# 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,  $\Delta H_{\rm soln}$ , 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,  $\Delta H_1^0$ , were determined from measurements of the heats of solution of SiO<sub>2</sub> ( $\alpha$ -quartz), Al(OH)<sub>3</sub> (gibbsite), NaF, KF, and the merlinoite samples in 24.4 wt% HF<sub>(aq)</sub> 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  $C_P^0$ ,  $S_T^0 - S_0^0$ ,  $(H_T^0 - H_0^0)/T$ , and  $-(G_T^0 - H_0^0)/T$  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  $S_{298}^0 - S_0^0$ . The following values for  $S_T^0$  and  $\Delta H_{1298}^0$  at 298.15 K (25 °C) were obtained:

	$S_{T,298}^{0}$	$\Delta H_{ m f,298}^0$
Merlinoite composition	$[J/(mol \cdot K)]$	(kJ/mol)
$(Na_{0.81}K_{0.19}AlSi_{1.94}O_{5.88} \cdot 2.13H_2O)$	$328.8 \pm 15.3$	$-3591.2 \pm 2.9$
$(K_{0.80}Na_{0.20}AlSi_{1.94}O_{5.88} \cdot 1.81H_2O)$	$324.4 \pm 15.8$	$-3519.0 \pm 2.9$
$(KAlSi_{1.94}O_{5.88} \cdot 1.69H_2O)$	$320.7 \pm 15.3$	$-3481.8 \pm 3.0$
$(Na_{0.81}K_{0.19}AlSi_{1.81}O_{5.62} \cdot 2.18H_2O)$	$319.2 \pm 14.7$	$-3488.3 \pm 2.8$
$(K_{0.91}Na_{0.09}AlSi_{1.81}O_{5.62} \cdot 1.79H_2O)$	$305.9 \pm 15.0$	$-3387.3 \pm 2.8$
(KAlSi <sub>1.81</sub> O <sub>5.62</sub> ·1.69H <sub>2</sub> O)	$304.3 \pm 14.7$	$-3360.0 \pm 2.8$

#### 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 min-

erals 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

TABLE 1.	Electron-microprobe analyses of	synthetic merlinoite	samples used for low-t	emperature heat-capacity measurem	ents
IADLE I.	LIECTI OH-HINGIODI ODE AHAIVSES OF	SVITUELLE IIICIIIIULE	Sallibles used for low-i	CITIDEI ALUI E TIEAL-CADACILY TITEASULETTI	CIILO

	P-9(NaK)	P-9(KNa)	P-9(K)	P-8(NaK)	P-8(KNa)	P-8(K)
		Weight percer	nt oxide (average of	f five analyses)		
SiO <sub>2</sub>	48.86	48.82	46.09	46.90	46.34	45.67
Al <sub>2</sub> O <sub>3</sub>	21.26	21.36	20.16	21.83	21.76	21.39
K₂O	3.634	13.82	21.74	3.742	17.07	20.20
Na <sub>2</sub> O	10.23	2.320	0.00	10.72	1.071	0.00
H <sub>2</sub> O*	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 (I	based on 64 oxyger	ns per ceil)		
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 <sub>2</sub> O	23.17	19.93	18.10	19.14	20.53	19.14

Chemical formula

KAISi<sub>1,81</sub>O<sub>5,62</sub>·1.69H<sub>2</sub>O

P-9(NaK) Na<sub>0.81</sub>K<sub>0.19</sub>AlSi<sub>1.94</sub>O<sub>5.88</sub>·2.13H<sub>2</sub>O P-9(KNa) K<sub>0.80</sub>Na<sub>0.20</sub>AlSi<sub>1.94</sub>O<sub>5.88</sub>·1.81H<sub>2</sub>O P-9(K) KAlSi<sub>1.94</sub>O<sub>5.88</sub>·1.69H<sub>2</sub>O P-8(NaK) Na<sub>0.81</sub>K<sub>0.19</sub>AlSi<sub>1.81</sub>O<sub>5.82</sub>·2.18H<sub>2</sub>O P-8(KNa) K<sub>0.91</sub>Na<sub>0.00</sub>AlSi<sub>1.81</sub>O<sub>5.82</sub>·2.179H<sub>2</sub>O

P-8(K)

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<sub>2</sub>O-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. 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<sub>2</sub>O) 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 ( $10-15~\mu m$ ). The crystals were repeatedly washed with distilled, deionized water in order to remove as much adsorbed (OH)<sup>-</sup> and NaCl as possible. The anhydrous compositions of the synthetic merlinoites were determined by electron-microprobe analysis using feld-spar 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 ( $40~\mu m$ ). 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%

<sup>\*</sup> Determined by TGA (25-800 °C at 6°/min).

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

	а	b	C	V	Number of lines
Sample		Angstroms		(ų)	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<sub>2</sub>O. Chloride and fluoride were below detection limits in all samples. High-resolution MAS <sup>27</sup>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<sub>2</sub> as an internal standard and  $CuK\alpha_1$  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<sub>2</sub>)

The  $\alpha$ -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  $\mu$ m).

#### Gibbsite [Al(OH)<sub>3</sub>]

The gibbsite sample used as the Al standard for these measurements was Fisher reagent Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O. 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
60	44	43	49	56
61	42	38	44	49
65	45	41	47	51
49	36	35	41	48
57	39	34	39	44
58	40	36	41	45
	60 61 65 49 57	60 44 61 42 65 45 49 36 57 39	60 44 43 61 42 38 65 45 41 49 36 35 57 39 34	60 44 43 49 61 42 38 44 65 45 41 47 49 36 35 41 57 39 34 39

#### 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

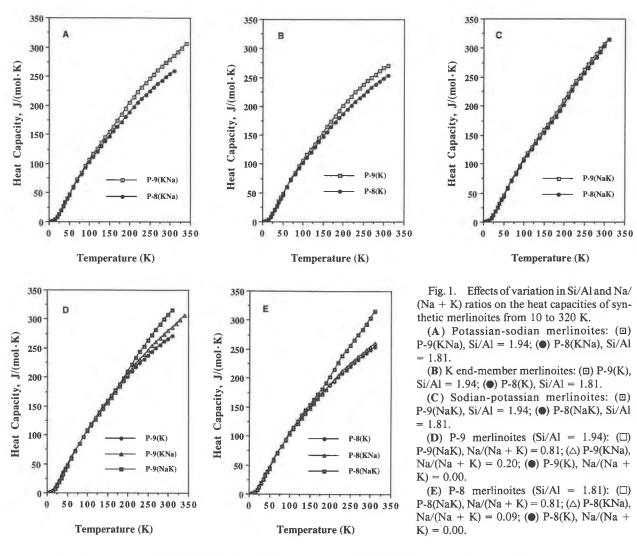
#### Low-temperature, adiabatic calorimetry

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.



The solution calorimeter was operated under constantpressure conditions for these measurements; therefore, the measured heats of solution are enthalpy changes at a pressure of 10<sup>5</sup> 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 merilinoite at various temperatures (in kelvins)

