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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

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ABSTRACT

The heat capacities, C_P, and heats of solution, ΔH_{soln}, of six synthetic merlinoite samples having various Si/Al and Na/(Na + K) ratios were measured by low-temperature, adiabatic calorimetry and hydrofluoric acid solution calorimetry, respectively. Merlinoite heat capacities were measured from 10 to 320 K, and enthalpies of formation from the elements, ΔH^0_f, were determined from measurements of the heats of solution of SiO_2 (α-quartz), $Al(OH)_3$ (gibbsite), NaF, KF, and the merlinoite samples in 24.4 wt% $HF_{(aq)}$ at 35 °C and 50 °C. The heat capacities of these samples show one large and two smaller glass-type transitions attributed to changes in the entropic state of the zeolitic water molecules. Tables of the thermodynamic functions C^0_P, $S^0_T - S^0_0$, $(H^0_T - H^0_0)/T$, and $-(G^0_T - H^0_0)/T$ are presented for these six samples from 5 to 310 K. Configurational entropy contributions to the third-law entropies resulting from mixing on exchangeable cation, tetrahedral, and water sites were estimated. The configurational entropy contribution was estimated to be about 17% of the calorimetrically determined value of $S^0_{298} - S^0_0$. The following values for S^0_T and $\Delta H^0_{f,298}$ at 298.15 K (25 °C) were obtained:

Merlinoite composition	$S^0_{T,298}$ [J/(mol·K)]	$\Delta H^0_{f,298}$ (kJ/mol)
$(Na_{0.81}K_{0.19}AlSi_{1.94}O_{5.88}\cdot 2.13H_2O)$	328.8 ± 15.3	−3591.2 ± 2.9
$(K_{0.80}Na_{0.20}AlSi_{1.94}O_{5.88}\cdot 1.81H_2O)$	324.4 ± 15.8	−3519.0 ± 2.9
$(KAlSi_{1.94}O_{5.88}\cdot 1.69H_2O)$	320.7 ± 15.3	−3481.8 ± 3.0
$(Na_{0.81}K_{0.19}AlSi_{1.81}O_{5.62}\cdot 2.18H_2O)$	319.2 ± 14.7	−3488.3 ± 2.8
$(K_{0.91}Na_{0.09}AlSi_{1.81}O_{5.62}\cdot 1.79H_2O)$	305.9 ± 15.0	−3387.3 ± 2.8
$(KAlSi_{1.81}O_{5.62}\cdot 1.69H_2O)$	304.3 ± 14.7	−3360.0 ± 2.8

INTRODUCTION

Zeolites constitute one of the largest groups of rock-forming silicates, occurring as vug-filling minerals in a variety of volcanic rocks and as major authigenic phases in many sedimentary environments. Although recent calorimetric measurements on zeolite minerals (Johnson et al., 1982, 1983, 1985, 1986) have doubled the existing thermodynamic data base, accurate thermochemical data are available for only a few minerals in this group. These data are necessary in order to model and understand mineral-solution equilibria in diagenesis, low-temperature hydrothermal alteration, and low-grade metamorphism. Many zeolites exhibit extensive solid solution with respect to both exchangeable cations and framework Si/Al ratio, and the thermodynamic properties of these minerals can be expected to vary as a function of composition. It is desirable, therefore, that thermochemical measurements for these minerals be made on synthetic zeolite samples whose compositions can be carefully controlled and that mixing models be developed that can be used to extend the data to naturally occurring zeolite compositions. As part of an on-going project to determine the thermodynamic properties of alkalic zeolites by calorimetric techniques, we measured the heat capacity and enthalpy of solution of six synthetic merlinoite samples having various Si/Al and Na/(Na + K) ratios.

Merlinoite, first discovered in Italy by Passaglia et al. (1977), is the naturally occurring equivalent of type W synthetic zeolite. Merlinoite has orthorhombic symmetry, space group *Immm*, and is quite similar structurally to phillipsite (Breck, 1974; Sherman, 1977). The crystal

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TABLE 1. Electron-microprobe analyses of synthetic merlinoite samples used for low-temperature heat-capacity measurements

	P-9(NaK)	P-9(KNa)	P-9(K)	P-8(NaK)	P-8(KNa)	P-8(K)
			Weight percent oxide (average of five analyses)			
SiO_2	48.86	48.82	46.09	46.90	46.34	45.67
Al_2O_3	21.26	21.36	20.16	21.83	21.76	21.39
K_2O	3.634	13.82	21.74	3.742	17.07	20.20
Na_2O	10.23	2.320	0.00	10.72	1.071	0.00
H_2O*	16.01	13.67	12.01	16.81	13.76	12.74
Total	100.00	100.00	100.00	100.00	100.00	100.00
			Unit cell (based on 64 oxygens per cell)			
Si	21.19	21.33	20.81	20.68	20.73	20.58
Al	10.87	11.00	10.73	11.34	11.47	11.36
K	2.01	7.70	12.52	2.10	9.74	11.61
Na	8.20	1.97	0.03	9.17	0.93	0.004
H_2O	23.17	19.93	18.10	19.14	20.53	19.14

Chemical formula

P-9(NaK)	$Na_{0.81}K_{0.19}AlSi_{1.94}O_{5.88}\cdot 2.13H_2O$
P-9(KNa)	$K_{0.80}Na_{0.20}AlSi_{1.94}O_{5.88}\cdot 1.81H_2O$
P-9(K)	$KAlSi_{1.94}O_{5.88}\cdot 1.69H_2O$
P-8(NaK)	$Na_{0.81}K_{0.19}AlSi_{1.81}O_{5.62}\cdot 2.18H_2O$
P-8(KNa)	$K_{0.91}Na_{0.09}AlSi_{1.81}O_{5.62}\cdot 1.79H_2O$
P-8(K)	$KAlSi_{1.81}O_{5.62}\cdot 1.69H_2O$

* Determined by TGA (25–800 °C at 6°/min).

structures of merlinoite and phillipsite are both composed of double octagonal rings joined laterally by four-membered rings that form S-shaped chains in the *c* direction (see Flanigen, 1977, and Galli et al., 1979). The difference between the two zeolite structures is found in the orientation of the tetrahedra in the eight-membered rings: six down and two up in phillipsite, eight down in merlinoite. This structural similarity results in very similar morphologies and X-ray diffraction patterns for the two minerals (Donahoe et al., 1984). The structure of type W zeolite (merlinoite) corresponds to one of the 17 theoretical structures based on linkages of eight- and four-membered rings proposed by Smith and Rinaldi (1962).

At present, the known natural occurrences of merlinoite are restricted to two localities in Italy (Passaglia et al., 1977; Gottardi and Galli, 1985), one in Germany (Alberti et al., 1979), one in Russia (Khomyakov et al., 1981), and one in the United States (Donahoe et al., 1984). However, as discussed in Donahoe et al. (1984), it seems probable that merlinoite is more common than is currently recognized because it can easily be misidentified as phillipsite. There have been no previous measurements of the thermochemical properties of merlinoite.

MATERIALS

Synthetic merlinoites

Donahoe and Liou (1985) discovered that monomineralic samples of zeolites with specific Si/Al ratios could be precipitated from clear solutions by varying solution pH. Two samples of merlinoite were synthesized from clear solutions at 80 °C in the system Na_2O-K_2O-Al_2O_3-SiO_2-H_2O. Approximately 40 g of each were obtained in 5 to 7 months. The synthesis method is described in Donahoe et al. (1984); however, because solution volumes of 8 L were required to produce 40-g zeolite samples, adequate mechanical stirring of the solutions was impossible. Instead, the solutions were alternately heated and shaken for 40 to 60 min in 2-gallon (that is, approximately 8 L) polypropylene bottles until the silicic acid dissolved. The two original samples synthesized for the study were potassian-sodian merlinoites with Si/Al ratios = 1.94 (P-9) and 1.81 (P-8), respectively. Splits from these synthesis products were ion-exchanged in saturated NaCl (33 to 40 g of zeolite in 1071 g of NaCl + 3 kg of H_2O) and KCl (20 to 30 g of zeolite in 1033 g of KCl + 3 kg of H_2O) solutions at 80 °C for 168 h with occasional agitation. In this manner, a sodian-potassian and a pure-K end-member composition were produced for each Si/Al ratio, making a total of six merlinoite samples. In this and the subsequent paper (Donahoe et al., 1990), the exchangeable-cation compositions of the samples are designated by (K) for the K-exchanged merlinoites, by (NaK) for the Na-exchanged merlinoites, and by (KNa) for the samples as originally synthesized.

