

## Thermodynamic studies of zeolites: natrolite, mesolite and scolecite<sup>1</sup>

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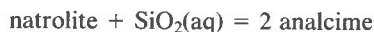
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### Abstract

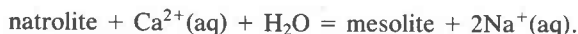
Calorimetric measurements have been carried out on specimens of natrolite, mesolite, and scolecite in order to assess the thermodynamic properties of a zeolite series having the same aluminosilicate framework. Low-temperature heat capacity and high-temperature enthalpy increments of natrolite and scolecite were measured by adiabatic and drop-calorimetric techniques. Standard enthalpies of formation at 298.15 K of all three zeolites were determined by solution calorimetry. Thermodynamic functions have been calculated for natrolite to 660 K and for scolecite to 470 K. The heat capacity and standard entropy at 298.15 K have been estimated for mesolite. The following values at  $T = 298.15$  K and a pressure of 1 bar have been obtained:

	$\Delta H_f^\circ(T)$	$C_p^\circ(T)$	$S^\circ(T) - S^\circ(0)$	$\Delta G_f^\circ(T)$
	kJ/mol	J/(mol · K)	J/(mol · K)	kJ/mol
natrolite	$-5718.6 \pm 5.0$	$359.23 \pm 0.72$	$359.73 \pm 0.72$	$-5316.6 \pm 5.0$
mesolite	$-5947.1 \pm 5.4$	$371 \pm 2$	$363 \pm 2$	$-5513.2 \pm 5.4$
scolecite	$-6049.0 \pm 5.0$	$382.81 \pm 0.77$	$367.42 \pm 0.73$	$-5597.9 \pm 5.0$

With reference to zeolitic water, it is concluded that the entropy of water molecules in both natrolite and scolecite is similar to that in ice. A consideration of the X-ray results for the present specimen of natrolite leads to the conclusion that a contribution of about 9.2 J/(mol · K) to the standard entropy is made by the Al-Si disorder in the aluminosilicate framework. The new results allow calculations to be made by which the pressure and temperature effect can be deduced for such equilibria as:



and



Results are consistent with observed parageneses in natural occurrences.

### Introduction

The thermodynamic properties of a zeolite are controlled largely by the aluminosilicate framework, but significant contributions can be made by the bonding of the exchangeable cations and water molecules. Few zeolites have unique compositions and this is one of the major problems that arise when systematic thermody-

amic studies of these materials are attempted. Examples of compositional variations include the Si content of the framework, the exchangeable cations, and the water content. The situation is further complicated by varying degrees of ordering of the Si-Al distribution in the framework as well as by variable cation positioning. Clearly then, in order to establish a basic understanding of the thermodynamics of zeolites in general, it is advantageous to study a group in which composition variables are minimal. Natrolite, mesolite, and scolecite are particularly suited to such a study because they have the same

<sup>1</sup> Work performed under the auspices of the Division of Engineering, Mathematical, and Geosciences, Office of Basic Energy Sciences, of the U.S. Department of Energy.

framework and the same ordered Si–Al distribution, and each has a unique cation content. Alberti *et al.* (1982) have shown that the Si content of the tetrahedral sites in each of these zeolites arises only slightly from the ideal 60 mol%. Furthermore, natrolites typically contain less than one per cent of cations other than Na<sup>+</sup>, and scolecites have less than two per cent of cations other than Ca<sup>2+</sup>. Mesolites have approximately equal contents of Na and Ca, with Ca/(Ca+Na+K) varying less than 5% from 0.50. The reader is referred to Alberti *et al.* (1982) for a summary of compositional ranges and atomic arrangements in these zeolites.

Low-temperature heat capacity and high-temperature enthalpy increment measurements were carried out on natrolite and scolecite, and enthalpy of reaction measurements were made on all three zeolites. The standard thermodynamic functions were derived for natrolite and scolecite and were estimated for mesolite. Our thermodynamic results suggest that the entropy of the zeolitic water in both natrolite and scolecite approaches that of ice. In addition, our calculations show that natrolite is stable only in solutions of low Ca<sup>2+</sup> activity and that the width of the mesolite field of stability is nearly four orders of magnitude in terms of Na<sup>+</sup> activity.

The question of structural disorder and the resulting contribution to the residual entropy of geologic materials continues to be a subject of great interest (Ulbrich and Waldbaum, 1976). We have also addressed this topic with respect to the specimen of natrolite used in our studies by calculating its configurational entropy based on the Al/Si distribution inferred from the experimental lattice parameters.