G <sub>P</sub> T         C <sub>P</sub> 309.7         206.88         217.9           314.1         212.28         224.6           34.21         212.28         224.6           54.21         223.06         224.1           67.22         215.64         228.0           67.22         215.64         228.0           67.22         215.64         228.0           74.07         220.9         228.4           89.33         236.61         228.1           103.1         226.01         224.4           103.5         220.03         238.4           115.7         225.74         224.4           115.7         225.73         224.1           115.7         226.15         224.7           115.7         226.15         224.7           115.7         226.15         224.7           115.7         226.15         224.7           115.1         226.15         224.7           115.1         226.25         226.3           115.0         226.3         230.9           114.5         226.3         230.9           114.6         226.3         230.9 <t< th=""><th>7 214.85 229.55 229.55 229.65 229.65 229.65 220.66 220.66 220.67</th><th>227.3 222.3 222.3 222.3 222.3 222.4 222.7 227.1</th><th>7 289 99. 289 99. 300 331 300 331 300 331 300 331 300 331 300 331 300 331 300 331 300 331 300 331 300 300</th><th>278.5 280.8 280.8 283.8 283.8 283.8 283.8 292.4 305.7 300.7 300.6 310.6</th><th>7 33,11 34,64 42,97 47,91 47,91 47,91 65,71 66,71 78,27 78,2</th><th>21.57 22.51 32.51 32.51 38.05 51.17 55.00 65.00 65.00 75.09 75.09 103.2 103.2 114.9</th><th>T 182.18 182.20 183.70</th><th>7 185 6 191 9 191</th><th>7 300.67 305.10 310.02 314.02 314.93 58.88 64.98 74.90 74.90 80.15 80.15 90.78</th><th>266.8 268.8 271.0 273.1</th><th>181.01 186.43 191.83</th><th>γ 184.2 189.0 193.9 198.7</th><th>309.40 314.57 7.83†</th><th>270.5</th></t<>	7 214.85 229.55 229.55 229.65 229.65 229.65 220.66 220.66 220.67	227.3 222.3 222.3 222.3 222.3 222.4 222.7 227.1	7 289 99. 289 99. 300 331 300 331 300 331 300 331 300 331 300 331 300 331 300 331 300 331 300 331 300 300	278.5 280.8 280.8 283.8 283.8 283.8 283.8 292.4 305.7 300.7 300.6 310.6	7 33,11 34,64 42,97 47,91 47,91 47,91 65,71 66,71 78,27 78,2	21.57 22.51 32.51 32.51 38.05 51.17 55.00 65.00 65.00 75.09 75.09 103.2 103.2 114.9	T 182.18 182.20 183.70	7 185 6 191 9 191	7 300.67 305.10 310.02 314.02 314.93 58.88 64.98 74.90 74.90 80.15 80.15 90.78	266.8 268.8 271.0 273.1	181.01 186.43 191.83	γ 184.2 189.0 193.9 198.7	309.40 314.57 7.83†	270.5
206.88 217.67 217.67 223.06 228.44 215.604 225.091 226.04 226.04 226.35 296.35 296.30 296.30 296.30 306.22 316.73 316.73 11.48 316.73 11.48 316.73 11.48 316.73 11.48 316.73 11.48 316.73 11.15 204.12 209.41 209.41 209.41	214 85 219 56 229 52 229 52 229 52 229 52 229 56 229 56 229 56 220 56 22	227.3 222.3 222.3 222.3 224.2 224.2 224.1 227.6 227.1 227.6	299 95 - 3003 31	278.5 289.8 289.8 289.8 289.8 292.4 295.7 300.5 300.5 0.1298 0.3046 0.3044 0.4868 0.6727 0.67	31.11 38.64 47.97 47.99 47.99 47.99 65.33 65.74 66.57 78.27	21.57 28.51 38.05 38.05 38.05 38.05 59.01 67.08 75.09 97.09 97.09 103.2 114.9	182 18 193 20 19	185 6 198 1 203 7 203 7 203 7 203 7 218 4 227 5 227 5 227 5 227 5 240 2 240 3 240 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	300,67* 305,10 310,02 314,93 58,88** 64,98 74,90 80,15 86,35 90,78	266,8 268,8 271,0 273,1 59,22	181.01 186.43 191.83	184.2 193.9 198.7	309.40 314.57 7.83†	270.5
217.67 223.06 228.44 228.44 228.45 231.21 236.61 237.70 237.70 247.40 247.40 247.40 247.40 247.40 247.40 247.40 247.40 247.40 247.40 248.88 296.30 296.30 306.22 311.48 311.48 311.48 311.44 311.42 311.42 311.42 311.43 311.43 311.43 311.44 311.44 311.45 311.44 311.43 311.43 311.43 311.44 311.44 311.44 311.44 311.44 311.45 311.43 311.44 311.44 311.44 311.44 311.44 311.44 311.44 311.45 311.44 31	224,43 224,52 224,52 225,68 226,64 261,64 261,74 281,14 1033,6 1033,6 11,14 11	237.2 247.4 247.3 247.7 252.4 252.4 252.6 278.0 287.7 287.1 287.1 287.1 287.1 1.936 1.936 1.936 1.936 1.936 1.936 1.936 1.137	308.23 313.16 318.22 323.27 323.22 333.28 343.19 5,14* 6,10 6,68 6,68 11,198 11,298 12	283.6 286.5 289.8 292.4 295.7 300.7 300.7 305.6 310.5 0.1298 0.2681 0.3069 0.3444 0.06727 0.9319 1.284 1.284 1.284 2.479 8.273 8.273 10.73	38 57 47 97 47 97 47 97 47 97 47 97 48 90 48 44 90 53 90 53 102 54 102 54 112 58 113 5	38.231 38.231 45.965 45.965 55.1.17 55.01 67.08 82.84 82.84 82.84 109.1 1114.9 1114.9 1114.9 1126.3 1136.5	1983 20 204, 77 209, 64 215, 10 220, 56 220, 56 220, 56 221, 46 221, 4	198.1 208.7 208.8 213.6 223.0 223.0 223.0 224.5 246.0 246.0	310,02 314,93 58,88** 64,98 74,90 74,90 85,35 90,78	271,0 273,1 59,22	191,83	193.9	7.83	2.272
228.44 228.44 221.57 220.91 220.91 220.91 247.01 247.01 247.01 247.01 247.01 247.01 247.01 247.01 247.02 268.88 268.85 268.88 268.85 268.88 274.24 277.01 187.91 187.91 187.91 187.91 187.91 187.91 187.91 187.91 198.74	224.65 229.97 229.97 220.68 220.68 220.69 220.77 200.77 20	247.3 247.3 252.4 252.7 252.7 262.7 273.1 273.1 282.6 287.1 2887.7 2901.6 3001.	313.22 323.27 323.22 333.28 343.19 5,14* 6,10 6,10 10.78 11.38 11.38 11.38 11.38 11.38 11.38 11.38 11.38 11.38 11.38 11.38 11.38 11.38 12.28 22.57 22.57 27.94	289,8 292,4 295,7 300,7 300,7 300,6 310,5 0,1296 0,304,9 0,304,9 0,309	47.2 33.3 33.3 33.3 33.3 33.3 33.3 33.3 3	45.96 59.1.17 59.01 76.08 76.08 82.84 82.84 82.84 103.2 1114.9 1114.9 1126.6 1126.6 1136.5 11	204, 77 209, 64 216, 10 226, 10 226, 10 227, 10 227, 10 227, 10 227, 10 227, 10 227, 10 227, 10 227, 10 22, 10 23, 10 24, 10 25, 10 26, 10 27, 10 28,	208 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	64.98 74.90 80.15 86.35 90.78	59.22			8.61	0.5096