The synthetic merlinoite samples were examined by X-ray diffraction analysis and scanning electron microscopy and found to be monomineralic and fairly uniform in grain size (10–15 μm). The crystals were repeatedly washed with distilled, deionized water in order to remove as much adsorbed $(OH)^-$ and NaCl as possible. The anhydrous compositions of the synthetic merlinoites were determined by electron-microprobe analysis using feldspar standards, 15-kV accelerating potential, a beam current of 50 nA, and the Bence-Albee (1968) data reduction method. Alkali migration was minimized by the use of 20-s counting times and a large beam size (40 μm). The water content of the samples was determined by thermogravimetric analysis. Microprobe oxide totals ranged from 88 to 94 wt% and were normalized to total 100 wt%

TABLE 2. X-ray unit-cell parameters of synthetic merlinoite samples

Sample	*a* (Angstroms)	*b* (Angstroms)	*c* (Angstroms)	*V* (Å³)	Number of lines used
P-9(NaK)	14.164(4)	14.258(5)	9.904(2)	2000(1)	25
P-9(KNa)	14.193(3)	14.297(3)	9.964(2)	2022(1)	35
P-9(K)	14.110(3)	14.223(3)	10.005(3)	2008(1)	47
P-8(NaK)	14.234(2)	14.272(1)	10.049(1)	2041(1)	37
P-8(KNa)	14.136(4)	14.273(3)	9.974(3)	2012(1)	37
P-8(K)	14.070(2)	14.256(2)	9.921(2)	1990(1)	36

Note: Refinements made using Job 9214 computer program (Appleman et al., 1972).

with the addition of water. Zeolite compositions are in Table 1. Crystals in each sample were found to be homogeneous and to consist entirely of K, Na, Al, Si, and H_2O. Chloride and fluoride were below detection limits in all samples. High-resolution MAS ^{27}Al NMR spectra taken of the samples (Donahoe and deJong, unpublished data) showed no adsorbed sodium aluminate component in the synthetic merlinoites.

X-ray diffraction patterns were obtained for the merlinoite samples with a Guinier-Hägg camera using BaF_2 as an internal standard and Cu$K\alpha_1$ radiation. Unit-cell parameters for the synthetic merlinoites are in Table 2. Calculated molar volumes (cm³) are as follows: P-9(K), 111.04; P-9(KNa), 111.82; P-9(NaK), 110.66; P-8(K), 105.18; P-8(KNa), 106.34; P-8(NaK), 107.89. Atomic weights for 1975 (Commission on Atomic Weights, 1976) were used to calculate the gram-formula weights for the merlinoite samples, which are as follows: P-9(K) = 245.0880, P-8(K) = 237.2771, P-9(KNa) = 244.0282, P-8(KNa) = 237.6288, P-9(NaK) = 239.9669, and P-8(NaK) = 233.0567 g/mol. The density used to correct the samples for buoyancy was 2.20 g/cm³.

α-Quartz (SiO_2)

The α-quartz used for the heat-of-solution measurements was a portion of Standard Reference Material 1654 from the National Bureau of Standards, sized by sieving to be −305 to +360 mesh (44 to 55 μm).

Gibbsite [$Al(OH)_3$]

The gibbsite sample used as the Al standard for these measurements was Fisher reagent $Al_2O_3 \cdot 3H_2O$. The sample was heated at 150 °C for 8 h without any detectable weight loss that might have been caused by dehydration.

NaF

"Baker analyzed" reagent sodium fluoride was heated for 8 h at 150 °C and stored in a tightly sealed plastic bag.

KF

"Baker analyzed" reagent potassium fluoride was heated for 8 h at 150 °C and stored in a tightly sealed plastic bag.

TABLE 3. Percent of total heat capacity represented by sample heat capacity at different temperatures

	10 K	50 K	100 K	200 K	300 K
P-9(NaK)	60	44	43	49	56
P-9(KNa)	61	42	38	44	49
P-9(K)	65	45	41	47	51
P-8(NaK)	49	36	35	41	48
P-8(KNa)	57	39	34	39	44
P-8(K)	58	40	36	41	45

HF

The hydrofluoric acid used was either Mallinckrodt reagent (49.5% HF) or "Baker analyzed" reagent (48.0% HF) diluted to the appropriate concentration with distilled water. Only HF lots with titrated concentration analyses were used.

APPARATUS AND PROCEDURES

Low-temperature, adiabatic calorimetry

The adiabatically shielded low-temperature heat-capacity calorimeter and the methods of data reduction used in this study have been described by Robie and Hemingway (1972), Robie et al. (1976), and Hemingway et al. (1984). The heat capacities of the merlinoite samples represented 34–65% of the total heat capacities measured (see Table 3).

HF solution calorimetry

The enthalpy of formation of a phase is derived from its measured enthalpy of solution by the construction of a thermochemical cycle. Construction of these thermochemical reaction schemes requires the measurement of heats of solution for elemental standard compounds. Quartz (Si), gibbsite (Al), NaF (Na), and KF (K) were selected for use as standards in this study and were dissolved sequentially in 24.4% HF. Descriptions of these materials and their measured heats of solution are given below.

The solution calorimeter used in this study and the methods of data reduction have been previously described by Robie and Hemingway (1972). Since that description, several modifications have been made to the calorimetric system. The calorimeter has been redesigned to allow reduction of the reaction vessel volume from 1 to 0.5 L. The immersion water heater is of slightly different design, and the copper resistance thermometer has been replaced by a quartz thermometer. The quartz thermometer was calibrated against a Pt resistance thermometer so as to conform with the 1968 International Practical Temperature Scale of the NBS (Comité International des Poids et Mesures, 1969). In the electrical-measurements circuit, the potentiometer was replaced by a digital voltmeter that measures the heater current and voltage. Data collection has been semi-automated by means of an HP 9825B computer. Operator intervention is required to begin and end the solution period.

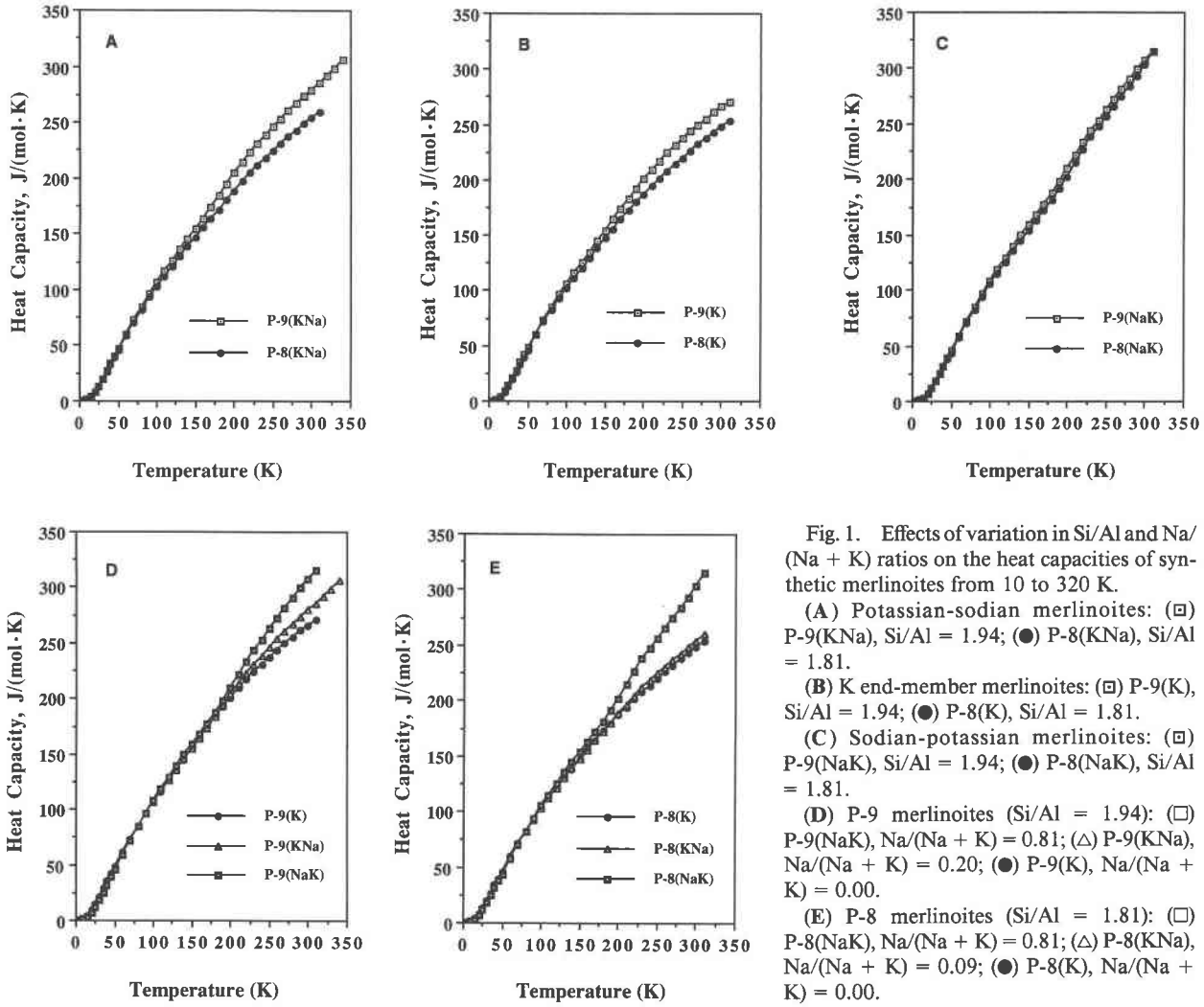

Fig. 1. Effects of variation in Si/Al and Na/(Na + K) ratios on the heat capacities of synthetic merlinoites from 10 to 320 K.

