^0/T against T^2 and smoothly extrapolated to $T \rightarrow 0$. For the calculation of thermodynamic properties at 5 K and below, it was assumed that $C_P^0(T) = AT^3$. Above 5 K, thermodynamic quantities were obtained by appropriate integration of the polynomials in the applicable temperature ranges. The results at rounded temperatures are given in Tables 4 and 5.

TABLE 5. Low-temperature thermodynamic functions of dehydrated mordenite (P^o = 0.1013 MPa)

T (K)	$C_p^o(T)$ [J/(mol·K)]	$S^o(T) - S^o(0)$ [J/(mol·K)]	$H^o(T) - H^o(0)$ (J/mol)	$-[G^o(T) - H^o(0)]/T$ [J/(mol·K)]
5	0.226	0.075	0.282	0.019
10	1.824	0.606	4.554	0.151
15	5.420	1.966	21.93	0.504
20	10.37	4.180	61.00	1.130
25	16.06	7.094	126.8	2.021
30	22.44	10.58	222.8	3.150
35	29.09	14.53	351.6	4.488
40	35.73	18.85	513.7	6.011
45	42.29	23.44	708.8	7.691
50	48.78	28.23	936.5	9.504
60	61.75	38.27	1489	13.45
70	74.91	48.78	2172	17.75
80	88.21	59.65	2988	22.30
90	101.41	70.80	3936	27.07
100	114.25	82.15	5015	32.01
120	138.50	105.16	7545	42.28
140	161.18	128.22	10544	52.91
160	182.74	151.17	13985	63.76
180	202.80	173.87	17844	74.74
200	220.98	196.19	22084	85.77
220	237.77	218.05	26673	96.80
240	254.03	239.43	31592	107.80
260	269.67	260.39	36831	118.74
280	283.82	280.91	42368	129.59
300	296.99	300.94	48177	140.35
320	311.29	320.55	54257	151.00
340	324.95	339.85	60626	161.54
350	329.82	349.35	63900	166.77
273.15	279.16	273.93	40440	125.88
298.15	295.76	299.10	47628	139.36

TABLE 6. Enthalpies of reaction (298.15 K) with HF(aq) of mordenite, dehydrated mordenite, Al, and gibbsite*

m (g)	$\Delta\theta_c$ (K)	ϵ(calor) (J/K)	ϵ(calor) $(-\Delta\theta_c)$ (J)	ΔH_{corr}** (J)	$\Delta H/M$ (J/g)
Mordenite, Ca$_{0.289}$Na$_{0.361}$Al$_{0.940}$Si$_{5.060}$O$_{12}$·3.468H$_2$O (M = 441.827 g/mol)					
0.14510	0.74815	403.20	−301.65	0.09	−2078.3
0.14500	0.74852	402.66	−301.40	0.09	−2078.0
0.14469	0.74570	403.26	−300.71	0.09	−2077.7
0.14458	0.74541	402.64	−300.13	0.09	−2075.3
0.14560	0.75045	403.21	−302.59	0.09	−2077.6
0.14587	0.75359	402.66	−303.40	0.09	−2079.3

$\langle\Delta H/M\rangle$ = −2077.7 ± 0.5 J/g†
ΔH_r = −917.98 ± 0.44 kJ/mol‡

Dehydrated mordenite, Ca$_{0.289}$Na$_{0.361}$Al$_{0.940}$Si$_{5.060}$O$_{12}$ (M = 379.350 g/mol)					
0.12139	0.80823	403.32	−325.98	0.08	−2684.7
0.12216	0.81371	404.14	−328.85	0.08	−2691.3
0.12166	0.80939	404.18	−327.14	0.08	−2688.3
0.11935	0.79496	403.96	−321.13	0.08	−2690.0
0.12283	0.81523	404.58	−329.83	0.08	−2684.6

$\langle\Delta H/M\rangle$ = −2687.8 ± 1.4 J/g†
ΔH_r = −1019.6 ± 1.1 kJ/mol‡

Gibbsite, Al(OH)$_3$ (M = 78.0036 g/mol)					
0.02585	0.13597	402.72	−54.76	0.08	−2115.3
0.02564	0.13463	403.47	−54.32	0.08	−2115.4
0.02562	0.13403	405.85	−54.40	0.08	−2120.2
0.02601	0.13752	403.08	−55.43	0.08	−2128.0
0.02532	0.13374	403.54	−53.97	0.08	−2128.4
0.02563	0.13481	403.50	−54.40	0.08	−2119.4
0.02570	0.13497	404.20	−54.55	0.08	−2119.5