225.60H 220.91 226.04 226.04 226.04 224.01 224.01 224.02 225.74 268.88 274.24 279.60 289.83 300.83	245.97 256.04 256.04 256.04 256.04 277.49 277.49 288.18 10.326 11.61 11.	252.4 252.7 262.7 273.1 273.1 273.1 282.6 292.6 293.7 296.1 396.1 396.1 396.1 396.2 1.936 1.936 1.936 1.936 1.193	228.22 238.24 393.28 393.28 393.28 393.12 5,14* 6,10 6,10 6,08 7,31 11.39 11.39 11.39 11.39 11.39 11.39 11.39 11.39 11.39 11.39 11.39 11.39 11.39 11.39 11.39 11.39 11.39 11.39 11.39 12.25 12.25 13.30 13.3	292.4 295.7 300.7 300.6 310.5 310.5 0.1298 0.3049 0.3049 0.444 0.6681 0.6727 0.9319 1.799 2.479 4.642 6.257 1.799 2.479 1.799 2.479 8.273 10.73	59.33 59.33 65.71 78.27 78.27 78.27 78.27 102.54 108.55 112.87 112.87 112.87 112.87 113.30 115.30 115.30 115.30	51.17 67.08 67.08 75.09 89.99 89.99 89.99 1003.2 1100.1 1100.1 1126.3 1126.3 1137.5 1143.0 1143.0 1153.5 1153.5 1153.5 1153.5	215 10 220 56 220 56 220 56 220 56 220 56 220 56 220 56 220 56 220 56 220 56 220 56 20 20 56 20	213 6 223 0 223 1 223 1 235 0 244 5 244 5 244 5 265 0 266 0 266 0 267 6 273 9 273 9 273 9 283 0 283 0 284 0 285 0	64.98 74.90 80.15 85.35 90.78 96.69	-	202,59	203.3	9.33	0.9236
226.94 226.04 226.04 242.01 242.01 242.01 252.78 258.15 268.88 290.33 296.53 306.22 306.22 306.23 306.22 316.73 11.48 316.73 117.156 177.01 182.47 187.41 187.41 187.41 19	245.68 255.04 255.04 256.04 226.74 227.2.13 277.2.13 277.4 10.328 11.61	265.7 2 265.7 2 267.8 2 267.8 2 207.8 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	333.28 333.28 333.28 333.19 343.19 5.14* 6.68 6.60 6.68 7.28 7.91 10.78 11.98 11.98 11.98 11.98 11.98 11.98 11.98 11.98 11.98 12.25 12.25 12.25 17.26 18.26	205.7 205.6 310.5 310.5 310.5 310.5 310.5 310.5 310.5 310.5 310.5 310.7	59,42 59,42 72,01 72,01 72,01 72,01 72,01 73,01 73,01 73,01 73,01 73,01 73,01 73,01 73,01 74	99-01 67-09 89-99 89-99 89-99 103-1 1114-9 1126-3 1114-9 1137-5 143.0 153.5 163.5 163.5	2255.10 226.00 226.00 228.14 242.40 242.40 242.40 242.40 242.40 242.40 242.40 243.40 245.40 226.40 226.40 226.40 226.40 236.68 300.67 311.17	223 0 227 5 227 5 227 5 236 0 240 2 248 5 266 0 266 0 267 6 277 2 277 2 283 0 283 0 288 8	90,78 90,78 90,78	66.88	207,95	207.5	10.23	1.278
231.27 236.51 242.01 242.01 242.01 252.74 258.15 268.38 268.38 268.38 296.63 306.29 306.29 306.29 306.29 316.30 11.48 316.30 316.	256 04 266 44 266 44 266 44 277.13 277.13 277.13 288.81 10.38 11.61 13.14 14.59 16.08 22.49 22.38 30.89 30.89 30.89 34.40 47.64 47.64 47.64 59.12	247 ; 7 273.1 278.2 67.8 282.9 282.6 282.9 282.6 282.7 282.6 282.7 282.6 282.7 282.6 282.7	338.24 93.119 6.10 6.66 6.10 7.26 7.26 7.26 1.19 10.78 11.39 11.39 11.39 11.479	305 6 310.5 310.5 310.5 0.2681 0.3044 0.4868 0.6727 0.6727 0.6727 0.8319 1.799 1.799 2.479 2.479 2.479 6.257 6.257 6.257 6.257 6.257 6.257	72.01 72.01 74.27 74.27 90.53 90.53 90.53 1108.45 111.58 113.58 113.73 113.73 113.73 114.86 115.83 1	75.09 89.84 89.89 97.09 97.09 1003.2 114.9 114.9 114.8 1131.5 1131.5 1131.5 1131.5 1131.5 1131.5 1131.5 1131.5 1131.5 1131.5 1131.5 1131.5 1131.5 1131.5 1131.5 1131.5	226,00 226,146 226,13 242,40 247,87 223,34 226,34 226,40 226,40 226,40 226,40 226,40 226,40 236,40 236,40 236,40 236,40 236,40 236,40 336,73 311,73	227 5 281 5 286 0 240 2 240 2 248 5 262 3 262 3 264 0 267 6 277 2 277 2 283 0 283 0 288 8	85.35 90.78 96.69	85,28	218,63	215.9	12.58	2.357
242.01 247.01 247.02 252.78 258.15 268.88 274.24 274.24 274.24 274.24 274.24 274.24 276.30 295.63 306.22 306.22 306.22 306.22 311.48 31	2661.42 2661.42 2772.13 2774.49 2872.88.18 288.18 288.15 11.61 11.61 11.62 20.11 11.62 20.11 20.11 20.11 20.11 30.88 30.88 30.88 30.88 47.64 47.64 47.64 59.12	273.1 282.9 282.5 282.7 282.7 282.6 287.1 390.1 390.1 390.1 1.953 1.356 1.356 1.356 1.356 1.197 1.197 11.97	343.19 5.14** 6.10 6.68 6.88 7.72 8.75 10.78 11.198 11.198 14.79 16.43 18.43 1	310.5 0 1298 0 2681 0 2681 0 3444 0 6486 0 6727 1 284 1 284 1 284 1 284 1 4 642 2 4 73 3 4 642 6 257 6	78.27 90.53 90.53 90.53 100.54 114.30 1125.87 137.32 137.32 148.66 154.30 154.30	82.84 97.09 97.09 1109.1 1114.9 126.3 1126.3 137.5 143.0 153.5 163.6	236,346 226,33 226,34 226,34 226,34 226,34 226,40 226,40 226,40 226,40 236,40 2	231 5 231 5 240 2 244 5 252 3 256 0 266 0 266 0 267 0 273 9 273 9 273 9 273 2 273 2 273 2 283 0 283 0 283 0 283 0 283 0 283 0	90.78 96.69	91,20	223,97	219.9	13.99	3.236
247.401 247.401 263.52 268.35 268.35 268.35 268.36 274.24 274.24 279.56 300.33 300.33 300.33 300.33 300.33 311.46 311.47 161.104 167.31 187.91 187.91 187.91 187.91 198.74	272.13 277.49 287.149 288.18 288.18 288.11 10.32§ 11.61 11.62 11.62 11.62 11.62 11.62 11.62 11.62 11.63 11.6	282.9 287.7 287.7 287.7 297.1 390.6 390.6 1.366 1.366 3.770 6.539 1.197 11.97 11.97 11.97 11.97 11.97 11.97 11.97 11.97 11.97 11.97 11.97 11.97 11.97 11.97 11.97 11.97 11.97	6.10 6.10 7.26 7.26 7.31 9.71 10.78 11.39 11.39 16.43 16.43 18.26 20.30 22.57 27.54	0.0289 0.3009 0.3009 0.3444 0.4868 0.6772 0.9319 1.799 2.473 2.473 4.642 6.257 8.273 10,73	905.34 905.54 102.54 114.30 125.87 137.32 143.01 154.86 143.01 154.30 154.30	97.09 97.09 1003.1 1104.9 126.3 137.5 143.0 153.5 163.6	242.45 247.87 253.34 286.33 286.33 286.34 225.06† 225.06† 225.68 300.46 300.87 311.77	244 5 244 5 244 5 244 5 244 5 252 3 255 3 260 0 260 0 260 0 273 9 273 9 283 0 288 8 288 8	0000	103.0	229,32	223.6	17.26	5.868