## Materials

### Natrolite, mesolite, and scolecite

Sources of the zeolites used in the present study were as follows: Larne, County Antrim, Northern Ireland (natrolite); Nasik, Poona District, India (mesolite); and Kosmos, Washington, U.S.A. (scolecite). Each mineral occurs as prismatic crystals, up to 8 cm in length, which may be colorless transparent or white and translucent. A stock of about 20 grams of each was prepared for the calorimetric measurements by crushing the clear ends of selected crystals to about 0.5 mm size. The grains were examined under a microscope and any that were opaque were discarded. A sample of about 25 grains taken from the stock of each zeolite was analyzed with an ARL electron microprobe to determine the average composition and compositional variations. For all elements an accelerating voltage of 15 kV was used with a sample current of 10 nA and a defocused beam. The elements commonly found in zeolites—Na, Al, Si, K, Ca, Mg, Fe, Sr, and Ba—were sought, but only the first five were detected. Standards used were albite, microcline and andesine. Water content was determined by heating a

sample that had been equilibrated with air of 50% relative humidity to 873 K for 24 hours and measuring the weight loss. Analytical results along with the cell dimensions are given in Table 1.

The natrolite analyses were slightly low in Na, and this was assumed to be due to analytical error (ion migration effect). The composition was taken to be Na<sub>2</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub> · 2H<sub>2</sub>O, and molar thermodynamic properties are based on this formula. The average mesolite composition varied somewhat from the ideal ratio, Ca:Na = 1:1. However, because there was a nearly perfect charge balance, the composition given in Table 1 was used in all calculations and in the thermochemical cycles as well, even though the unit cell contents (Z = 24) are very much larger than this formula indicates. The scolecite analyses yielded a composition very close to CaAl<sub>2</sub>Si<sub>3</sub>O<sub>10</sub> · 3H<sub>2</sub>O (Table 1), and all calculations are based on this formula.

### Gibbsite

The gibbsite, Al(OH)<sub>3</sub>, was Fisher Reagent Al<sub>2</sub>O<sub>3</sub> · 3H<sub>2</sub>O which had been heated for approximately 6 hours at 423 K before use. The source of the gibbsite and its thermal treatment were, therefore, identical to those reported by Hemingway and Robie (1977) for their determination of ΔH<sub>f</sub><sup>0</sup>[Al(OH)<sub>3</sub>].

Table 1. Analytical results and structural parameters for the zeolites

	Natrolite		Mesolite		Scolecite	
Sample composition (mass per cent)						
SiO <sub>2</sub>	47.40		46.53		45.90	
Al <sub>2</sub> O <sub>3</sub>	26.79		26.13		26.00	
CaO	0.04		9.49		14.31	
Na <sub>2</sub> O	15.97		5.39		0.04	
K <sub>2</sub> O	0.03		0.02		0.00	
H <sub>2</sub> O	9.2		12.3		13.8	
Total	99.43		99.86		100.05	
Cell contents (number of atoms)*						
	A	B	A	B	A	B
Si	24.01	3.00	24.07	3.01	23.98	3.00
Al	15.99	2.00	15.93	1.99	16.01	2.00
Ca	0.02	—	5.26	0.657	8.01	1.00
Na	15.68	2.00	5.40	0.676	0.02	—
K	0.01	—	0.01	—	0.00	—
H <sub>2</sub> O	15.52	2.00	21.17	2.647	24.04	3.00
Cell dimensions (Å)						
a	18.309(3)		18.405(4)		18.504(4)	
b	18.623(4)		56.609(13)		18.972(5)	
c	6.592(2)		6.546(2)		6.519(2)	
β					90.61(2)	
*A - cell contents based on 80 framework oxygens; B - idealized composition used as basis for calculation of molar thermodynamic properties.						

### Sodium fluoride

Ultrapure sodium fluoride was obtained from Alfa Inorganics (Danvers, MA). The sample was heated to 475 K for approximately 8 hours and then transferred to a helium-atmosphere glovebox where it was stored.

### Hydrofluoric acid

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

### Apparatus, experimental procedures, and results

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

### Heat capacity measurements (5 to 350 K)

In this part of the study, we employed the same calorimeter (laboratory designation 6-GS-1) as in our earlier work on analcime (Johnson *et al.*, 1982). This calorimeter was constructed from oxygen-free, high-conductivity copper, and has an internal volume of 5.976 cm<sup>3</sup> at 298.15 K. Both natrolite, 7.8125 g, and scolecite, 7.4913 g, were loaded into the calorimeter in a glovebox filled with dry helium. After removal from the glovebox, the natrolite was found to have been reduced in mass by approximately 0.3% and the scolecite by approximately 0.03%. This loss of water will be discussed later. To promote rapid thermal equilibration, a small amount of helium, about  $7 \times 10^{-6}$  mol, was left in the calorimeter. Separate experiments were performed to determine the heat capacity of the empty calorimeter.