(**A**) Potassian-sodian merlinoites: (⊡) P-9(KNa), Si/Al = 1.94; (●) P-8(KNa), Si/Al = 1.81.

(**B**) K end-member merlinoites: (⊡) P-9(K), Si/Al = 1.94; (●) P-8(K), Si/Al = 1.81.

(**C**) Sodian-potassian merlinoites: (⊡) P-9(NaK), Si/Al = 1.94; (●) P-8(NaK), Si/Al = 1.81.

(**D**) P-9 merlinoites (Si/Al = 1.94): (□) P-9(NaK), Na/(Na + K) = 0.81; (△) P-9(KNa), Na/(Na + K) = 0.20; (●) P-9(K), Na/(Na + K) = 0.00.

(**E**) P-8 merlinoites (Si/Al = 1.81): (□) P-8(NaK), Na/(Na + K) = 0.81; (△) P-8(KNa), Na/(Na + K) = 0.09; (●) P-8(K), Na/(Na + K) = 0.00.

The solution calorimeter was operated under constant-pressure conditions for these measurements; therefore, the measured heats of solution are enthalpy changes at a pressure of 10^5 Pa.

Experimental results

Heat capacities

The heat-capacity measurements for the synthetic merlinoite samples are listed in their chronologic order of measurement as series 1, 2, 3, etc. in Table 4 and are shown graphically in Figure 1. The first compound measured, P-9(KNa), revealed that the heat-capacity curve changes slope abruptly at temperatures above 320 K. This change resulted from the beginning of dehydration of the synthetic merlinoite (see Figs. 1A and 1D). Although previous experience had shown that merlinoite dehydration is completely reversible at temperatures below 390 K, it was decided not to risk any possible nonreversible structural changes in the remaining samples by limiting heat-capacity measurements to a maximum of 320 K.

Figures 1A through 1C compare the effect of variation in Si/Al ratio on the heat capacity of potassian-sodian, potassian, and sodian-potassian merlinoites. The more siliceous merlinoite has higher heat capacity. The difference in heat capacity for the two silica series is larger for the K-rich merlinoites than for the sodian-potassian merlinoites (Figs. 1B and 1C).

Figures 1D and 1E show the effect of exchangeable-cation composition on the heat capacity of merlinoite for a fixed framework composition. For both Si/Al ratios, the heat capacity of merlinoite decreases as its Na content increases at temperatures below 75 K, although heat-capacity differences between samples are small. At temperatures greater than 200 K, however, the heat capacity of merlinoite increases as its Na content increases because the water content of merlinoite increases markedly with increasing Na content (see Table 1).

Compositional differences have less effect on heat capacity at lower temperatures for all samples measured. This relationship suggests that entropic contributions from zeolitic water molecules may cause most of the merlinoite

TABLE 4. Experimental heat capacities [in J/(mol·K)] of merlinoite at various temperatures (in kelvins)

P-9(NaK)					
T	C_p	T	C_p	T	C_p
304.26*	309.7	206.88	217.9	214.85	227.3
309.18	314.1	212.28	224.6	219.56	232.3
314.14	319.1	217.67	230.6	224.43	237.2
56.85**	54.21	223.06	236.0	229.52	242.4
61.88	60.99	228.44	241.3	234.65	247.3
66.56	67.22	215.60††	228.0	239.97	252.4
71.68	74.07	220.91	233.5	245.32	257.7
77.74	81.93	226.04	238.4	250.68	262.7
83.69	89.33	231.21	243.7	256.04	267.8
89.66	96.39	236.61	249.1	261.42	273.1
95.63	103.1	242.01	254.4	266.79	278.0
101.58	109.5	247.40	259.5	272.13	282.9
107.47	115.7	252.78	264.7	277.49	287.7
113.31	121.8	258.15	270.0	282.84	292.6
119.11	127.9	263.52	275.3	288.18	297.1
124.87	133.8	268.88	280.1	293.50	301.6
130.58	139.7	274.24	284.7	298.81	306.2
136.27	145.4	279.60	289.7	10.32§	0.985
141.93	151.0	284.96	294.5	11.61	1.356
147.56	156.5	290.30	299.4	13.14	1.963
124.45†	133.4	295.63	303.3	14.59	2.736
130.17	139.2	300.93	308.2	16.24	3.770
135.42	144.5	306.22	312.5	18.08	5.175
140.75	149.8	311.48	316.8	20.11	6.959
146.37	155.2	316.73	320.9	22.38	9.188
151.95	160.6	161.10‡	168.9	24.92	11.97
157.51	165.8	166.30	173.8	27.74	15.31
163.06	171.0	171.55	178.6	30.89	19.35
168.59	176.2	177.01	183.8	34.40	24.10
174.11	181.2	182.47	189.1	38.32	29.75
179.61	186.5	187.91	194.6	42.72	35.55
185.11	192.0	193.33	200.7	47.64	41.69
190.59	197.8	198.74	207.3	53.12	49.09
196.05	204.2	204.12	214.1	59.12	57.22
201.48	210.9	209.49	221.0	65.41	65.63

P-9(KNa)					
T	C_p	T	C_p	T	C_p
299.95*	278.5	31.11	21.57	182.18	185.6
303.31	280.8	34.64	26.51	187.70	191.9
308.23	283.6	38.57	32.31	193.20	198.1
313.16	286.5	42.97	38.05	198.69	203.7
318.22	289.8	47.91	43.98	204.17	208.8
323.27	292.4	53.39	51.17	209.64	213.6
328.29	295.7	59.42	59.01	215.10	218.4
333.28	300.7	65.71	67.08	220.56	223.0
338.24	305.6	72.01	75.09	226.00	227.5
343.19	310.5	78.27	82.84	231.46	231.5
5.14**	0.1298	84.44	89.99	236.93	236.0
6.10	0.2681	90.53	97.09	242.40	240.2
6.68	0.3009	96.57	103.2	247.87	244.5
7.26	0.3444	102.54	109.1	253.34	248.5
7.91	0.4868	108.45	114.9	258.82	252.3
8.75	0.6727	114.30	120.6	264.31	256.0
9.71	0.9319	120.10	126.3	269.80	260.0
10.78	1.284	125.87	131.9	275.08†	264.0
11.98	1.799	131.61	137.5	280.34	267.6
13.31	2.479	137.32	143.0	285.40	270.5
14.79	3.431	143.01	148.3	290.46	273.9
16.43	4.642	148.66	153.5	295.68	277.2
18.26	6.257	154.30	158.5	300.87	280.1
20.30	8.273	159.91	163.6	306.03	283.0
22.57	10.73	165.50	168.8	311.17	285.9
25.11	13.75	171.07	174.1	316.27	288.8
27.94	17.32	176.63	179.6		

P-9(K)					
T	C_p	T	C_p	T	C_p
300.67*	266.8	181.01	184.2	309.40	270.5
305.10	268.8	186.43	189.0	314.57	272.2
310.02	271.0	191.83	193.9	7.83†	0.5096
314.93	273.1	197.22	198.7	8.61	0.6929
58.88**	59.22	202.59	203.3	9.33	0.9236
64.98	66.88	207.95	207.5	10.23	1.278
74.90	79.06	213.29	211.7	11.34	1.727
80.15	85.28	218.63	215.9	12.58	2.357
85.35	91.20	223.97	219.9	13.99	3.236
90.78	96.97	229.32	223.6	15.53	4.387
96.69	103.0	234.70	227.3	17.26	5.868
102.54	108.8	240.08	230.9	19.20	7.763
108.37	114.4	245.46	234.4	21.36	10.10
114.16	119.9	250.84	237.8	23.76	12.92
119.91	125.5	256.22	241.3	26.44	16.29
125.62	130.9	261.60	244.6	29.44	20.25
131.28	136.3	266.98	247.6	32.79	24.91
136.91	141.8	272.37	250.8	36.53	30.17
142.51	147.1	277.74	254.0	40.69	36.25
148.09	152.4	283.08	257.1	45.35	41.83
153.64	157.6	288.39	260.1	50.57	48.50
159.16	163.0	293.68	262.9	56.35	55.97
170.12	174.1	298.95	265.6	62.52	63.77
175.57	179.2	304.19	268.4	68.80	71.57

P-8(NaK)					
7.81*	0.4094	101.33	106.2	224.59	232.1
8.83	0.4209	107.13	112.0	229.80	237.2
9.65	0.6832	112.87	117.8	235.02	242.3
10.57	0.9067	118.55	123.5	240.23	247.6
11.76	1.291	124.18	129.1	245.44	252.3
14.55	2.589	129.77	134.8	250.66	257.2
16.17	3.575	123.53**	128.5	255.88	261.9
18.01	4.915	129.25	134.2	261.09	266.2
20.06	6.630	134.44	139.3	266.32	271.0
22.31	8.830	139.71	144.4	271.56	275.7
24.82	11.46	145.18	149.6	276.78	280.6
27.63	14.69	150.60	154.7	281.98	285.6
30.76	18.53	156.01	159.6	287.16	290.3
34.25	23.11	161.40	164.5	292.32	295.3
38.14	28.60	166.76	169.4	297.45	300.4
42.49	34.10	172.10	174.1	302.55	306.7
47.37	39.91	177.43	178.9	307.63	312.5
52.78	47.11	182.73	183.7	312.69	317.6
58.74	55.17	188.02	188.9	284.75†	286.4
64.99	63.33	193.30	194.3	288.73	291.2
71.25	71.30	198.56	200.0	293.60	295.9
77.46	79.33	203.80	206.5	298.51	301.2
83.56	86.79	209.01	213.4	303.46	307.6
89.54	93.67	214.20	220.4	308.39	314.1
95.46	100.1	219.39	226.7	313.32	318.1