262.74 263.85 263.85 263.85 263.85 274.84 274.84 274.86 290.30 300.83 300.83 300.83 306.25 306.25 306.25 316.74 11.10‡ 16.30 177.07 182.47 182.47 187.91 193.33 198.74 209.49 209.49 107.13	2277.40 288.84 288.84 298.81 10.326 11.61 11.161 11	287.7 287.6 287.1 300.1 300.1 300.1 1.936 1.936 1.936 3.770 8.599 9.188 9.188 19.35 24.10 28.73 5.745 3.770 6.599 9.188 9.188 4.10 28.73 4.10 28.73 4.10 28.73 4.10 28.73 4.10 28.73 4.10 28.73 4.10 28.73 4.10 28.73 4.10 4.10 4.10 4.10 4.10 4.10 4.10 4.10	6.68 7.26 7.91 10.78 11.38 11.39 11.39 11.39 11.30 11.	0.3009 0.344 0.486 0.6727 0.9319 1.284 1.789 2.479 2.43 6.257 6.257 8.273 10,73	96.57 102.54 108.45 114.30 120.10 125.87 131.61 137.32 143.01 148.66 154.30	103.2 109.1 1114.9 120.6 120.6 131.5 137.5 148.3 153.5 158.5 163.6	247,87 258,334 258,334 264,31 264,31 265,08 275,08 280,34 285,40 290,68 300,87 306,03	244.5 248.5 252.3 256.0 266.0 264.0 267.0 277.3	102.54	108.8	240.08	230.9	19.20	7.763
258 15 258 15 268 36 268 88 274 24 279 40 279 40 290 30 290 30 290 30 390 29 39	288.28 288.50 288.50 288.50 10.328 10.328 11.61 13.16 13.16 14.59 16.08 27.74 27.74 27.74 30.89 30.80 30 30.80 30 30.80 30.80 30.80 30.80 30.80	292.6 292.6 297.1 301.6 306.2 1.336 1.336 1.336 1.336 1.336 1.137 1.157 1.157 1.197	7.26 7.91 8.75 8.75 10.78 11.38 13.31 14.79 16.45 18.26 18.26 22.57 22.57 22.57	0.3444 0.04868 0.6727 0.6319 1.284 1.799 2.479 3.431 4.642 6.257 8.257 8.273 10.73	102.54 108.45 120.10 125.87 131.61 137.32 143.01 143.01 159.91	109.1 114.9 126.3 131.9 137.5 143.0 148.3 158.5 163.6	253.34 258.82 264.81 269.80 280.34 285.40 290.46 295.68 300.03 311.17	248 5 252 3 252 3 256 0 264 0 270 5 277 2 283 0 283 0 285 9	108.37	114.4	245,46	234.4	21.36	10.10
274.24 274.24 274.24 274.24 274.24 274.24 274.24 286.30 296.32 306.22 306.22 306.22 311.48 311.104 161.701 165.30 177.01 187.47 187.47 187.47 187.47 187.47 198.74 198.74 198.74	288.18 298.81 298.81 11.61 11.62 14.58 16.24 16.24 16.24 16.24 16.24 16.24 17.74 27.74 27.74 27.74 27.74 47.64 47.64 47.64 59.12	2014. 2016. 2016. 2016. 2019. 2017. 2017. 2017. 2017. 2017. 2017. 2019. 2017. 2017. 2017. 2017. 2017. 2017. 2017. 2017.	8.75 8.75 9.71 10.78 11.38 13.31 14.79 16.45 20.30 22.57 27.54	0.64869 0.64864 0.69319 1.284 1.799 2.479 3.441 4.642 6.257 8.257 10.73	108.45 120,10 125,87 131,61 143,01 148,66 159,91	114.9 120.6 120.6 137.5 143.0 148.3 158.5 158.5	28.82 268.31 269.80 285.40 285.40 290.46 300.87 311.77	250.2 250.0 260.0 264.0 277.5 277.2 277.2 280.1 285.9 285.9	114.16	119.9	250,84	237.8	23.76	12.92
279.60 279.60 290.30 290.30 300.93 300.93 300.93 311.48 316.73 31	283.50 283.50 10.328 116.14 13.14 16.28 22.238 22.238 20.11	300.16 300.16 1.356 1.356 1.366 3.770 6.539 11.97 11.9	9.77 9.77 11.98 11.38 14.79 16.43 20.30 22.57 22.57 27.54	0.9319 0.9319 1.284 1.799 2.479 3.431 6.257 6.257 10.73	125.87 131.61 137.32 143.01 154.30 154.30	126.3 131.9 137.5 143.0 148.3 158.5 163.6	269-831 275,08† 280,34 280,34 290,87 300,87 311,17	250.0 264.0 267.6 270.5 273.9 273.9 273.9 287.1 283.0 285.9	125.82	130.9	261.60	244.6	29 44	20.25
279.50 290.30 290.30 290.30 300.33 300.33 306.22 316.73 177.55 177.50 182.47 182.47 182.47 182.47 187.91 193.33 198.74 193.33 198.74 197.91 19	10.326 10.326 13.14 14.59 18.08 22.38 24.92 30.74 30.89 30.74 47.64 47.64 59.12	0.985 1.336 1.936 1.953 3.770 5.175 6.959 9.188 11.97 15.31 19.35 24.10 29.75 4.16 4.169	10.78 11.38 11.39 14.79 16.43 18.26 20.30 22.57 22.57 25.11	1.284 1.799 2.479 3.431 4.642 6.257 8.273 10.73	125.87 131.61 137.32 143.01 148.66 154.30	131.9 137.5 143.0 148.3 153.5 158.5	275,081 280,34 285,40 290,46 390,87 300,03 311,17	264.0 267.6 270.5 273.9 277.2 287.1 283.0 285.9 285.9	131.28	136.3	266.98	247.6	32.79	24.91
294.36 294.36 295.63 306.23 306.22 311.48 311.48 311.46 311.70 171.55 171.55 177.01 187.47 187.47 187.47 198.74 19	11.61 14.59 16.24 16.24 16.24 20.11 22.38 24.92 27.74 39.32 47.64 47.64 47.64 59.12	1,356 1,993 2,736 2,776 5,175 6,999 6,999 11,97 15,31 15,31 19,35 24,10 29,75 38,55 4,169	11.98 14.79 16.43 16.43 18.26 20.30 22.57 25.11	1,799 2,479 3,431 4,642 6,257 8,273 10,73 13,75	131.61 137.32 143.01 148.66 154.30	137.5 148.3 153.5 158.5 163.6	280,34 285,40 290,46 295,68 300,87 306,03 311,17	267.6 270.5 273.9 277.2 280.1 283.0 285.9 285.9	136.91	141,8	272.37	250,8	36.53	30.17
290.30 290.62 300.92 300.92 311.48 316.73 16.70 177.01 182.47 187.91 198.74 198.74 204.12 209.49 P-8(NaK)	13.14 16.28 16.28 22.38 22.4.92 27.74 30.89 34.40 42.72 42.72 42.72 53.12	1,963 2,736 3,770 6,859 9,188 11,97 11,97 11,97 12,31 24,10 29,75 35,55 4,169	13.31 16.43 16.43 18.26 22.57 22.57 25.11	2.479 3.431 4.642 6.257 8.273 10.73	137.32 143.01 148.66 154.30 159.91	143.0 148.3 153.5 158.5 163.6	285,40 290,46 295,68 300,87 311,17 316,27	270.5 273.9 277.2 280.1 283.0 285.9 285.9	142.51	147.1	277.74	254.0	40.69	36.25