$\langle\Delta H/M\rangle$ = −2120.9 ± 2.0 J/g†
ΔH_r = −165.44 ± 0.31 kJ/mol‡§

Al (M = 26.981 539 g/mol)					
0.01626	0.89622	403.64	−361.75	−0.85	−22300
0.01600	0.88098	403.90	−355.83	−0.83	−22291
0.01623	0.89813	403.99	−362.84	−0.85	−22409
0.01598	0.88030	403.50	−355.20	−0.83	−22280
0.01602	0.88276	403.97	−356.61	−0.83	−22312
0.01615	0.88868	404.22	−359.22	−0.84	−22295
0.01591	0.87356	404.24	−353.13	−0.83	−22248

$\langle\Delta H/M\rangle$ = −22305 ± 19 J/g†
Impurity corr. = −41 ± 8 J/g†
$\Delta H/M$(Al) = −22346 ± 42 J/g‡
ΔH_f(Al) = −602.93 ± 1.13 kJ/mol‡

Gibbsite, Al(OH)$_3$ (M = 78.0036 g/mol)					
0.04691	0.24941	402.54	−100.40	0.09	−2138.4
0.04653	0.24773	402.36	−99.68	0.09	−2140.3
0.04661	0.24768	401.88	−99.54	0.09	−2133.7
0.04690	0.24960	401.43	−100.20	0.09	−2134.5
0.04666	0.24882	401.50	−99.90	0.09	−2139.1
0.04647	0.24823	401.12	−99.57	0.09	−2140.7

$\langle\Delta H/M\rangle$ = −2137.8 ± 1.2 J/g†
ΔH_r = −166.76 ± 0.19 kJ/mol‡||

* The column headings are m, the mass of the sample reacted; $\Delta\theta_c$, the temperature change of the calorimeter corrected for heat exchange with the environment; ϵ(calor), the mean energy equivalent of the calorimetric system before and after the experiment; 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 $\langle\Delta H/M\rangle$, the mean specific enthalpy of reaction or solution.

** The ΔH_{corr} includes the enthalpy effect of opening the ampoule, 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.
‡ The uncertainty is twice the standard deviation of the mean.
§ This result used in Table 8.
|| This result used in Table 7.

Enthalpy of reaction measurements at 298.15 K

An LKB-8700 precision calorimetric system, with a 100-cm³ reaction vessel and stirrer both constructed of 18-carat Au, was used for the enthalpy of reaction measurements. The reaction vessel was modified for quartz-crystal thermometry by the addition of a reentry well in which was placed the sensor of a quartz-crystal thermometer (Hewlett-Packard model 2804 A). Calorimetric 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 of mordenite, dehydrated mordenite, Al, and gibbsite, with approximately 24.4 mass% HF(aq). The mordenite was quickly loaded into the ampoules and weighed after equilibration with a 50% relative humidity atmosphere. The dehydrated mordenite and Al were loaded into ampoules in the glove box. The amounts of mordenite and gibbsite reacted were fixed by the stoichiometry of the mordenite and the base reaction in the cycle: 0.001 664 3 mol of SiO$_2$ and 100 cm³ of 24.4 mass%

TABLE 7. Thermochemical cycle for the derivation of ΔH°_f(gibbsite) at 298.15 K and $P^\circ = 0.1013$ MPa

Reaction	ΔH (kJ/mol)
1. Al(cr) + 2218.39HF·7632.87H$_2$O = ⅗H$_2$(g) + [A]*	−602.93 ± 1.13**
2. [A] = Al(OH)$_3$(cr) + 2218.39HF ·7629.87H$_2$O	166.76 ± 0.19**
3. 2218.39HF·7629.87H$_2$O + 3H$_2$O(l) = 2218.39HF·7632.87H$_2$O	−1.26 ± 0.20†
4. 3H$_2$(g) + ³⁄₂O$_2$(g) = 3H$_2$O(l)	−857.49 ± 0.13‡
5. Al(cr) + ⅗H$_2$(g) + ³⁄₂O$_2$(g) = Al(OH)$_3$(cr)	−1294.9 ± 1.2§

* [A] = AlF$_3$·2215.39HF·7632.87H$_2$O.
** Enthalpy of reaction from Table 6.
† Johnson et al. (1973).
‡ Cox et al. (1989).
§ The ΔH°_f(gibbsite) is the sum of items 1 through 4.