P-8(KNa)					
301.06*	255.0	62.32	61.35	203.60	191.4
305.50	256.7	68.59	68.68	219.43	204.2
310.36	260.4	74.85	76.15	224.68	208.1
315.26	262.3	80.99	83.28	229.93	211.6
6.60**	0.3821	87.02	89.85	235.19	215.0
7.41	0.4395	92.98	95.90	240.45	218.3
8.25	0.6254	98.91	101.7	245.72	221.7
9.13	0.8005	104.75	106.9	250.98	225.0
10.21	1.092	110.54	112.3	255.73†	227.7
11.36	1.499	116.27	117.4	260.45	231.1
12.60	2.046	121.94	122.6	265.44	234.0
14.01	2.825	127.58	127.6	270.47	237.0
15.56	3.867	133.17	132.6	275.58	240.0
17.30	5.185	138.74	137.5	280.67	242.9
19.23	6.920	144.26	142.4	285.74	245.9
21.38	9.073	149.76	147.0	290.80	249.2
23.78	11.70	155.24	151.4	295.84	252.0
26.45	14.89	160.69	156.0	300.87	254.9
29.43	18.66	166.12	160.4	310.66††	260.0
32.76	23.12	171.53	164.6	315.53	262.8
36.48	28.18	176.91	169.1	287.93‡	246.9
40.62	34.14	182.28	173.4	301.20	254.5
45.26	39.43	187.64	177.8	306.18	257.0
50.45	46.14	192.98	182.2	311.14	260.6
56.19	53.92	198.30	186.7	316.09	263.3

P-8(K)					
300.49*	248.7	69.60	71.16	208.40	193.3
305.17	251.0	75.84	77.78	213.61	196.8
310.00	253.4	81.94	84.40	218.80	200.5
314.87	256.3	87.90	90.68	224.00	204.0
319.78	258.9	93.81	96.58	229.20	207.1
8.97**	0.7385	99.69	102.1	234.42	210.4
9.74	0.9263	105.49	107.4	239.63	213.8
10.58	1.216	111.23	112.7	244.84	216.7
11.58	1.620	116.91	117.8	250.06	220.0
12.82	2.225	122.53	122.9	245.26†	216.9
14.21	3.061	128.12	127.9	250.30	220.0
15.77	4.138	133.66	132.8	255.25	223.1
17.54	5.546	139.16	137.7	260.20	226.3
19.50	7.367	144.64	142.5	265.26	229.3
21.70	9.631	150.08	147.1	270.34	232.3
24.16	12.46	155.50	151.6	275.41	235.2
26.89	15.75	160.89	156.3	280.45	238.1
29.95	19.68	166.25	161.0	285.49	240.7
33.37	24.32	171.57	165.6	290.51	243.7
37.16	29.76	176.88	170.0	295.51	246.3
41.40	35.20	182.18	174.2	300.51	248.3
46.15	40.87	187.46	178.3	305.49	251.1
51.41	47.84	192.71	182.1	310.44	254.3
57.22	56.12	197.96	185.9	315.39	256.8
63.36	64.30	203.19	189.7		

Note: Beginning of each series of experiments indicated as follows: (*) series 1, (**) series 2, (†) series 3, (††) series 4, (‡) series 5, (§) series 6.

heat-capacity variation with composition at higher temperature.

The heat-capacity curves for the zeolites (Figs. 1A through 1E) do not exhibit the normal, sigmoidal pattern typical of anhydrous compounds, but show a transition region in the temperature range from 150 to 225 K. This anomalous region is analogous to a glass transition, caused by an increase in the degrees of freedom of the zeolitic water as it changes from an icelike to a waterlike state with increasing temperature (see, for example, Haida et al., 1974). The temperature region and size of the glass-type transition are a function of merlinoite composition and therefore vary from sample to sample. Data for additional merlinoite compositions are needed to determine a systematic relationship between composition and glass-type transition characteristics.

Thermodynamic properties

Smoothed values for the C_P^0 and the derived thermodynamic functions $S_T^0 - S_0^0$, $(H_T^0 - H_0^0)/T$ and $-(G_T^0 - H_0^0)/T$ for the six synthetic merlinoite compositions are listed in Table 5.

As for feldspar minerals, the third-law entropies of zeolites may be quite different from the values of $S_{298}^0 - S_0^0$ measured by calorimetric methods. The discrepancy can be even more significant for zeolites than for feldspars because in addition to configurational contributions from disorder and mixing on framework Si-Al sites, there are also contributions to third-law entropy from mixing on zeolitic water sites and mixing on exchangeable-cation sites.

On the basis of their structural refinement of a natural merlinoite from Cupaello, Italy, Galli et al. (1979) found no evidence for Si-Al ordering on the tetrahedral sites T_1 and T_2 and identified five cation sites and six partially filled water sites in the merlinoite structure. The occupancy factors determined by Galli et al. (1979) for this merlinoite were used to estimate the site occupancies of the six synthetic merlinoite samples. The configurational entropy contribution, S_{ci}, to the third-law entropy for each sample was calculated using the method described by Ulbrich and Waldbaum (1976). Estimated values of S_{ci} for the synthetic merlinoites range between 44.6 and 47.8 J/(mol·K) and are given in Table 6 along with corrected values of S_{298}^0. The configurational entropy term is nontrivial, amounting to about 17% of the calorimetrically determined value of $S_{298}^0 - S_0^0$.

Heats of solution

Enthalpies of solution were determined for α-quartz, gibbsite, NaF, KF, and six synthetic merlinoite samples in 477 g of 24.4 wt% $HF_{(aq)}$. Measurement of heats of solution for the standard materials were made to obtain values appropriate for the dissolution-reaction stoichiometry of merlinoite in 24.4 wt% $HF_{(aq)}$.

α-Quartz (SiO_2). Quartz is the most commonly used reference material for Si in heat of solution measurements by both hydrofluoric acid and molten-salt calorimetry. Despite its importance as a primary standard, problems exist in the determination of accurate heat-of-solution measurements (Hemingway and Robie, 1977; Hemingway et al., 1988).

Discrepancies between values obtained for the enthalpy of reaction of α-quartz with $HF_{(aq)}$ exist not only between laboratories, but also for data obtained within one laboratory (see Hemingway et al., 1988). Hemingway et al. (1988) identified two possible causes for such discrepancies: heat contributed from the abrasion of the calorimeter by quartz particles and the excess enthalpy contributed by the dissolution of quartz particles smaller than 2 μm. Both of these factors would cause the measured enthalpy of solution of quartz to be higher than the true enthalpy of solution at a particular temperature. In addition, the contribution of such factors will be proportionately greater at lower temperature; therefore, the enthalpy of solution at 25 °C obtained by extrapolation will be even more negative than if the contribution were the same at all temperatures.

Such discrepancies in the measured heat of solution of NBS SRM 1654 were encountered in this study. Sixteen measurements were made of ΔH_{soln} for α-quartz at approximately 35 and 50 °C. Measured heats of solution varied by 3.6 kJ/mol at 49.45 °C. Enthalpy of solution values clustered about −137.33 kJ/mol at 34.7 °C, approximately 1 kJ/mol smaller than the value determined by Nitkiewicz et al. (unpublished data, 1983). Because the 44- to 55-μm size fraction of the quartz reference material was used in this study, surface-energy contributions to the measured enthalpy of solution are believed to be negligible. Subsequent to the measurements made in this study, Nitkiewicz et al. (unpublished data, 1983) measured the enthalpy of abrasion of quartz on the same Au calorimeter by varying the surface area of the fins used to stir the solution. The apparent enthalpy of solution of α-quartz was increased from −136.55 kJ/mol to −140.70 kJ/mol at 34.8 °C by an increase in fin surface area of approximately 68%. This increase was attributed to heat of abrasion by Hemingway et al. (1988). A similar effect may have occurred in this study when the stirring speed of the smaller-surface-area fins was increased from 144 rpm to 600 rpm in an effort to decrease the time required for complete dissolution of the quartz. At 49.45 °C, the increase in stirring rate resulted in an increase in the apparent enthalpy of solution of quartz from −137.63 to −141.30 kJ/mol.