205.63 300.23 306.22 316.73 316.73 316.73 11.05 17.00 17.00 17.00 182.47 182.47 182.47 183.33 198.74 209.49 209.49 198.74	14.59 18.08 20.11 22.38 24.92 27.74 30.89 38.32 44.0 38.32 42.72 42.72 53.12	2.736 3.770 5.170 6.959 9.188 11.97 11.37 19.35 29.75 35.55 4.1.69	14.79 16.43 18.26 20.30 22.57 25.11 27.94	3.431 4.642 6.257 8.273 10.73	143 01 148 66 154 30 159 91	148.3 153.5 158.5 163.6	290 46 295.68 300.87 306.03 311.17	273.9 277.2 280.1 285.9 285.9	148.09	152.4	283.08	257,1	45.35	41.83
306.29 306.22 311.48 311.48 311.48 16.73 17.15 17.70 187.91 187.91 187.91 187.91 187.91 187.91 198.74 198.7	16.24 18.08 20.31 22.38 27.74 30.89 38.32 42.72 47.64 53.12	3,770 5,175 6,959 9,188 11,97 15,31 19,35 24,10 24,15 35,55 41,69	16.43 18.26 20.30 22.57 25.11 27.94	4.642 6.257 8.273 10.73	148 66 154 30	153.5 158.5 163.6	295.68 300.87 306.03 311.17	277.2 280.1 285.9 286.9	153.64	157.6	288 39	260,1	50.57	48.50
311.48 316.73 116.73 116.70 116.30 177.01 182.47 182.47 198.74 198.74 204.12 209.49 P-8(NaK)	18.08 22.38 22.38 27.74 30.89 34.40 38.32 42.72 47.64 53.12	5.175 6.959 9.188 11.97 15.31 19.36 24.10 29.75 35.55	18.26 20.30 22.57 25.11 27.94	6257 8273 1073 13.75	159.91	158.5	300 87 306 03 311 17 316 27	283 0 285 9 286.8	159.16	163.0	293,68	6797	50.35	20.97
311.48 316.73 316.73 16.1.00 16.30 177.50 177.50 182.47 182.47 183.73 193.73 193.73 209.49 209.49 107.13 107.13	2011 22.38 24.93 27.74 30.89 34.40 38.32 47.64 53.12	6.359 9.188 11.97 15.31 19.36 24.10 29.75 35.55	20.30 22.57 25.11 27.94	10.73 10.73 13.75	200	03.0	311.17	285.9	176.67	179.1	304 19	268.4	68.80	71.57
16.30 17.01 17.01 187.91 187.91 187.91 187.91 187.91 187.91 187.91 187.91 198.74 198.7	24.30 27.74 27.74 30.89 34.40 38.32 47.64 53.12 59.12	2.186 11.97 15.31 19.35 24.10 29.75 35.55 41.69	25.11 27.94	13.75	185.50	1888	316.27	288.8	10.01	7.671	6	1000	8	
166.30 177.55 177.01 182.47 187.91 193.33 198.74 204.12 209.49 P-8(NaK) P-8(NaK)	27.74 30.89 34.40 38.32 42.72 47.64 53.12 59.12	29.75 29.75 29.75 35.55 41.69	27.94	000	171 07	174.1								
171.55 177.55 182.47 182.47 193.33 198.74 204.12 209.41 209.49 107.13 107.13	30.89 34.40 38.32 42.72 47.64 53.12	24.10 29.75 35.55 41.69		14.7	176.63	179.6								
17.01 187.91 187.91 187.91 187.91 198.74 204.12 204.12 204.12 204.12 101.33 101.33 112.87	34.40 38.32 42.72 47.64 53.12 59.12	24.10 29.75 35.55 41.69												
182.47 187.91 193.33 193.34 204.12 209.49 P-8(NaK) P-101.33 107.13	38.32 42.72 47.64 53.12 59.12	29.75 35.55 41.69												
193.33 198.74 198.74 2094.12 2094.12 2094.19 209.11 101.33 107.13 107.13	42.72 47.64 53.12 59.12	35.55 41.69												
198.74 204.12 209.49 209.49 P-8(NaK) 4 101.33 107.13	47.64 53.12 59.12	41.69												
204.12 204.12 204.12 209.49 P-8(NaK) 107.13 107.13	59.12 59.12	40.00												
P-8(NaK) P-8(NaK) 4 101.33 9 107.13	20.00	49.09 67.23												
P-8(NaK) 101.33 107.13 112.87	65.41	65.63												
101.33 107.13 112.87					P-8(KNa)	Va)					P-6	P-8(K)		
107.13	924 59	232 1	301.06*	255.0	62.32	61.35	203.60	191.4	300.49*	248.7	69.60	71.16	208.40	193.3
112.87	229.80	237.2	305.50	256.7	68.59	68.68	219.43	204.2	305.17	251.0	75.84	77.78	213.61	196.8
	235.02	242.3	310.36	260.4	74.85	76.15	224.68	208.1	310.00	253.4	81.94	84.40	218.80	200.5
118.55	240.23	247.6	315.26	262.3	80.99	83.28	229.93	211.6	314.87	256.3	87.90	90.68	224.00	204.0
124.18	245.44	252.3	6.60**	0.3821	87.02	89.85	235.19	215.0	319.78	258.9	93.81	96.58	229.20	207.1
129.77	250.66	257.2	7.41	0.4395	95.98	95.90	240.45	218.3	8.97**	0.7385	69.66	102.1	234.42	210.4
123.53**	255.88	261.9	8.25	0.6254	98.91	101.7	245.72	221.7	9.74	0.9263	105.49	107.4	239.63	213.6
129.25	261.09	266.2	9.13	0.8005	104.75	6.901	250.98	225.0	10.00	0.2.1	11.23	147.0	260.05	2000
134.44	266.32	0.172	12.01	1.092	110.04	117.5	253.73	221.1	12 83	200.0	122 53	122 0	245 261	2169
139.71	271.50	7.27	1.30	0.499	121 04	100 8	265 44	234.0	14.21	3.061	128.12	127.9	250.30	220.0
150.60	281 98	285.6	14 01	2.825	127.58	127.6	270.47	237.0	15.77	4.138	133.66	132.8	255.25	223.1
156.01	287.16	290.3	15.56	3.867	133.17	132.6	275.58	240.0	17.54	5.546	139.16	137.7	260.20	226.3
161.40	292.32	295.3	17.30	5.185	138.74	137.5	280.67	242.9	19.50	7.367	144.64	142.5	265.26	229.3
166.76	297.45	300.4	19.23	6.920	144.26	142.4	285.74	245.9	21.70	9.631	150.08	147.1	270.34	232.3
172.10	302.55	306.7	21.38	9.073	149.76	147.0	290.80	249.2	24.15	15.75	160.89	156.3	280.45	238.1
177.43	307.63	312.5	23.78	14.80	153.24	156.0	300 R7	254 9	29.62	19.68	166.25	161.0	285.49	240.7
188.03	212.09	286.4	29.43	18.66	166.12	160.4	310,6614	260.0	33.37	24.32	171.57	165.6	290.51	243.7
103.30	288.73	2912	32.76	23.12	171.53	164.6	315.53	262.8	37.16	29.76	176.88	170.0	295.51	246.3
198 56	293.60	295.9	36.48	28.18	176.91	169.1	287.93‡	246.9	41.40	35.20	182.18	174.2	300.51	248.3
203.80	298.51	301.2	40.62	34.14	182.28	173.4	301.20	254.5	46.15	40.87	187.46	178.3	305.49	251.1
209:01	303.46	307.6	45.26	39.43	187.64	177.8	306.18	257.0	51.41	47.84	192.71	182.1	310.44	254.3
	308.39	314.1	50.45	46.14	192.98	182.2	311.14	260.6	57.22	56.12	197.96	185.9	315.39	256.8
219.39	313.32	318.1	56.19	53.92	198.30	186.7	316.09	263.3	63.36	04.30	203.19	1.69.7		