HF(aq). It was assumed that the CaF$_2$ precipitated quantitatively. In separate experiments, no enthalpy change was detected when pure CaF$_2$ was introduced into an HF(aq) solution. For the Al reactions, it was assumed that the H$_2$ gas that escaped from the calorimeter was saturated with HF and H$_2$O vapor, and the vapor pressures and enthalpies of vaporization of HF and H$_2$O from HF(aq) were taken from the work of Brosheer et al. (1947). The detailed results for the calorimetric reactions are given in Table 6. The molar masses of mordenite, dehydrated mordenite, Al, and gibbsite in Table 6 are based on the 1987 atomic weights (IUPAC, 1988).

Standard enthalpies of formation at 298.15 K

The reactions and enthalpy values necessary to derive the standard enthalpy of formation of gibbsite are given in Table 7. The reactions and enthalpy values used to derive the enthalpies of formation of mordenite and dehydrated mordenite are given in Table 8. The standard molar enthalpy of formation of mordenite, −6756.2 ± 4.5 kJ/mol, is given by the sum of items 1 through 12 in Table 8, and the standard molar enthalpy of formation of dehydrated mordenite, −5661.8 ± 4.6 kJ/mol, is given by a similar summation with items 13, 14, and 15 substituted for items 5, 6, and 8.

Enthalpy-increment measurements

The drop calorimeter used for the enthalpy increment measures on dehydrated mordenite has been described in detail (Fredrickson et al., 1969). The system consisted essentially of a resistance-heated, Mo-core furnace and a Cu-block calorimeter. Measurements of the furnace temperature were made with thermocouples of Pt and Pt + 10 mass% of Rh. The temperature of the calorimeter was determined with a quartz-crystal thermometer (Hewlett-Packard model 2804 A). The energy equivalent of the empty calorimeter was determined by electrical calibration. For the present experiments, the calorimeter and furnace were filled with He at a pressure of about 1.3 kPa, which substantially decreased equilibration times

TABLE 8. Thermochemical equations used for the derivation of ΔH°_f of mordenite and dehydrated mordenite at 298.15 K and $P^\circ = 0.1013$ MPa[A]

Reaction	ΔH (kJ/mol)
1. 5.060SiO$_2$(cr, silicalite) + 4015.74HF ·13817.54H$_2$O = [A]	−732.69 ± 0.51[B]
2. 0.94Al(OH)$_3$(cr, gibbsite) + [A] = [B]	−155.51 ± 0.29[C]
3. 0.361NaF(cr) + [B] = [C]	−1.75 ± 0.12[D]
4. 0.289CaF$_2$(cr) + [C] = [D]	0 ± 0.06[D]
5. [D] = Ca$_{0.289}$Na$_{0.361}$Al$_{0.940}$·Si$_{5.060}$O$_{12}$ ·3.468H$_2$O(cr) + 4016.68HF ·13815.01H$_2$O	917.98 ± 0.44[C]
6. 4016.68HF·13815.01H$_2$O + 5.762H$_2$O(l) = 4016.68HF·13820.77H$_2$O	−2.40 ± 0.24[E]
7. 0.94HF·3.234H$_2$O = 0.47H$_2$(g) + 0.47F$_2$(g) + 3.234H$_2$O(l)	301.69 ± 0.63[F]
8. 2.528H$_2$(g) + 1.264O$_2$(g) = 2.528H$_2$O(l)	−722.58 ± 0.11[G]
9. 5.060Si(cr) + 5.060O$_2$(g) = 5.060SiO$_2$(cr, silicalite)	−4580.31 ± 4.25[B]
10. 0.94Al(cr) + 1.41O$_2$(g) + 1.41H$_2$(g) = 0.94Al(OH)$_3$(cr, gibbsite)	−1217.22 ± 1.10[H]
11. 0.361Na(cr) + 0.1805F$_2$(g) = 0.361NaF(cr)	−208.14 ± 0.24[I]
12. 0.289Ca(cr) + 0.289F$_2$(g) = 0.289CaF$_2$(cr)	−355.26 ± 0.12[I]
13. [D] = Ca$_{0.289}$Na$_{0.361}$Al$_{0.940}$·Si$_{5.060}$O$_{12}$(cr) + 4016.86HF·13818.48H$_2$O	1019.6 ± 1.1[C]
14. 4016.68HF·13818.48H$_2$O + 2.29H$_2$O(l) = 4016.68HF·13820.77H$_2$O	−0.94 ± 0.09[E]
15. 0.94H$_2$O(l) = 0.94H$_2$(g) + 0.47O$_2$(g)	268.68 ± 0.04[G]
16. 0.289 Ca(cr) + 0.361Na(cr) + 0.940Al(cr) + 5.060Si(cr) + 3.468H$_2$(g) + 7.734O$_2$(g) = Ca$_{0.289}$Na$_{0.361}$Al$_{0.940}$Si$_{5.060}$O$_{12}$ ·3.468H$_2$O(cr)	−6756.2 ± 4.5[J]
17. 0.289Ca(cr) + 0.361Na(cr) + 0.940Al(cr) + 5.060Si(cr) + 6.00O$_2$(g) = Ca$_{0.289}$Na$_{0.361}$Al$_{0.940}$Si$_{5.060}$O$_{12}$(cr)	−5661.8 ± 4.6[K]