Because of the possible errors introduced by abrasion, we discard all data for the enthalpy of solution of α-quartz collected at 35 °C and only retain the value of −137.63 kJ/mol measured at 49.45 °C prior to the use of an increased stirring rate. To obtain $d\Delta H_{soln}/dT$, values for the enthalpy of solution of NBS SRM 1654 at 34.5 °C and 25 °C were taken from Nitkiewicz et al. (unpublished data, 1983) and from Johnson et al. (1982), respectively (see Table 7). Both of these studies were conducted using 24.4% $HF_{(aq)}$; therefore, the measured heats of solution are directly comparable with our 49.45 °C value. In addition,

TABLE 5. Molar thermodynamic properties of merlinoite

Temp. T (K)	Heat capacity C_p^o	Entropy $S_T^o - S_0^o$	Enthalpy function $(H_T^o - H_0^o)/T$	Gibbs energy function $-(G_T^o - H_0^o)/T$
	[J/(mol·K)]			
P-9(NaK): $Na_{0.81}K_{0.19}AlSi_{1.94}O_{5.88}\cdot 2.13H_2O$, GFW = 239.9669				
5	0.109	0.035	0.026	0.009
10	0.863	0.283	0.212	0.071
15	2.974	0.968	0.727	0.241
20	6.865	2.315	1.738	0.576
25	12.05	4.381	3.262	1.120
30	18.20	7.110	5.228	1.882
35	24.94	10.42	7.558	2.859
40	31.79	14.20	10.16	4.036
45	38.44	18.33	12.93	5.392
50	45.02	22.72	15.81	6.903
60	58.42	32.11	21.79	10.31
70	71.80	42.12	27.98	14.13
80	84.68	52.55	34.27	18.28
90	96.69	63.23	40.55	22.68
100	107.9	74.00	46.73	27.27
110	118.5	84.78	52.77	32.01
120	128.9	95.54	58.68	36.86
130	139.1	106.3	64.47	41.78
140	149.0	116.9	70.16	46.77
150	158.6	127.5	75.74	51.80
160	168.0	138.1	81.21	56.87
170	177.3	148.5	86.59	61.95
180	187.0	158.9	91.89	67.05
190	197.6	169.3	97.17	72.16
200	209.2	179.8	102.5	77.28
210	221.1	190.3	107.8	82.41
220	232.4	200.8	113.3	87.55
230	242.8	211.4	118.7	92.70
240	252.7	221.9	124.0	97.87
250	262.3	232.4	129.4	103.0
260	271.7	242.9	134.7	108.2
270	281.0	253.3	139.9	113.4
280	290.0	263.7	145.1	118.6
290	298.7	274.0	150.3	123.8
300	307.1	284.3	155.4	128.9
310	315.4	294.5	160.4	134.1
273.15	283.8	256.6	141.6	115.0
298.15	305.5	282.4	154.4	128.0
P-9(KNa): $K_{0.80}Na_{0.20}AlSi_{1.94}O_{5.88}\cdot 1.81H_2O$, GFW = 244.0282				
5	0.124	0.040	0.029	0.010
10	1.029	0.328	0.246	0.081
15	3.591	1.159	0.875	0.284
20	7.969	2.753	2.067	0.686
25	13.61	5.117	3.793	1.324
30	20.08	8.160	5.959	2.201
35	27.03	11.77	8.470	3.305
40	33.95	15.84	11.22	4.614
45	40.53	20.22	14.12	6.102
50	46.92	24.82	17.08	7.742
60	59.77	34.51	23.12	11.39
70	72.54	44.69	29.27	15.41
80	84.80	55.18	35.45	19.73
90	96.19	65.84	41.58	24.26
100	106.6	76.52	47.57	28.95
110	116.5	87.15	53.39	33.76
120	126.3	97.71	59.06	38.65
130	135.9	108.2	64.60	43.59
140	145.3	118.6	70.03	48.58
150	154.6	129.0	75.36	53.60
160	163.8	139.2	80.60	58.63
170	173.5	149.4	85.78	63.67
180	183.7	159.7	90.93	68.72
190	194.2	169.9	96.09	73.77
200	204.3	180.1	101.3	78.83
210	213.8	190.3	106.4	83.90
220	222.5	200.4	111.5	88.96
230	230.7	210.5	116.5	94.03
240	238.5	220.5	121.4	99.09

TABLE 5—*Continued*

Temp. T (K)	Heat capacity C_p^o	Entropy $S_T^o - S_0^o$	Enthalpy function $(H_T^o - H_0^o)/T$	Gibbs energy function $-(G_T^o - H_0^o)/T$
	[J/(mol·K)]			
250	246.0	230.4	126.2	104.1
260	253.3	240.2	131.0	109.2
270	260.2	249.9	135.6	114.2
280	266.9	259.4	140.2	119.2
290	273.1	268.9	144.7	124.2
300	279.1	278.3	149.1	129.2
310	285.0	287.5	153.4	134.2
320	291.4	296.7	157.6	139.1
330	298.5	305.8	161.7	144.0
340	306.1	314.8	165.9	148.9
273.15	262.4	252.9	137.1	115.8
298.15	278.0	276.6	148.3	128.3
P-9(K): $KAlSi_{1.94}O_{5.88}\cdot 1.69H_2O$, GFW = 245.0880				
5	0.128	0.040	0.030	0.010
10	1.167	0.356	0.270	0.086
15	3.980	1.292	0.980	0.312
20	8.600	3.031	2.273	0.758
25	14.45	5.562	4.108	1.454
30	21.04	8.770	6.372	2.398
35	28.01	12.53	8.963	3.571
40	34.95	16.73	11.78	4.950
45	41.53	21.23	14.72	6.507
50	47.92	25.94	17.72	8.213
60	60.61	35.80	23.82	11.98
70	73.09	46.08	29.97	16.11
80	85.03	56.63	36.11	20.52
90	96.10	67.29	42.17	25.12
100	106.3	77.95	48.08	29.87
110	116.0	88.55	53.82	34.73
120	125.6	99.05	59.40	39.65
130	135.1	109.5	64.86	44.62
140	144.7	119.8	70.22	49.62
150	154.3	130.2	75.50	54.65
160	164.0	140.4	80.73	59.69
170	173.8	150.7	85.92	64.74
180	183.2	160.9	91.06	69.80
190	192.3	171.0	96.15	74.86
200	201.0	181.1	101.2	79.92
210	209.2	191.1	106.1	84.97
220	216.8	201.0	111.0	90.02
230	224.1	210.8	115.7	95.06
240	230.9	220.5	120.4	100.1
250	237.4	230.0	125.0	105.1
260	243.6	239.5	129.4	110.1
270	249.6	248.8	133.7	115.0
280	255.3	258.0	138.0	120.0
290	260.9	267.0	142.1	124.9
300	266.0	276.0	146.2	129.8
310	270.9	284.8	150.1	134.6
273.15	251.4	251.7	135.1	116.6
298.15	265.1	274.3	145.4	128.9
P-8(NaK): $Na_{0.81}K_{0.19}AlSi_{1.81}O_{5.62}\cdot 2.18H_2O$, GFW = 233.0567				
5	0.086	0.027	0.020	0.007
10	0.767	0.237	0.179	0.058
15	2.854	0.880	0.671	0.209
20	6.598	2.175	1.650	0.525
25	11.66	4.172	3.129	1.044
30	17.58	6.811	5.034	1.777
35	24.18	10.01	7.291	2.719
40	30.88	13.68	9.825	3.855
45	37.16	17.68	12.52	5.167
50	43.47	21.92	15.29	6.629
60	56.74	31.02	21.09	9.925
70	69.80	40.75	27.12	13.63
80	82.42	50.90	33.25	17.65
90	94.14	61.30	39.38	21.92
100	104.8	71.77	45.39	26.38