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<sub>1</sub> and T<sub>2</sub> 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 Sci 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  $\alpha$ -quartz, gibbsite, NaF, KF, and six synthetic merlinoite samples in 477 g of 24.4 wt% HF<sub>(aq)</sub>. 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<sub>(aq)</sub>.

α-Quartz (SiO<sub>2</sub>). 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  $\alpha$ -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  $\Delta H_{\rm soln}$  for  $\alpha$ -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  $\alpha$ -quartz was increased from -136.55 kJ/mol to -140.70kJ/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 guartz. 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  $\alpha$ -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  $d\Delta H_{\rm soln}/dT$ , 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<sub>( $\alpha q$ )</sub>; therefore, the measured heats of solution are directly comparable with our 49.45 °C value. In addition,

TABLE 5. Molar thermodynamic properties of merlinoite

TABLE 5—Continued

Temp,	Heat capacity	Entropy S <sub>7</sub> – S <sub>8</sub>	Enthalpy function (H <sup>o</sup> <sub>7</sub> – H <sup>o</sup> <sub>8</sub> )/T	Gibbs energy function –(G? – H8)/T	Temp.	Heat capacity	Entropy S% – S%	Enthalpy function (H <sup>o</sup> r - H <sub>o</sub> r)/T	Gibbs energy function $-(G_T^0 - H_0^0)/T$
<i>T</i> (K)			mol·K)]	(	(K)		[J/(m	iol·K)]	
P-9(Na	aK): Na <sub>0.81</sub> K <sub>0,19</sub> A	AISi <sub>1,94</sub> O <sub>5,88</sub> ·2.1	13H <sub>2</sub> O, GFW = 2	39.9669					
5	0.109	0.035	0.026	0.009	250 260	246.0 253.3	230.4 240.2	126.2 131.0	104.1 109.2
10	0.863 2.974	0.283 0.968	0.212 0.727	0.071 0.241	270	260.2	249.9	135.6	114.2
15 20	6.865	2,315	1.738	0.576	280	266.9	259.4	140.2	119.2
25	12.05	4.381	3.262	1.120	290	273.1	268.9	144.7	124.2
30	18.20	7.110	5.228	1.882	300	279.1	278.3	149.1	129.2
35	24.94	10.42	7.558	2.859	310	285.0	287.5	153.4	134.2
40	31.79	14.20	10.16	4.036	320	291.4	296.7	157.6	139.1
45	38.44	18.33	12.93	5.392	330	298.5	305.8	161.7	144.0
50	45.02	22.72	15.81	6.903	340	306.1	314.8	165.9	148.9
60	58.42	32.11	21.79	10.31	273.15	262.4	252.9	137.1	115.8
70	71.80	42.12	27.98	14.13	298.15	278.0	276.6	148.3	128.3
80	84.68	52.55	34.27	18.28			101 0 401	NI O OFW (	45 0000
90	96.69	63.23	40.55	22.68	_	P-9(K): KA	ISI <sub>1,94</sub> O <sub>5.88</sub> · 1.69	9H <sub>2</sub> O, GFW = 2	45.0880
100	107.9	74.00	46.73	27.27	5	0.128	0.040 0.356	0.030 0.270	0.010 0.086
110	118.5	84.78	52.77	32.01	10	1.167 3.980	1.292	0.980	0.312
120	128.9	95.54	58.68	36.86	15 20	8.600	3.031	2.273	0.758
130	139.1	106.3	64.47 70.16	41.78 46.77	25	14.45	5.562	4.108	1.454
140	149.0 158.6	116.9 127.5	75.74	51.80	30	21.04	8.770	6.372	2.398
150 160	168.0	138.1	81.21	56.87	35	28.01	12.53	8.963	3.571
170	177.3	148.5	86.59	61.95	40	34.95	16.73	11.78	4.950
180	187.0	158.9	91.89	67.05	45	41.53	21,23	14.72	6.507
190	197.6	169.3	97.17	72.16	50	47.92	25.94	17.72	8.213
200	209.2	179.8	102.5	77.28	60	60.61	35.80	23.82	11.98
210	221.1	190.3	107.8	82.41	70	73.09	46.08	29.97	16.11
220	232.4	200.8	113.3	87.55	80	85.03	56.63	36.11	20.52
230	242.8	211.4	118.7	92.70	90	96.10	67.29	42.17	25.12
240	252.7	221.9	124.0	97.87	100	106.3	77.95	48.08	29.87
250	262.3	232.4	129.4	103.0	110	116.0	88.55	53.82	34.73
260	271.7	242.9	134.7	108.2	120	125.6	99.05	59.40	39.65
270	281.0	253.3	139.9	113.4	130	135.1	109.5	64.86	44.62
280	290.0	263.7	145.1	118.6	140	144.7	119.8	70.22	49.62
290	298.7	274.0	150.3	123.8	150	154.3	130.2	75.50	54.65
300	307.1	284.3	155.4	128.9	160	164.0	140.4	80.73	59.69
310	315.4	294.5	160.4	134.1	170	173.8	150.7	85.92	64.74 69.80
273.15	283.8	256.6	141.6	115.0	180	183.2	160.9	91.06 96.15	74.86
298.15	305.5	282.4	154.4	128.0	190 200	192.3 201.0	171.0 181.1	101.2	79.92
D 0///	VI=V- M - M - 4	NO: 0 46	04H O OEW - 0	44 0000	210	209.2	191.1	106.1	84.97
P-9(KI	Na): K <sub>0,80</sub> Na <sub>0,20</sub> A	0.040	$81H_2O$ , GFW = 2 0.029	0.010	220	216.8	201.0	111.0	90.02
5 10	0.124 1.029	0.040	0.029	0.081	230	224.1	210.8	115.7	95.06
15	3.591	1.159	0.875	0.284	240	230.9	220.5	120.4	100.1
20	7.969	2.753	2.067	0.686	250	237.4	230.0	125.0	105.1
25	13.61	5.117	3.793	1.324	260	243.6	239.5	129.4	110.1
30	20.08	8.160	5.959	2.201	270	249.6	248.8	133.7	115.0
35	27.03	11.77	8.470	3.305	280	255.3	258.0	138.0	120.0
40	33.95	15.84	11.22	4.614	290	260.9	267.0	142.1	124.9
45	40.53	20.22	14.12	6.102	300	266.0	276.0	146.2	129.8
50	46.92	24.82	17.08	7.742	310	270.9	284.8	150.1	134.6
60	59.77	34.51	23.12	11.39	273.15	251.4	251.7	135.1	116.6
70	72.54	44.69	29.27	15.41	298.15	265.1	274.3	145.4	128.9
80	84.80	55.18	35.45	19.73					
90	96.19	65.84	41.58	24.26				<sub>82</sub> -2.18H <sub>2</sub> O, GF	W = 233.0567
100	106.6	76.52	47.57	28.95	5	0.086	0.027	0.020	0.007
110	116.5	87.15	53.39	33.76	10	0.767	0.237	0.179	0.058
120	126.3	97.71	59.06	38.65	15	2.854	0.880	0.671	0.209
130	135.9	108.2	64.60	43.59	20	6.598	2.175	1.650	0.525 1.044
140	145.3	118.6	70.03	48.58	25	11.66	4.172	3.129 5.034	1.044
150	154.6	129.0	75.36	53.60	30	17.58 24.18	6.811 10.01	7.291	2.719
160	163.8	139.2	80.60 85.78	58.63 63.67	35 40	30.88	13.68	9.825	3.855
170	173.5	149.4	85.78 90.93	63.67 68.72	45	37.16	17.68	12.52	5.167
180	183.7 194.2	159.7 169.9	96.09	73.77	50	43.47	21.92	15.29	6.629
190 200	194.2 204.3	180.1	101.3	78.83	60	56.74	31.02	21.09	9.925
				83.90	70	69.80	40.75	27.12	13.63
	217 2								
210	213.8 222.5	190.3 200.4	106.4 111.5					33.25	17.65
	213.8 222.5 230.7	200.4 210.5	111.5 116.5	88.96 94.03	80 90	82.42 94.14	50.90 61.30	33.25 39.38	17.65 21.92

TAI

209.5

218.5

227.4

236.2

244.9

253.6

262.1

270.5

239.0

260.5

 $\begin{array}{lll} \textbf{P-8(K): KAISi}_{1.8}, \textbf{O}_{5.82} \cdot \textbf{1.69H}_2\textbf{O}, \ \textbf{GFW} = \textbf{237.2771} \\ 0.115 & 0.036 & 0.027 & 0 \\ 1.022 & 0.317 & 0.240 & 0 \end{array}$ 

1.150

2.727

240

250

260

270

280

290

300

310

273.15

298.15

5

10

15

20

218.2

224.5

230.6

236.7

242.6

248.5

254.1

259.7

238.6

253.1

3.591

7.865

114.2

118.5

122.7

126.8

130.8

134.8

138.7

142.5

128.1

138.0

0.873

2.050

95.23

99.98

104.7

109.4

114.1

118.8

123.4

128.0

110.9

122.5

0.009

0.077

0.278

0.677

Temp.	Heat capacity	Entropy S? – S?	Enthalpy function $(H_T^0 - H_0^0)/T$	Gibbs energy function -(G? - H%)/T	Temp.	Heat capacity	Entropy S% – S%	Enthalpy function $(H_T^0 - H_0^0)/T$	Gibbs energy function -(G <sup>o</sup> <sub>7</sub> - H <sup>o</sup> <sub>8</sub> )/T
<i>T</i> (K)	Vi	IJ/(n	nol·K)]		<i>T</i> (K)		ſJ/(r	nol·K)]	
6.7		1-/(-			- (14)		[-/(-		
110	115.0	82.24	51.26	30.98	25	13.44	5.062	3.753	1.309
120	125.0	92.68	56.99	35.69	30	19.78	8.062	5.886	2.177
130	134.9	103.1	62.60	40.47	35	26.60	11.62	8.355	3.266
140 150	144.7	113.4	68.12	45.32	40	33.29	15.61	11.06	4.556
	154.1	123.7	73.54	50.20	45	39.67	19.90	13.88	6.021
160 170	163.2	134.0 144.1	78.86	55.12	50	46.17	24.42	16.78	7.633
180	172.1 181.2	154.2	84.08 89.22	60.05 65.01	60 70	59.62 71.66	34.03 44.15	22.81 28.95	11.22 15.20
190	191.1	164.3	94.32	69.97	80	82.43	54.43	34.97	19.46
200	202.3	174.4	99.43	74.94	90	92.72	64.74	40.82	23.92
210	214.6	184.5	104.6	79.91	100	102.4	75.01	46.50	28.51
220	226.6	194.8	109.9	84.90	110	111.6	85.20	52.00	33.20
230	237.5	205.1	115.2	89.90	120	120.6	95.30	57.34	37.96
240	247.3	215.4	120.5	94.92	130	129.6	105.3	62.55	42.76
250	256.6	225.7	125.8	99.94	140	138.4	115.2	67.66	47.58
260	265.4	236.0	131.0	105.0	150	147.0	125.1	72.66	52.42
270	274.2	246.1	136.1	110.0	160	155.6	134.8	77.58	57.26
280	283.2	256.3	141.2	115.1	170	164.2	144.5	82.42	62.11
290	292.9	266.4	146.3	120.1	180	172.4	154.1	87.19	66.96
300	303.5	276.5	151.3	125.1	190	180.1	163.7	91.88	71.80
310	314.7	286.6	156.4	130.2	200	187.4	173.1	96.47	76.63
273.15	277.0	249.3	137.7	111.6	210	194.4	182.4	101.0	81.45
298.15	301.5	274.6	150.4	124.2	220	201.2	191.6	105.4	86.25
				, _ , , _	230	207.6	200.7	109.7	91.02
P-1	3(KNa): KNa	anaAlSi, a,O. as	1.79H₂O, GFW =	= 237.6288	240	213.9	209.7	113.9	95.78
5	0.134	0.044	0.032	0.011	250	220.0	218.5	118.0	100.0
10	1.041	0.347	0.259	0.088	260	226.1	227.3	122.1	105.2
15	3.481	1.159	0.867	0.292	270	232.0	235.9	126.0	109.9
20	7.675	2.693	2.008	0.685	280	237.7	244.5	129.9	114.6
25	13.13	4.971	3.668	1.303	290	243.2	252.9	133.7	119.2
30	19.42	7.911	5.759	2.152	300	248.4	261.2	137.5	123.8
35	26.18	11.41	8.190	3.218	310	253.7	269.5	141.1	128.3
40	32.95	15.35	10.86	4.485	273.15	233.9	238.6	127.3	111.4
45	39.37	19.60	13.68	5.926	298.15	247.5	259.7	136.8	122.9
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			1.1	4.1.	1 41
80	82.08	53.65	34.48	19.17				this study ar	
90	92.83	63.95	40.37	23.57	Johnson e	t al. (1982)	and Nitkie	wicz et al. (u	inpublished
100	102.6	74.24	46.12	28.13				$-44 \mu m$ , and	
110 120	111.9	84.46	51.68	32.79					
130	120.9	94.58	57.07	37.51	respective	ly. For part	icle sizes of	$f > 2 \mu m$ , no	surface-en-
	129.8	104.6	62.32	42.29	ergy contr	ibution is e	expected (H	emingway et	al., 1988).
140 150	138.6 147.1	114.6 124.4	67.45 72.48	47.10 51.92				comparable.	
160	155.4	134.2	77.40		_				-
170	163.5	143.8	82.23	56.76 61.60	line fit thr	ough the da	ita produce	s the equatio	n
180	171.6	153.4	86.97	66.43		-	100.16	2000 10	2.77
190	171.6	162.9	91.64		$\Delta F$	$I_{\text{soln},\alpha\text{-qtz}} = -$	133.46 - 8	$8.3989 \times 10^{-3}$	$^{-2}I$ ,
200	188.3	172.3	96.27	71.26 76.08					
210	196.6	181.7	100.8	80.89	where $T$ i	s in degree	s Celsius.	The calculate	ed value of
220	204.4	191.1	105.4	85.68		-			
230	211.6	200.3	109.8	90.46					
240	211.0	200.5	114.0	05.22					