[A] [A] = 5.060H$_2$SiF$_6$·3985.38HF·13827.66H$_2$O.
[B] Johnson et al. (1982).
[C] Table 6.
[D] Johnson et al. (1985).
[E] Johnson et al. (1973).
[F] Based on the selected ΔH°_f (F⁻, aq, 298.15 K) = −335.35 ± 0.65 kJ/mol (Cox et al., 1989).
[G] Cox et al. (1989).
[H] Table 7.
[I] Parker et al. (1976).
[J] ΔH°_f (mordenite).
[K] ΔH°_f (dehydrated mordenite).

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

The sample of dehydrated mordenite was loaded into a Pt$_{90}$Rh$_{10}$ capsule in the He atmosphere glove box. The filling tube of the capsule was crimped and welded shut inside the glove box. The capsule (1.2 cm in diameter, 4.8 cm long, and with internal volume of 5.35 cm³) had a mass of 19.55065 g and contained 4.07818 g of dehydrated mordenite and 1.73 × 10⁻⁴ mol of He.

TABLE 9. Drop calorimetric results for dehydrated mordenite*

Expt. no.	T (K)	$\Delta\theta_c$ (K)	ϵ(calor) $(\Delta\theta_c)$ (J)	ΔH(capsule) (J)	ΔH_{corr} (J)	$\Sigma(\Delta H)$ (J)	$f\Sigma(\Delta H)$ (J)	$H^0(T) - H^0$ (298.15 K)** (J/mol)
1	351.47	0.07595	332.43	−148.65	−0.16	183.62	180.00	16744
2	351.47	0.07597	332.52	−148.65	−0.22	183.65	180.03	16746
3	401.42	0.15112	661.43	−287.18	−0.35	373.90	366.52	34093
14	450.41	0.22783	997.16	−426.57	−0.33	570.26	559.01	51999
4	450.79	0.22833	999.35	−427.64	−0.29	571.42	560.15	52105
5	500.91	0.30883	1351.65	−572.37	−0.37	778.91	763.54	71024
6	550.80	0.39040	1708.62	−717.71	−0.47	990.44	970.90	90313
7	600.32	0.47356	2072.53	−861.98	−0.60	1209.95	1186.08	110329
8	650.72	0.55942	2448.24	−1009.68	−0.65	1437.91	1409.54	131115
9	700.84	0.64745	2833.43	−1157.15	−0.82	1675.46	1642.40	152775
10	751.72	0.73624	3221.93	−1307.79	−0.85	1913.29	1875.54	174462
11	801.75	0.82449	3608.05	−1456.97	−1.01	2150.07	2107.65	196052
12	850.00	0.91041	3983.95	−1601.74	−1.15	2381.06	2334.08	217115
13	900.04	1.01426	4438.32	−1817.76	−1.30	2619.26	2567.58	238835