TABLE 5—*Continued*

Temp. T (K)	Heat capacity C_P°	Entropy $S_T^\circ - S_0^\circ$	Enthalpy function $(H_T^\circ - H_0^\circ)/T$	Gibbs energy function $-(G_T^\circ - H_0^\circ)/T$
	[J/(mol·K)]			
110	115.0	82.24	51.26	30.98
120	125.0	92.68	56.99	35.69
130	134.9	103.1	62.60	40.47
140	144.7	113.4	68.12	45.32
150	154.1	123.7	73.54	50.20
160	163.2	134.0	78.86	55.12
170	172.1	144.1	84.08	60.05
180	181.2	154.2	89.22	65.01
190	191.1	164.3	94.32	69.97
200	202.3	174.4	99.43	74.94
210	214.6	184.5	104.6	79.91
220	226.6	194.8	109.9	84.90
230	237.5	205.1	115.2	89.90
240	247.3	215.4	120.5	94.92
250	256.6	225.7	125.8	99.94
260	265.4	236.0	131.0	105.0
270	274.2	246.1	136.1	110.0
280	283.2	256.3	141.2	115.1
290	292.9	266.4	146.3	120.1
300	303.5	276.5	151.3	125.1
310	314.7	286.6	156.4	130.2
273.15	277.0	249.3	137.7	111.6
298.15	301.5	274.6	150.4	124.2
P-8(KNa): $K_{0.91}Na_{0.09}AlSi_{1.81}O_{5.62}\cdot 1.79H_2O$, GFW = 237.6288				
5	0.134	0.044	0.032	0.011
10	1.041	0.347	0.259	0.088
15	3.481	1.159	0.867	0.292
20	7.675	2.693	2.008	0.685
25	13.13	4.971	3.668	1.303
30	19.42	7.911	5.759	2.152
35	26.18	11.41	8.190	3.218
40	32.95	15.35	10.86	4.485
45	39.37	19.60	13.68	5.926
50	45.73	24.08	16.56	7.516
60	58.46	33.55	22.49	11.06
70	70.51	43.47	28.50	14.98
80	82.08	53.65	34.48	19.17
90	92.83	63.95	40.37	23.57
100	102.6	74.24	46.12	28.13
110	111.9	84.46	51.68	32.79
120	120.9	94.58	57.07	37.51
130	129.8	104.6	62.32	42.29
140	138.6	114.6	67.45	47.10
150	147.1	124.4	72.48	51.92
160	155.4	134.2	77.40	56.76
170	163.5	143.8	82.23	61.60
180	171.6	153.4	86.97	66.43
190	179.9	162.9	91.64	71.26
200	188.3	172.3	96.27	76.08
210	196.6	181.7	100.8	80.89
220	204.4	191.1	105.4	85.68
230	211.6	200.3	109.8	90.46
240	218.2	209.5	114.2	95.23
250	224.5	218.5	118.5	99.98
260	230.6	227.4	122.7	104.7
270	236.7	236.2	126.8	109.4
280	242.6	244.9	130.8	114.1
290	248.5	253.6	134.8	118.8
300	254.1	262.1	138.7	123.4
310	259.7	270.5	142.5	128.0
273.15	238.6	239.0	128.1	110.9
298.15	253.1	260.5	138.0	122.5
P-8(K): $KAlSi_{1.81}O_{5.62}\cdot 1.69H_2O$, GFW = 237.2771				
5	0.115	0.036	0.027	0.009
10	1.022	0.317	0.240	0.077
15	3.591	1.150	0.873	0.278
20	7.865	2.727	2.050	0.677
25	13.44	5.062	3.753	1.309
30	19.78	8.062	5.886	2.177
35	26.60	11.62	8.355	3.266
40	33.29	15.61	11.06	4.556
45	39.67	19.90	13.88	6.021
50	46.17	24.42	16.78	7.633
60	59.62	34.03	22.81	11.22
70	71.66	44.15	28.95	15.20
80	82.43	54.43	34.97	19.46
90	92.72	64.74	40.82	23.92
100	102.4	75.01	46.50	28.51
110	111.6	85.20	52.00	33.20
120	120.6	95.30	57.34	37.96
130	129.6	105.3	62.55	42.76
140	138.4	115.2	67.66	47.58
150	147.0	125.1	72.66	52.42
160	155.6	134.8	77.58	57.26
170	164.2	144.5	82.42	62.11
180	172.4	154.1	87.19	66.96
190	180.1	163.7	91.88	71.80
200	187.4	173.1	96.47	76.63
210	194.4	182.4	101.0	81.45
220	201.2	191.6	105.4	86.25
230	207.6	200.7	109.7	91.02
240	213.9	209.7	113.9	95.78
250	220.0	218.5	118.0	100.0
260	226.1	227.3	122.1	105.2
270	232.0	235.9	126.0	109.9
280	237.7	244.5	129.9	114.6
290	243.2	252.9	133.7	119.2
300	248.4	261.2	137.5	123.8
310	253.7	269.5	141.1	128.3
273.15	233.9	238.6	127.3	111.4
298.15	247.5	259.7	136.8	122.9

the particle-size ranges used in this study and those of Johnson et al. (1982) and Nitkiewicz et al. (unpublished data, 1983) were 44–55 μm, 37–44 μm, and 3–149 μm, respectively. For particle sizes of >2 μm, no surface-energy contribution is expected (Hemingway et al., 1988), and again the results are directly comparable. A straight-line fit through the data produces the equation

$$\Delta H_{\text{soln},\alpha\text{-qtz}} = -133.46 - 8.3989 \times 10^{-2}T,$$

where T is in degrees Celsius. The calculated value of

TABLE 6. Calculated values for the configurational entropy contribution (S_{cl}) to third-law entropy and corrected values of S_{298}° for the synthetic merlinoites

Sample	$S_{298}^\circ - S_0^\circ$	S_{cl} (= S_0°)	S_{298}°
	[J/(mol·K)]		
P-9(NaK)	282.4 ± 0.4	46.4 ± 15.3	328.8 ± 15.3
P-9(KNa)	276.6 ± 0.4	47.8 ± 15.8	324.4 ± 15.8
P-9(K)	274.3 ± 0.4	46.4 ± 15.3	320.7 ± 15.3
P-8(NaK)	274.6 ± 0.4	44.6 ± 14.7	319.2 ± 14.7
P-8(KNa)	260.5 ± 0.3	45.4 ± 15.0	305.9 ± 15.0
P-8(K)	259.7 ± 0.3	44.6 ± 14.7	304.3 ± 14.7

TABLE 7. Heats of solution of α-quartz, gibbsite, NaF, KF, and synthetic merlinoite samples in 24.4 wt% $HF_{(aq)}$

Sample mass (g)	ΔT_{corr} (°C)	$\bar{T}_{soln}$ (°C)	Heat capacities (J/deg) Initial	Heat capacities (J/deg) Final	ΔH_{soln} at $\bar{T}_{soln}$ (kJ/mol)
α-Quartz, SiO_2 (Reaction 3)					
0.2511	0.2927	49.4546	2037.6638	2037.7442	−137.629
—	—	34.5*	—	—	−136.32*
0.10801†	—	25.0†	—	—	−135.588†
$\Delta H^0_{soln,298}$ = −135.560 ± 0.402 kJ/mol					
Gibbsite, $Al(OH)_3$ (Reaction 4)					
0.1850	0.1936	34.0542	2003.0945	2003.2055	−163.446
0.1849	0.1943	34.7443	2006.6022	2004.1228	−163.350
0.1850	0.1935	34.7367	2001.2734	2004.2756	−163.350
0.1850	0.1919	34.7336	2008.4348	2009.9482	−163.351
0.1850	0.1918	34.7363	2011.6377	2009.5413	−163.351
0.5002	0.5222	34.7794	2002.7272	2009.2098	−163.345
0.5002	0.5239	34.7352	2003.3829	2004.5841	−163.351
0.1850	0.1877	49.4976	2034.2726	2037.5874	−161.280
0.1850	0.1881	49.4637	2035.2460	2035.4680	−161.285
0.1850	0.1897	49.4882	2035.3316	2035.1094	−161.281
0.1850	0.1862	49.4924	2035.4161	2034.8779	−161.281
$\Delta H^0_{soln,298}$ = −164.716 ± 0.494 kJ/mol					
NaF (Reaction 5)					
0.0995	0.0028	34.7640	2003.8043	2005.6377	−2.763
0.0995	0.0029	34.7722	1996.8064	1996.5406	−2.762
0.0995	0.0037	34.7647	1989.5663	1991.1727	−2.763
0.0995	0.0037	34.7102	2008.3733	2009.6097	−2.769
0.0995	0.0016	49.4485	2026.1229	2030.6961	−1.247
0.0995	0.0009	49.2719	2037.0750	2035.8670	−1.265
0.0995	0.0019	49.2716	2036.0322	2038.8048	−1.265
$\Delta H^0_{soln,298}$ = −3.771 ± 0.011 kJ/mol					
KF (Reaction 6)					
0.1377	0.0304	34.8112	2007.6749	2007.4401	−26.255
0.1377	0.0314	34.7894	1996.0952	1999.8678	−26.256
0.1377	0.0316	34.7870	1991.9284	1990.6086	−26.256
0.1377	0.0296	49.4215	2038.4139	2041.1811	−25.595
0.1377	0.0299	49.2870	2032.8533	2036.1297	−25.601
0.1377	0.0299	49.2849	2033.4513	2034.4967	−25.601
$\Delta H^0_{soln,298}$ = −26.699 ± 0.080 kJ/mol					
P-9(NaK): $Na_{0.81}K_{0.19}AlSi_{1.94}O_{5.88}\cdot 2.13H_2O$ (Reaction 7)					
0.5437	0.5455	34.6876	2003.8701	2008.7259	−482.0255
0.5437	0.5425	34.6456	2008.1388	2010.6252	−482.0255
0.5437	0.5436	34.6375	2006.8680	2010.6850	−482.0254
0.5437	0.5340	49.4553	2038.1286	2041.2964	−482.0444
0.5437	0.5358	49.4691	2039.8805	2040.4925	−482.0444
0.5437	0.5361	49.4609	2041.2669	2040.5441	−482.0444
$\Delta H^0_{soln,298}$ = −482.013 ± 1.446 kJ/mol					
P-9(KNa): $K_{0.80}Na_{0.20}AlSi_{1.94}O_{5.88}\cdot 1.81H_2O$ (Reaction 7)					
0.5660	0.5528	35.1614	1984.4266	1985.6354	−474.0136
0.5660	0.5542	35.1513	1980.4332	1984.3488	−474.0121
0.5660	0.5557	35.1637	1983.6769	1983.7031	−474.0140
0.5660	0.5426	49.8736	2037.8611	2036.4589	−476.2669
0.5660	0.5427	49.5090	2037.0383	2035.1587	−474.2111
0.5660	0.5422	49.4679	2034.8864	2036.3456	−476.2048
$\Delta H^0_{soln,298}$ = −472.457 ± 1.417 kJ/mol					
P-9(K): $KAlSi_{1.94}O_{5.88}\cdot 1.69H_2O$ (Reaction 7)					
0.5639	0.5385	49.2787	2041.6575	2043.1955	−477.3117
0.5639	0.5382	49.2805	2041.0301	2039.6569	−477.3117
0.5639	0.5359	49.2840	2045.1027	2047.5173	−477.3115
0.5639	0.5463	34.5402	2011.9146	2013.6364	−478.0403
0.5639	0.5465	34.5603	2012.7756	2013.7332	−478.0393
0.5639	0.5470	34.5407	2010.8403	2010.5017	−478.0403
$\Delta H^0_{soln,298}$ = −478.512 ± 1.436 kJ/mol					
P-8(NaK): $Na_{0.81}K_{0.19}AlSi_{1.81}O_{5.62}\cdot 2.18H_2O$ (Reaction 7)					
0.5226	0.5169	34.7367	2017.0488	2016.9822	−465.4808
0.5226	0.5170	34.6919	2015.2989	2018.9931	−465.4703
0.5226	0.5186	34.6767	2015.8131	2017.6409	−465.4667
0.5226	0.5152	49.4528	2039.3445	2041.3185	−468.9338
0.5226	0.5156	49.4576	2036.6378	2042.5992	−468.9350
0.5226	0.5163	49.4795	2036.5444	2037.5916	−468.9401
$\Delta H^0_{soln,298}$ = −463.196 ± 1.390 kJ/mol					
P-8(KNa): $K_{0.91}Na_{0.09}AlSi_{1.81}O_{5.62}\cdot 1.79H_2O$ (Reaction 7)					
0.5457	0.5367	35.0888	1983.3887	1983.2693	−463.7429
0.2729	0.2687	34.9213	1978.8899	1980.9681	−463.7502
0.2757	0.2688	34.8740	2003.7101	2005.9529	−463.7522
0.5457	0.5215	49.4533	2037.6192	2036.6808	−463.1196
0.5457	0.5234	49.4518	2036.0863	2037.0007	−463.1197
0.5457	0.5208	49.4461	2037.9160	2041.4240	−463.1199
$\Delta H^0_{soln,298}$ = −464.181 ± 1.393 kJ/mol					
P-8(K): $KAlSi_{1.81}O_{5.62}\cdot 1.69H_2O$ (Reaction 7)					
0.5459	0.5235	49.2592	2041.1372	2042.9278	−464.7440
0.5459	0.5230	49.2598	2040.9644	2044.3993	−464.7440
0.5449	0.5334	49.2880	2043.3161	2043.1089	−464.7444
0.5459	0.5328	34.7884	2013.4455	2014.9555	−464.5256
0.5459	0.5288	34.6009	2013.7245	2014.5625	−464.5228
0.5459	0.5307	34.6162	2012.6574	2013.3736	−464.5230
0.5459	0.5307	34.6194	2010.8174	2015.7806	−464.5231
$\Delta H^0_{soln,298}$ = −464.378 ± 1.393 kJ/mol					