TABLE 6. Calculated values for the configurational entropy contribution (Sc) to third-law entropy and corrected values

of  $S_{298}^0$  for the synthetic merlinoites

	$S_{298}^{\circ} - S_{0}^{\circ}$	$S_{cl} (= S_0^0)$	S <sub>298</sub>
Sample		[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)	$274.6 \pm 0.4$	44.6 ± 14.7	319.2 ± 14.7
P-8(KNa)	$260.5 \pm 0.3$	45.4 ± 15.0	305.9 ± 15.0
P-8(K)	$259.7 \pm 0.3$	44.6 ± 14.7	304.3 ± 14.7

**TABLE 7.** Heats of solution of  $\alpha$ -quartz, gibbsite, NaF, KF, and synthetic merlinoite samples in 24.4 wt% HF<sub>(ac)</sub>

Sample mass	$\Delta T_{corr}$	$ar{\mathcal{T}}_{soin}$	Heat capa	acities (J/deg)	$\Delta H_{ m soin}$ at $ar{ au}_{ m soin}$	Sample mass	$\Delta T_{corr}$	T <sub>solo</sub>	Heat capac	ities (J/deg)	$\Delta H_{\text{soin}}$ at $T_{\text{soin}}$
(g)	(°C)	(°C)	Initial	Final	(kJ/mol)	(g)	(°C)	(°C)	Initial	Final	(kJ/mol)
		α-Quartz	, SiO <sub>2</sub> (React	ion 3)			P-9(KNa): I	( <sub>0.80</sub> Na <sub>0.20</sub> A	Si <sub>1,94</sub> O <sub>5,88</sub> -1.8	1H <sub>2</sub> O (Reaction	on 7)
0.2511	0.2927	49.4546	2037.6638	2037.7442	-137.629	0.5660	0.5528	35.1614	1984.4266	1985.6354	-474.0136
_	_	34.5*	_	_	-136.32*	0.5660	0.5542	35.1513	1980.4332	1984.3488	-474.0121
0.10801†	_	25.0†	_	_	-135.588 †	0.5660	0.5557	35.1637	1983.6769	1983.7031	-474.0140
	$\Delta H$	0 = -1	35.560 ± 0.4	102 kJ/mol		0.5660	0.5426	49.8736	2037.8611	2036.4589	-476.2669
		3011,200				0.5660	0.5427	49.5090	2037.0383	2035.1587	-474.2111
		Gibbsite, /	AI(OH) <sub>3</sub> (Read	ction 4)		0.5660	0.5422	49.4679	2034.8864	2036.3456	-476.2048
0.1850	0.1936	34.0542	2003.0945	2003.2055	-163.446		$\Delta H$	$\frac{0}{\text{soln.298}} = -4$	172.457 ± 1.4	417 kJ/mol	
0.1849	0.1943	34.7443	2006.6022	2004.1228	-163.350						
0.1850	0.1935	34.7367	2001.2734	2004.2756	-163.350		P-9(K	: KAISI 1.94	O <sub>8.88</sub> 1.69H <sub>2</sub> O	(Reaction 7)	
0.1850	0.1919	34.7336	2008.4348	2009.9482	-163.351	0.5639	0.5385	49.2787	2041.6575	2043.1955	-477.3117
0.1850	0.1918	34.7363	2011.6377	2009.5413	-163.351	0.5639	0.5382	49.2805	2041.0301	2039.6569	-477.3117
0.5002	0.5222	34.7794	2002.7272	2009.2098	-163.345	0.5639	0.5359	49.2840	2045.1027	2047.5173	-477.3115
0.5002	0.5239	34.7352	2003.3829	2004.5841	-163.351	0.5639	0.5463	34.5402	2011.9146	2013.6364	-478.0403
0.1850	0.1877	49.4976	2034.2726	2037.5874	-161.280	0.5639	0.5465	34.5603	2012.7756	2013.7332	-478.0393
0.1850	0.1881	49.4637	2035,2460	2035.4680	-161.285	0.5639	0.5470	34.5407	2010.8403	2010.5017	-478.0403
0.1850	0.1897	49.4882	2035.3316	2035.1094	-161.281		$\Delta H$	0 soln 298 = -4	478.512 ± 1.4	436 kJ/mol	
0.1850	0.1862	49.4924	2035.4161	2034.8779	-161.281			,			
	$\Delta H$	$\frac{0}{900,298} = -1$	164.716 ± 0.4	194 kJ/mol			P-8(NaK): N	la <sub>0.81</sub> K <sub>0.19</sub> A	Si <sub>1,81</sub> O <sub>5,52</sub> · 2.1	8H <sub>2</sub> O (Reaction	on 7)
		,				0.5226	0.5169	34.7367	2017.0488	2016.9822	-465.4808
		NaF	(Reaction 5)	)		0.5226	0.5170	34.6919	2015.2989	2018.9931	-465.4703
0.0995	0.0028	34.7640	2003.8043	2005.6377	-2.763	0.5226	0.5186	34.6767	2015.8131	2017.6409	-465.4667
0.0995	0.0029	34.7722	1996.8064	1996.5406	-2.762	0.5226	0.5152	49.4528	2039.3445	2041.3185	-468.9338
0.0995	0.0037	34.7647	1989.5663	1991.1727	-2.763	0.5226	0.5156	49.4576	2036.6378	2042.5992	-468.9350
0.0995	0.0037	34.7102	2008.3733	2009.6097	-2.769	0.5226	0.5163	49.4795	2036.5444	2037.5916	-468.9401
0.0995	0.0016	49.4485	2026.1229	2030.6961	-1.247		$\Delta H$	0 soln,298 = -4	463.196 ± 1.3	390 kJ/mol	
0.0995	0.0009	49.2719	2037.0750	2035.8670	-1.265						
0.0995	0.0019	49.2716	2036.0322	2038.8048	-1.265		P-8(KNa): I	(0.91 Na <sub>0.09</sub> A	Si 1.81 O 5.62 · 1.7	'9H₂O (Reacti	on 7)
	$\Delta l$	$H_{\text{soin,298}}^{0} = -$	$-3.771 \pm 0.01$	I1 kJ/mol		0.5457	0.5367	35.0888	1983.3887	1983.2693	-463.7429
						0.2729	0.2687	34.9213	1978.8899	1980.9681	-463.7502
		KF	(Reaction 6)			0.2757	0.2688	34.8740	2003.7101	2005.9529	-463.7522
0.1377	0.0304	34.8112	2007.6749	2007.4401	-26.255	0.5457	0.5215	49.4533	2037,6192	2036.6808	-463.1196
0.1377	0.0314	34.7894	1996.0952	1999.8678	-26.256	0.5457	0.5234	49.4518	2036,0863	2037.0007	-463.1197
0.1377	0.0316	34.7870	1991.9284	1990.6086	-26.256	0.5457	0.5208	49.4461	2037,9160	2041.4240	-463.1199
0.1377	0.0296	49.4215	2038.4139	2041.1811	-25.595		$\Delta H$	0 soln,298 =	464.181 ± 1.3	393 kJ/mol	
0.1377	0.0299	49.2870	2032.8533	2036.1297	-25.601						
0.1377	0.0299	49.2849	2033.4513	2034.4967	-25.601		P-8(K	: KAISi1,81	O <sub>5,62</sub> 1.69H <sub>2</sub> O	(Reaction 7)	
	$\Delta F$	10 = -	$26.699 \pm 0.0$	80 kJ/mol		0.5459	0.5235	49.2592	2041.1372	2042.9278	-464.7440
						0.5459	0.5230	49.2598	2040.9644	2044.3993	-464.7440
P	-9(NaK): I	Va <sub>0.81</sub> K <sub>0.19</sub> A	ISi <sub>1,94</sub> O <sub>5.88</sub> · 2.1	3H₂O (Reaction		0.5449	0.5334	49.2880	2043.3161	2043.1089	-464.7444
0.5437	0.5455	34.6876	2003.8701	2008.7259	-482.0255	0.5459	0.5328	34.7884	2013.4455	2014.9555	-464.5256
0.5437	0.5425	34.6456	2008.1388	2010.6252	-482.0255	0.5459	0.5288	34.6009	2013.7245	2014.5625	-464.5228
0.5437	0.5436	34.6375	2006.8680	2010.6850	-482.0254	0.5459	0.5307	34.6162	2012.6574	2013.3736	-464.5230
0.5437	0.5340	49.4553	2038.1286	2041.2964	-482.0444	0.5459	0.5307	34.6194	2010.8174	2015.7806	-464.5231
0.5437	0.5358	49.4691	2039.8805	2040.4925	-482.0444		$\Delta H$	0 soin,298 = -	464.378 ± 1.3	393 kJ/mol	
0.5437	0.5361	49.4609	2041.2669	2040.5441	-482.0444						
	$\Delta H$	0 soln 298 = -4	182.013 ± 1.4	46 kJ/mol							