* The entries in the table are T, the temperature of the furance and sample; $\Delta\theta_c$, the change in temperature of the calorimeter corrected for heat exchange with the surroundings; ϵ(calor)($\Delta\theta_c$), the energy absorbed by the calorimetric system; ΔH(capsule), the enthalpy contribution due to the capsule; ΔH_{corr}, the correction for the enthalpy of the He in the capsule and the difference of the final calorimetric temperature from 298.15 K; $\Sigma(\Delta H) = [\epsilon$(calor)($\Delta\theta_c$) $+ \Delta H$(capsule) $+ \Delta H$(corr)], $f = 0.98027$; and $H^0(T) - H^0$ (298.15 K), the standard enthalpy at T relative to 298.15 K.
** The capsule contained $1.075\,044 \times 10^{-2}$ mol of dehydrated mordenite.

Enthalpy-increment results

The results of the drop-calorimetric experiments are given in Table 9 in order of increasing temperatures. The energy equivalent of the calorimeter ϵ(calor) varied slightly as a function of $\Delta\theta_c$, the change in temperature of the calorimeter corrected for heat exchange with the environment, from 4376.46 J/K for $\Delta\theta_c \approx 0.5$ K to 4375.35 J/K for $\Delta\theta_c = 1.5$ K. The enthalpy contribution of the capsule was determined in a separate series of experiments with an empty capsule of dimensions, mass, and material similar to those used for the present experiments. The measured enthalpy was corrected for the enthalpy of the He in the capsule and for the deviation (usually less than 0.01 K) of the final calorimetric temperature from 298.15 K.

Unlike our previous studies with zeolites, the enthalpy increments for dehydrated mordenite obtained by drop calorimetry did not, for some unknown reason, merge smoothly at $T \approx 350$ K with those from the low-temperature measurements. The sequence of the experiments, essentially from low to high temperatures, and the agreement between experiments 14 and 4 argue that the poor overlap is not due to some unidentified structural change. Therefore, in order to force overlap at this temperature, the high-temperature results were arbitrarily multiplied by a factor of 0.98027 (f in Table 9), and the adjusted enthalpy increments for dehydrated mordenite, 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 900 K by the method of least-squares. The following equation adequately represented the results:

$$H^0(T) - H^0(298.15\text{ K})$$
$$= 7\,704\,565T^{-1} - 129\,172.45$$
$$+ 305.9516T + 0.152\,234\,T^2$$
$$- 5.361\,109\,6 \times 10^{-5}T^3 \text{ (J/mol).} \quad (6)$$

This fit was constrained to give at $T = 298.15$ K, $H^0(T) - H^0(298.15\text{ K}) = 0$, and $C_p^0(T) = 295.76$ J/(mol·K) (Table 5). The root-mean-square deviation of the experimental results from Equation 6 was 0.27%.

The first derivative of Equation 6 with respect to T yielded the following expression for the heat capacity of dehydrated mordenite between 298.15 and 900 K:

$$C_p^0(T) = -7\,704\,565T^{-2} + 305.95 + 0.30447T$$
$$- 1.60833 \times 10^{-4}T^2 \text{ J/(mol·K).} \quad (7)$$

The anticipated high H_2O-vapor pressure over mordenite, even at temperatures as low as 500 K (for the comparable case of heulandite, see Johnson et al., 1985), led us to decide not to perform any drop-calorimetric measurements on this zeolite. Instead, we extrapolated the low-temperature calorimetric measurements (5–350 K) to 500 K with the results for dehydrated mordenite as a guide. For mordenite, therefore, the following expressions have been estimated:

$$H^0(T) - H^0(298.15\text{ K})$$
$$= 8\,196\,591T^{-1} - 192\,163.9 + 528.091T$$
$$+ 8.12444 \times 10^{-2}T^2 \text{ J/(mol·K)} \quad (8)$$

and

$$C_p^0(T) = -8\,196\,591T^{-2} + 528.09$$
$$+ 0.16249T \text{ J/(mol·K).} \quad (9)$$

Thermodynamic functions for mordenite and dehydrated mordenite

Table 10 gives the thermodynamic functions for mordenite between 298.15 and 500 K and for dehydrated mordenite between 298.15 and 900 K. For the calculation of $\Delta H_f^0(T)$ and $\Delta G_f^0(T)$, we have used heat capacities