Note: Column headings: Sample mass, the mass of the sample reacted. ΔT_{corr}, the temperature rise for the dissolution reaction corrected for heat exchange. $\bar{T}_{soln}$, the mean temperature of the solution period. Initial and final heat capacities, the heat capacity of the calorimetric system before and after the experiment as determined by electrical calibration. ΔH_{soln} at $\bar{T}_{soln}$, the enthalpy of solution at the mean temperature of the solution period. Reaction numbers refer to reactions listed in Table 8.

* Data taken from Nitkiewicz et al. (unpublished data, 1983).

† Data taken from Johnson et al. (1982).

ΔH_{soln} for α-quartz is −135.56 ± 0.40 kJ/mol at 298.15 K. This agrees with the value (−135.59 kJ/mol) measured by Johnson et al. (1982), but is 0.83% less negative than the value (−136.69 kJ/mol) recommended by Kilday and Prosen (1973) for the enthalpy of solution of NBS SRM 1654 in 24.4% $HF_{(aq)}$. However, because the data measured by Kilday and Prosen (1973) may contain heat contributions from abrasion (Hemingway et al., 1988), we accept the value of −135.56 ± 0.40 kJ/mol obtained from the equation above for the enthalpy of solution of α-quartz at 25 °C.

Gibbsite [$Al(OH)_3$]. The heat of solution of $Al(OH)_3$ was measured at 35 and 50 °C using the solution that resulted from the dissolution of quartz reaction (Table 7). The value for ΔH_{soln} of gibbsite at 25 °C (−164.716 ± 0.494 kJ/mol) agrees with that determined by Johnson et al. (1982) for the enthalpy of reaction of gibbsite with 24.4 wt% $HF_{(aq)}$ (−165.180 ± 0.125 kJ/mol). This was expected because our findings and those of Hemingway and Robie (1977) show that the presence of dissolved SiO_2 in the initial $HF_{(aq)}$ solution has very little effect upon ΔH_{soln} of $Al(OH)_3$. Comparison of our values with those determined by Hemingway and Robie for 20.1 wt% $HF_{(aq)}$ suggests that ΔH_{soln} of gibbsite is approximately 4 kJ/mol more negative for 24.4 wt% HF from 25 to 50 °C.

NaF and KF. The heat of solution of NaF was mea-

TABLE 8. Thermochemical reaction scheme for the derivation of the standard enthalpy of formation at 298.15 K of P-9(NaK) synthetic merlinoite

Reaction	ΔH (kJ/mol)
1. $[A] \rightarrow [HF \cdot 3.44H_2O] + [2566.65HF \cdot 8831.24H_2O]$	0
2. $1.13H_2O + [2566.65HF \cdot 8834.68H_2O] \rightarrow [B]$	−0.458 ± 0.049
3. $1.94SiO_2 + [B] \rightarrow [C]$	−262.986 ± 0.781
4. $Al(OH)_{3(c)} + [C] \rightarrow [D]$	−164.716 ± 0.494
5. $0.81NaF + [D] \rightarrow [E]$	−3.055 ± 0.009
6. $0.19KF + [E] \rightarrow [F]$	−5.073 ± 0.015
7. $[F] \rightarrow Na_{0.81}K_{0.19}AlSi_{1.94}O_{5.88} \cdot 2.13H_2O + [A]$	482.013 ± 1.446
8. $1.94Si_{(c)} + 1.94O_{2(g)} \rightarrow 1.94SiO_{2(c)}$	−1766.758 ± 1.940
9. $Al_{(c)} + 1.5H_{2(g)} + 1.5O_{2(g)} \rightarrow Al(OH)_{3(c)}$	−1293.128 ± 1.192
10. $0.81Na_{(c)} + 0.405F_{2(g)} \rightarrow 0.81NaF_{(c)}$	−467.006 ± 0.543
11. $0.19K_{(c)} + 0.095F_{2(g)} \rightarrow 0.19KF_{(c)}$	−108.257 ± 0.128
12. $[HF \cdot 3.44H_2O] \rightarrow 3.94H_{2(g)} + 1.72O_{2(g)} + 0.5F_{2(g)}$	321.26 ± 0.40
13. $1.13H_{2(g)} + 0.565O_{2(g)} \rightarrow 1.13H_2O$	−322.988 ± 0.047
14. $[2566.65HF \cdot 8831.24H_2O] + 3.44H_{2(g)} + 1.72O_{2(g)} \rightarrow [2566.65HF \cdot 8834.68H_2O]$	0
$[A] = [2567.65HF \cdot 8834.68H_2O]$	
$[B] = [2566.65HF \cdot 8835.81H_2O]$	
$[C] = [1.94H_2SiF_6 \cdot 2555.01HF \cdot 8839.69H_2O]$	
$[D] = [AlF_3 \cdot 1.94H_2SiF_6 \cdot 2552.01HF \cdot 8842.69H_2O]$	
$[E] = [0.81NaF \cdot AlF_3 \cdot 1.94H_2SiF_6 \cdot 2552.01HF \cdot 8842.69H_2O]$	
$[F] = [0.19KF \cdot 0.81NaF \cdot AlF_3 \cdot 1.94H_2SiF_6 \cdot 2552.01HF \cdot 8842.69H_2O]$	

sured at 35 and 50 °C in the solution that resulted from the dissolution of both gibbsite and quartz (Table 7). The value at 25 °C (−3.771 ± 0.011 kJ/mol) compares well with that determined for the dissolution of NaF in pure 24.4 wt% $HF_{(aq)}$ by Johnson et al. (1982) (−4.056 ± 0.063 kJ/mol). The heat of solution of KF in the solution resulting from the dissolution of NaF, gibbsite, and quartz was measured at 35 and 50 °C (Table 7). We could find no previously determined values for ΔH_{soln} of KF.