Note: Column headings: Sample mass, the mass of the sample reacted.  $\Delta T_{\text{corr.}}$  the temperature rise for the dissolution reaction corrected for heat exchange.  $\bar{T}_{\text{soin}}$ , 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.  $\Delta H_{\text{soin}}$  at  $\bar{T}_{\text{soin}}$ , the enthalpy of solution at the mean temperature of the solution period. Reaction numbers refer to reactions listed in Table 8.

 $\Delta H_{\rm soln}$  for  $\alpha$ -quartz is  $-135.56 \pm 0.40$  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<sub>(aq)</sub>. 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  $-135.56 \pm 0.40$  kJ/mol obtained from the equation above for the enthalpy of solution of  $\alpha$ -quartz at 25 °C.

Gibbsite [Al(OH)<sub>3</sub>]. The heat of solution of Al(OH)<sub>3</sub> was measured at 35 and 50 °C using the solution that

resulted from the dissolution of quartz reaction (Table 7). The value for  $\Delta H_{\rm soln}$  of gibbsite at 25 °C ( $-164.716\pm0.494$  kJ/mol) agrees with that determined by Johnson et al. (1982) for the enthalpy of reaction of gibbsite with 24.4 wt% HF<sub>(aq)</sub> ( $-165.180\pm0.125$  kJ/mol). This was expected because our findings and those of Hemingway and Robie (1977) show that the presence of dissolved SiO<sub>2</sub> in the initial HF<sub>(aq)</sub> solution has very little effect upon  $\Delta H_{\rm soln}$  of Al(OH)<sub>3</sub>. Comparison of our values with those determined by Hemingway and Robie for 20.1 wt% HF<sub>(aq)</sub> suggests that  $\Delta H_{\rm soln}$  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-

<sup>\*</sup> Data taken from Nitkiewicz et al. (unpublished data, 1983).

<sup>†</sup> Data taken from Johnson et al. (1982).

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	$\Delta H$ (kJ/mol)
1. [A] → [HF·3.44H <sub>2</sub> O] + [2566.65HF·8831.24H <sub>2</sub> O]	0
2. 1.13H <sub>2</sub> O + [2566.65HF⋅8834.68H <sub>2</sub> O] → [B]	$-0.458 \pm 0.049$
3. 1.94SiO <sub>2</sub> + [B] → [C]	$-262.986 \pm 0.781$
4. $AI(OH)_{3(c)} + [C] \rightarrow [D]$	$-164.716 \pm 0.494$
5. 0.81NaF + [D] → [E]	$-3.055 \pm 0.009$
6. 0.19KF + [E] → [F]	$-5.073 \pm 0.015$
7. [F] $\rightarrow \text{Na}_{0.81}\text{K}_{0.19}\text{AlSi}_{1.94}\text{O}_{5.88} \cdot 2.13\text{H}_{2}\text{O} + [A]$	$482.013 \pm 1.446$
8. $1.94Si_{c0} + 1.94O_{200} \rightarrow 1.94SiO_{200}$	$-1766.758 \pm 1.940$
9. $A _{(a)} + 1.5H_{2(a)} + 1.5O_{2(a)} \rightarrow A (OH)_{3(a)}$	$-1293.128 \pm 1.192$
10. $0.81 \text{Na}_{(c)} + 0.405 \text{F}_{2(c)} \rightarrow 0.81 \text{NaF}_{(c)}$	$-467.006 \pm 0.543$
11. $0.19K_{(c)} + 0.095F_{2(g)} \rightarrow 0.19KF_{(c)}$	$-108.257 \pm 0.128$
12. $[HF \cdot 3.44H_2O] \rightarrow 3.94H_{2(q)} + 1.72O_{2(q)} + 0.5F_{2(q)}$	$321.26 \pm 0.40$
13. $1.13H_{2(a)} + 0.565O_{2(a)} \rightarrow 1.13H_{2}O$	$-322.988 \pm 0.047$
14. $[2566.65HF \cdot 8831.24H_2O] + 3.44H_{2(g)} + 1.72O_{2(g)} \rightarrow [2566.65HF \cdot 8834.68H_2O]$	0
$[A] = [2567.65HF \cdot 8834.68H_2O]$	
$[B] = [2566.65HF \cdot 8835.81H_2O]$	
$[C] = [1.94H_2SiF_6 \cdot 2555.01HF \cdot 8839.69H_2O]$	
$[D] = [AIF_3 \cdot 1.94H_2SiF_6 \cdot 2552.01HF \cdot 8842.69H_2O]$	
$[E] = [0.81 \text{NaF} \cdot \text{AiF}_3 \cdot 1.94 \text{H}_2 \text{SiF}_6 \cdot 2552.01 \text{HF} \cdot 8842.69 \text{H}_2 \text{O}]$	
$[F] = [0.19KF \cdot 0.81NaF \cdot AlF_3 \cdot 1.94H_2SiF_6 \cdot 2552.01HF \cdot 8842.69H_2O]$	

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 ( $-3.771 \pm 0.011 \text{ kJ/mol}$ ) compares well with that determined for the dissolution of NaF in pure 24.4 wt% HF<sub>(aq)</sub> by Johnson et al. (1982) ( $-4.056 \pm 0.063 \text{ kJ/mol}$ ). 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  $\Delta H_{\text{solp}}$  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  $\Delta H_{\rm soln}$  for mixtures of NaF and KF are stoichiometric additions of the end-member values. Therefore, values of  $\Delta H_{\rm soln}$  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  $\Delta H_{\rm soln}$  values measured for P-8(K), P-8(KNa) and P-8(NaK) are reasonable approximations to true values, however values of  $\Delta H_{\rm soln}$  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·3.44H<sub>2</sub>O] (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  $\Delta H$  yields a value of  $-3591.2 \pm 2.9$  kJ/mol for the standard enthalpy of formation from the elements ( $\Delta H_{\rm f}^2$ ) 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 ( $\Delta H_{\rm f}^0$  in kJ/mol) are P-9(KNa),  $-3519.0 \pm 2.9$ ; P-9(K),  $-3481.8 \pm 3.0$ ; P-8(NaK),  $-3488.3 \pm 2.8$ ; P-8(KNa),  $-3387.3 \pm 2.8$ ;

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

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

<sup>\*</sup> Percent deviation in estimated values shown in parentheses.

and P-8(K),  $-3360.0 \pm 2.8$ . 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  $S_{298}^0$  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)	% Erro
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  $S_{298}^0 - S_0^0$  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 ( $\Delta H_T^o - \Delta H_0^o$ ) 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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