TABLE 10. Thermodynamic properties of mordenite and dehydrated mordenite

T (K)	$C_p^0(T)$ [J/(mol·K)]	$H^0(T) - H^0$ (298.15 K) (kJ/mol)	$S^0(T) - S^0(0)$ [J/(mol·K)]	$\Delta H_f^0(T)$ (kJ/mol)	$\Delta G_f^0(T)$ (kJ/mol)
		Mordenite			
298.15	484.33	0	486.54	−6756.20	−6247.65
300	485.74	0.90	489.54	−6756.17	−6244.50
320	500.06	10.76	521.36	−6755.74	−6210.42
340	511.80	20.88	552.05	−6755.12	−6177.39
360	523.34	31.25	581.66	−6754.35	−6142.34
380	533.07	41.81	610.22	−6754.40	−6108.32
400	541.86	52.56	637.79	−6753.40	−6074.33
420	549.87	63.48	664.42	−6752.30	−6040.40
440	557.25	74.55	690.18	−6751.12	−6006.53
460	564.10	85.77	715.10	−6749.86	−5972.71
480	570.51	97.11	739.24	−6748.54	−5938.96
500	576.55	108.59	762.66	−6747.14	−5905.26
		Dehydrated mordenite			
298.15	295.76	0	299.10	−5661.80	−5338.55
300	296.99	0.55	300.94	−5661.84	−5336.54
400	353.85	33.40	395.04	−5662.65	−5227.95
500	387.16	70.57	477.86	−5659.79	−5134.60
600	409.33	110.46	550.53	−5655.48	−5011.91
700	424.55	152.21	614.85	−5650.43	−4905.05
800	434.56	195.20	672.24	−5645.32	−4798.90
900	440.19	238.97	723.79	−5640.08	−4693.39

and entropies of Na, Ca, Al, Si, O_2, and H_2 from the compilation of Robie et al. (1978). At 298.15 K, the standard molar entropy of formation ΔS_f^0 and standard molar Gibbs energy of formation ΔG_f^0 are -1705.7 ± 1.1 J/(mol·K) and -6247.6 ± 4.5 kJ/mol for mordenite and -1084.18 ± 0.77 J/(mol·K) and -5338.6 ± 4.6 kJ/mol for dehydrated mordenite.

DISCUSSION

We are not aware of any other studies on mordenite that have yielded thermodynamic properties with which the present results may be compared. However, if one estimates ΔH_f^0(dehydrated mordenite) by taking the sum of the ΔH_f^0s of the constituent oxides and the appropriate coefficients, as is often done, $\Delta H_f^0 = -5655.7$ kJ/mol is obtained, very close to the experimental value of -5661.8 ± 4.6 kJ/mol.

For gibbsite, however, there are several other studies that yield $\Delta H_f^0[\text{Al(OH)}_3]$. Donahoe et al. (1990) and Hemingway and Robie (1977) have reported $\Delta H_f^0[\text{Al-(OH)}_3$, 298.15 K] = -1293.13 ± 1.19 kJ/mol based on reactions of Al(OH)_3 and Al with HF(aq). Gross et al. (1970) have measured the enthalpies of reaction of Al(OH)_3 and AlCl_3 with HF(aq). From these measurements, Hemingway and Robie (1977) derived $\Delta H_f^0[\text{Al(OH)}_3$, 298.15 K] = -1294.24 ± 2.93 kJ/mol. Barany and Kelley (1961) measured the enthalpies of reaction of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, Al(OH)_3, H_2O, and HCl(aq) with HF(aq) to derive $\Delta H_f^0[\text{Al(OH)}_3$, 298.15 K] = -1281.89 ± 1.26 kJ/mol. Our result, -1294.9 ± 1.2 kJ/mol, agrees within the combined uncertainties with the results of Hemingway and Robie (1977) and Gross et al. (1970) but not with that of Barany and Kelley (1961). The latter value is be-

lieved (Hemingway and Robie, 1977) to be discrepant because of erroneous values for the enthalpies of mixing of H_2O and HCl(aq) with HF(aq).