Experiments were also performed to measure the heat of solution of 50/50 molar mixtures of NaF and KF in the solution resulting from the dissolution of gibbsite and quartz. It was found that ΔH_{soln} for mixtures of NaF and KF are stoichiometric additions of the end-member values. Therefore, values of ΔH_{soln} at 25 °C were calculated for NaF and KF mixtures corresponding to the stoichiometries of the sodian-potassian and potassian-sodian merlinoites using the data for pure NaF and KF from Table 7.

Synthetic merlinoite samples. The heat of solution of merlinoite in 24.4 wt% $HF_{(aq)}$ was determined at approximately 35 and 50 °C for samples P-8 and P-9 (Table 7). Dissolution reactions were complete for all P-9 merlinoite samples. For the P-8 merlinoites, the dissolution reaction was complete only for the K-end member at 50 °C. At lower temperatures and higher Na contents, a small amount (<0.001 g) of material remained floating at the solution surface at the end of the dissolution reactions. This material was found to be amorphous by X-ray diffraction analysis and was insoluble in 24.4 wt% $HF_{(aq)}$ over periods of several weeks. The composition of the material was not determined. Pelletization of the sample reduced the amount of amorphous material remaining at the end of the experiment, but did not eliminate it. There was no correlation between the amount of remaining material and the observed heat of solution (i.e., samples leaving more residual amorphous material were not less exothermic). It was assumed, therefore, that the ΔH_{soln} values measured for P-8(K), P-8(KNa) and P-8(NaK) are reasonable approximations to true values, however values of ΔH_{soln} at 25 °C should be viewed as maxima.

Standard enthalpies of formation at 298.15 K

The thermochemical cycle used to derive the enthalpy of formation of P-9(NaK) synthetic merlinoite is shown in Table 8. The enthalpy of solution of 24.40 wt% HF in 24.41 wt% HF (Reaction 1) is assumed to be zero. The molar enthalpies of Reactions 3, 4, 5, and 7 are taken from Table 7. The enthalpy of dilution of $HF_{(aq)}$ (Reaction 2) and the enthalpy of formation of $[HF \cdot 3.44H_2O]$ (Reaction 12) are taken from Johnson et al. (1982). The enthalpy of formation for Reaction 14 is based on the findings of Johnson et al. (1973) and approximated as zero (actual value = −0.0002 kJ/mol). The standard enthalpies of formation for Reactions 8, 9, 10, and 13 are based on standard molar enthalpies of formation taken from Robie et al. (1979). The standard enthalpy of formation for KF (Reaction 11) is based on the standard molar enthalpy of formation from Parker et al. (1976).

Summation of the reactions and corresponding values of ΔH yields a value of −3591.2 ± 2.9 kJ/mol for the standard enthalpy of formation from the elements (ΔH_f^0) for P-9(NaK) merlinoite. Similar thermochemical cycles have been written for the reaction stoichiometries of the other merlinoite samples. Their standard enthalpies of formation from the elements (ΔH_f^0 in kJ/mol) are P-9(KNa), −3519.0 ± 2.9; P-9(K), −3481.8 ± 3.0; P-8(NaK), −3488.3 ± 2.8; P-8(KNa), −3387.3 ± 2.8;

TABLE 9. Comparison of estimated entropy values with calorimetry values for the six synthetic merlinoite samples

Zeolite sample	Measured entropy	Estimated entropy* Helgeson et al. (1978)	Robinson and Haas (1983)	Holland (1989)
	(J/mol·K)			
P-9(NaK)	282.4	314.9(11.5)	288.7(2.3)	225.7(20.1)
P-9(KNa)	276.6	296.0(7.0)	268.5(2.9)	231.7(16.2)
P-9(K)	274.3	287.6(4.9)	261.0(4.8)	233.0(15.1)
P-8(NaK)	274.6	312.5(13.8)	285.9(4.1)	214.3(22.0)
P-8(KNa)	260.5	285.5(9.6)	261.3(0.3)	209.6(19.5)
P-8(K)	259.7	278.4(7.2)	255.5(1.6)	218.6(15.8)
Avg % deviation		(9.0)	(2.7)	(18.1)

* Percent deviation in estimated values shown in parentheses.

and P-8(K), -3360.0 ± 2.8. The standard enthalpy of merlinoite decreases with increasing Na content and also with increasing Si/Al ratio. The relationship between Na content and enthalpy may result from the greater bond strength of Na-O relative to K-O and/or from the higher water contents of the Na-rich merlinoites. The contribution of enthalpy to the thermodynamic stability of these merlinoites is discussed in the following paper (Donahoe et al., 1990).

COMPARISON OF MEASURED DATA TO ESTIMATED VALUES

Third-law entropies

Numerous techniques have been devised for the estimation of entropy values for minerals (e.g., Craig and Barton, 1973; Nriagu, 1975; Saxena, 1976; Cantor, 1977; Helgeson et al., 1978; Robinson and Haas, 1983; Holland, 1989). The entropy values for the six merlinoite samples were estimated using the methods of Helgeson et al. (1978), Robinson and Haas (1983), and Holland (1989). The results are compared with the measured calorimetric entropies in Table 9.

The entropy estimation method of Helgeson et al. (1978) is a path-dependent method that employs volume and entropy changes of reactions involving the phase of interest and structurally related minerals and oxides for which measured entropy values are known. Entropy values were calculated using reactions between each merlinoite composition and microcline and/or albite. Relatively large deviations (5–14%) are associated with merlinoite entropy values estimated by this technique (see Table 9). Estimated entropy values are systematically higher than calorimetric entropies, and errors increase with increasing Na content. The higher estimated values reflect the use of data with configurational contributions in the model. Predicted values for the merlinoite samples therefore lie between the entropy determined from calorimetry and the value of S^0_{298} corrected for configurational entropy contributions. Estimated values might be improved if calorimetric data for minerals more closely related structurally to merlinoite were available (e.g., phillipsite).

TABLE 10. Comparison of measured enthalpies of formation for the synthetic merlinoite samples with enthalpy values estimated by the technique of Chermak and Rimstidt (1989)

Sample	Measured enthalpy (kJ/mol)	Estimated enthalpy (kJ/mol)	% Error
P-9(NaK)	−3591.2	−3595.7	0.13
P-9(KNa)	−3519.0	−3517.5	0.04
P-9(K)	−3481.8	−3487.4	0.24
P-8(NaK)	−3488.3	−3492.1	0.11
P-8(KNa)	−3387.3	−3396.2	0.26
P-8(K)	−3359.9	−3369.1	0.27

The estimation techniques of Holland (1989) and Robinson and Haas (1983) are based on a polyhedral approach where the entropies of structural components of minerals in various coordination states are determined by linear regression of calorimetric data for a variety of minerals. The technique developed by Holland (1989) refines that of Robinson and Haas (1983) by including the effect of volume on entropy. Entropies estimated by the models are compared in Table 9.

The method of Robinson and Haas (1983) predicts $S^0_{298} - S^0_0$ to within 5% or better; however, entropy values are systematically high and low for Na-rich and potassian merlinoite compositions, respectively. Although Holland's (1989) method is more sophisticated and easier to use, it produces estimated entropies for the merlinoite samples that are 15–22% lower than those measured. Holland's (1989) method predicts the entropy of natrolite (Johnson et al., 1983) with only 0.4% deviation; however, calorimetric entropies for analcime, scolecite, and mesolite (Johnson et al., 1982, 1983) range from 7.4 to 12.6% higher than the estimated values. Holland's (1989) model was constructed using only data for extremely stable phases and therefore may not be useful for predicting the entropy of a metastable phase. This interpretation is supported by the fact that a polyhedral model constructed by Chermak (unpublished data, 1989) using a number of metastable phases produces estimated entropies for zeolites with even smaller average deviations than the model of Robinson and Haas (1983).

Enthalpies of formation

Few methods have been developed to estimate the enthalpies of silicate minerals (Robinson and Haas, 1983; Chermak and Rimstidt, 1989). The method of Robinson and Haas (1983) empirically predicts only the relative enthalpy ($\Delta H^0_T - \Delta H^0_0$) of silicates and so cannot be evaluated with respect to our merlinoite enthalpy-of-formation data. Chermak and Rimstidt (1989) have developed a model based on breaking silicate minerals into structural polyhedra by which enthalpies of formation can be estimated. Chermak and Rimstidt (1989) determined the polyhedral contribution to the enthalpy of silicate minerals by multiple regression of calorimetric enthalpy-of-formation data for a selected group of feldspar, clay, and

zeolite minerals. Simple stoichiometric addition of the polyhedral enthalpy contributions yields the estimated enthalpy of formation for a mineral.

Table 10 compares calorimetrically determined enthalpies of formation for the six merlinoite samples with enthalpy values estimated using the method of Chermak and Rimstidt (1989). Correlation between estimated and measured enthalpies of formation for these samples is high, with errors of less than 0.3% and an average error of only 0.18% (about 6 kJ). Chermak and Rimstidt (1989) obtained similarly low errors in predicted enthalpies for other zeolite minerals not used in the construction of the model.

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