In previous publications (Johnson et al., 1982, 1983, 1985), we used our results for the standard molar entropies in an attempt to obtain a qualitative description of the disposition of H_2O in the cavities of several zeolites. The basis of our approach was that the largest entropy effects would be contributed by those zeolites with the most mobile H_2O molecules in their cavities. The average contribution of each H_2O is given in the present case as $S_{\text{H}_2\text{O}}^0 = [S^0(\text{mordenite}) - S^0(\text{dehydrated mordenite})]/3.468 = 54.1 \pm 0.3$ J/(mol·K). This result is similar to the values for analcime, 55.0 ± 0.3 J/(mol·K) (Johnson et al., 1982); heulandite, 50.5 J/(mol·K) (Johnson et al., 1985); and clinoptilolite, 57 J/(mol·K) (Hemingway and Robie, 1984), and it lies about midway between $S^0(\text{H}_2\text{O},\text{l}) = 70$ J/(mol·K) (Cox et al., 1989) and $S^0(\text{H}_2\text{O},\text{cr}) = 38$ J/(mol·K) (Giauque and Stout, 1936). Clearly, therefore, the H_2O in these zeolites, which is so weakly bonded and possesses such high mobility that it can be removed by simply lowering the ambient humidity, is significantly more mobile than the tightly bound zeolitic H_2O in such as natrolite and scolecite for which $S_{\text{H}_2\text{O}}^0 \approx 32$ J/(mol·K) (Johnson et al., 1983).

REFERENCES CITED

Barany, R., and Kelley, K.K. (1961) Heats and free energies of formation of gibbsite, kaolinite, halloysite, and dickite. U.S. Bureau of Mines Report 5825.
Breck, D.W. (1974) Zeolite molecular sieves: Structure, chemistry, and use. Wiley, New York.
Brosheer, J.C., Lenfesty, F.A., and Elmore, K.L. (1947) Vapor pressure of hydrofluoric acid solutions. Industrial and Engineering Chemistry, 39, 423–427.
Cox, J.D., Wagman, D.D., and Medvedev, V.A. (1989) CODATA key values for thermodynamics. Hemisphere, New York.
Donahoe, R.J., Hemingway, B.S., and Liou, J.G. (1990) Thermochemical data for merlinoite: 1. Low-temperature heat capacities, entropies, and enthalpies of formation at 298.15 K of six synthetic samples having various Si/Al and Na/(Na + K) ratios. American Mineralogist, 75, 188–200.
Fredrickson, D.R., Barnes, R.D., Chasanov, M.G., Nuttall, R.L., Kleb, R., and Hubbard, W.N. (1969) The enthalpy of uranium diboride from 600 to 1500 K by drop calorimetry. High Temperature Science, 1, 373–380.
Giauque, W.F., and Stout, J.W. (1936) The entropy of water and the third law of thermodynamics. The heat capacity of ice from 15 to 273 K. Journal of the American Chemical Society, 58, 1144–1150.
Gottardi, G., and Galli, E. (1985) Natural zeolites. Springer, Berlin.
Gross, P., Christie J., and Hayman, C. (1970) Heats of formation of gibbsite and light element double oxides. Fulmer Research Institute Report 6, PG/JMN/R.
Hemingway, B.S., and Robie, R.A. (1977) Enthalpies of formation of low albite ($\text{NaAlSi}_3\text{O}_8$), gibbsite ($\text{Al(OH)}_3$), and NaAlO_2; Revised values for $\Delta H_{f,298}^0$ and $\Delta G_{f,298}^0$ of some aluminosilicate minerals. Journal of Research of the U.S. Geological Survey, 5, 413–429.
——— (1984) Thermodynamic properties of zeolites: Low-temperature

heat capacities and thermodynamic functions of phillipsite and clinoptilolite. Estimates of the thermochemical properties of zeolitic water at low temperatures. American Mineralogist, 69, 692–700.

Howell, D.A., Johnson, G.K., Tasker, I.R., O'Hare, P.A.G., and Wise, W.S. (1990) Thermodynamic properties of the zeolite stilbite. Zeolites, 10, 525–531.

IUPAC (1988) Report of the commission on atomic weights and isotopic abundances. Pure and Applied Chemistry, 60, 841–854.

Johnson, G.K., Smith, P.N., and Hubbard, W.N. (1973) The enthalpies of solution and neutralization of HF(l); enthalpies of dilution and derived thermodynamic properties of HF(aq). Journal of Chemical Thermodynamics, 5, 793–809.

Johnson, G.K., Papatheodorou, G.N., and Johnson, C.E. (1980) The enthalpies of formation and high-temperature thermodynamic functions of As₄S₄ and As₄S₃. Journal of Chemical Thermodynamics, 12, 545–557.

Johnson, G.K., Flotow, H.E., O'Hare, P.A.G., and Wise, W.S. (1982) Thermodynamic studies of zeolites: Analcime and dehydrated analcime. American Mineralogist, 67, 736–748.

——— (1983) Thermodynamic studies of zeolites: Natrolite, mesolite, and scolecite. American Mineralogist, 68, 1134–1145.

——— (1985) Thermodynamic studies of zeolites: Heulandite. American Mineralogist, 70, 1065–1071.

Johnson, G.K., Tasker, I.R., Howell, D.A., and Smith, J.V. (1987) Thermodynamic properties of silicalite (SiO₂). Journal of Chemical Thermodynamics, 19, 617–632.

Johnson, G.K., Flotow, H.E., O'Hare, P.A.G., and Wise, W.S. (1989) Erratum. Thermodynamic studies of zeolites: Heulandite. American Mineralogist, 74, 697.

Osborne, D.W., Schreiner, F., Flotow, H.E., and Malm, J.G. (1972) Xenon tetrafluoride: Heat capacity and thermodynamic functions from 5 to 350 K. Reconciliation of the entropies from molecular and thermal data. Journal of Chemical Physics, 57, 3401–3408.

Parker, V.B., Wagman, D.D., and Garvin, D. (1976) Selected thermochemical data compatible with the CODATA recommendations. National Bureau of Standards Report NBSIR 75-968.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10⁵ Pascals) pressure and at high temperatures. U.S. Geological Survey Bulletin 1452.

Van Reeuwijk, L.P. (1974) The thermal dehydration of natural zeolites. Mededelingen Landbouwhogeschool, p. 74–79. Wageningen, The Netherlands.

Westrum, E.F., Jr., Hatcher, J.B., and Osborne, D.W. (1953) The entropy and low-temperature heat capacity of neptunium dioxide. Journal of Chemical Physics, 21, 419–423.

APPENDIX 1.

We are taking this opportunity to update the thermodynamic results for zeolites previously reported from this laboratory (Johnson et al., 1982, 1983, 1985, 1989) for changes in the base reactions for SiO_2 from α quartz to silicalite. This amounts to a correction of -3.51 kJ/mol for each Si atom in the formula for both ΔH_f^0 and ΔG_f^0. We are also modifying these values so that they are based on the $\Delta H_f^0[Al(OH)_3]$ result obtained in the present study. This change amounts to a correction of -1.8 kJ/mol for each Al atom in the formula. The revised values ($T = 298.15$ K), with which, we point out, the present results for ΔH_f^0 and ΔG_f^0 of mordenite and dehydrated mordenite are consistent, are given in Appendix Table 1.

APPENDIX TABLE 1. Standard enthalpies and Gibbs energies of formation (kJ/mol) at 298.15 K of zeolites, revised as outlined in the text

	ΔH_f	ΔG_f
Analcime, $Na_{0.96}Al_{0.96}Si_{2.04}O_6 \cdot H_2O$	-3305.8 ± 3.3	-3086.1 ± 3.3
Dehydrated analcime, $Na_{0.96}Al_{0.96}Si_{2.04}O_6$	-2979.1 ± 3.5	-2812.6 ± 3.5
Natrolite, $Na_2Al_2Si_3O_{10} \cdot 2H_2O$	-5732.7 ± 5.0	-5330.7 ± 5.0
Scolecite, $CaAl_2Si_3O_{10} \cdot 3H_2O$	-6063.1 ± 5.0	-5612.0 ± 5.0
Mesolite, $Na_{0.676}Ca_{0.657}Al_{1.990}Si_{3.01}O_{10} \cdot 2.647H_2O$	-5961.2 ± 5.4	-5527.3 ± 5.4
Heulandite, $Ba_{0.065}Sr_{0.175}Ca_{0.585}K_{0.132}Na_{0.383}Al_{2.165}Si_{6.835}O_{18} \cdot 6.00H_2O$	-10622.5 ± 10.2	-9807.0 ± 10.2