Only a brief description of the apparatus and measuring techniques will be given here; this information has been published in detail previously (Osborne *et al.*, 1972). The temperature of the adiabatic shields surrounding the calorimeter was controlled automatically so that it was close ( $\pm 0.001$  K) to that of the calorimeter at all times. The temperature of the calorimeter was measured by means of a calibrated platinum resistance thermometer (Westrum *et al.*, 1953) in conjunction with a calibrated double potentiometer and a photoelectric galvanometer. The temperature scale of the thermometer is believed to agree with the thermodynamic scale to within 0.1 K from 3 to 14 K, to within 0.03 K from 14 to 90 K, and to within 0.05 K between 90 and 373 K. Temperature differences, however, are reliable to 0.01 K at 4.2 K, to 0.0008 K at 14 K, to 0.0001 K from 25 to 58 K, and to 0.001 K above 58 K. Time and potentiometer readings were relayed to an on-line computer which, in turn, printed a record of the temperature as a function of time. Corrections for small deviations from truly adiabatic behavior were derived from observations of the steady-state drift of the temperature both before and after the calorimeter was heated. While the calorimeter was being heated, the current and voltage drop across the heater (from which the resistance was computed) were automatically recorded at predetermined time intervals. A preset timer calibrated against NBS Station WWV was used to fix the heating time to better than 0.01%. All standards of mass, resistance, and voltage used in this research are traceable to the National Bureau of Standards.

The heat capacity of each zeolite was calculated as the difference between the results obtained for the loaded and for the empty calorimeter. Minor heat capacity corrections had to be made because different amounts of helium, Apiezon T grease, copper, and gold were used with the loaded and empty calorimeter. A small curvature correction equal to  $-(d^2C_p/dT^2)(\Delta T)^2/24$  was applied to each heat capacity determination.

### Heat capacity results

As mentioned earlier, the preliminary evacuation of the calorimeter resulted in a loss in mass of about 0.3% of the natrolite and about 0.03% of the scolecite; in both cases, this loss was attributed to removal of zeolitic water. In the case of scolecite, this water loss did not significantly alter the sample composition and, thus, the initial mass of material placed in the calorimeter was simply assumed to have been reduced by this amount. For natrolite, the water loss did significantly alter the sample composition and it was assumed that the composition of the sample on which the measurements were actually made was  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 1.94\text{H}_2\text{O}$ . We accordingly adjusted the experimental results to refer to a composition of  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ . This adjustment was made as follows. It was assumed that the molar heat capacity contribution of the zeolitic water was the same in natrolite as in analcime, *i.e.*,  $\bar{C}_p^\circ(T)(\text{H}_2\text{O}) = C_p^\circ(T)(\text{analcime}) - C_p^\circ(T)(\text{dehydrated analcime})$ . It was further assumed that this relationship was valid over the entire range (4–350 K) of the experimental temperatures. Next,  $\bar{C}_p^\circ(T)(\text{H}_2\text{O})$  was calculated based on our earlier studies of analcime and dehydrated analcime (Johnson *et al.*, 1982). From 4 to 10 K,  $\bar{C}_p^\circ(T)(\text{H}_2\text{O})$  was plotted as a function of  $T$ . From 10.4 to 72.5 K,  $\bar{C}_p^\circ(T)(\text{H}_2\text{O})$  was fitted to a polynomial in  $T$  of order 6. Above 72.5 K,  $\bar{C}_p^\circ(T)(\text{H}_2\text{O})$  could be reliably interpolated. The  $\bar{C}_p^\circ(T)(\text{H}_2\text{O})$  computed at a given experimental temperature was then multiplied by 0.06 and added to the corresponding molar experimental heat capacity for the natrolite with composition 1.94 H<sub>2</sub>O. These new heat capacities are taken to refer to a composition of  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$  and are used as such in subsequent computations.

The corrected heat capacities,  $C_p^\circ(T)$ , are given in order of ascending mean temperatures,  $\langle T \rangle$ , for natrolite in Table 2 and scolecite in Table 3. The temperature increment,  $\Delta T$ , for each experiment below 20 K was approximately 2 K, between 20 K and 100 K,  $\Delta T \approx 0.1 \langle T \rangle$ , and above 100 K,  $\Delta T \approx 10$  K.

Individual heat capacity values are estimated to be uncertain by 5% near 6 K, by 1% near 14 K, and by 0.2% above 25 K. No impurity corrections were necessary. No anomalous behavior was observed, and plots of  $C_p^\circ(T)$  against  $\langle T \rangle$  had the normal sigmoid shape.

### Derivation of the standard entropy and other thermodynamic functions

Heat capacity results in Tables 2 and 3 were fitted by two polynomials in  $T$  using a weighted, least-squares

Table 2. Adjusted heat capacities of natrolite,  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ , based on experimental results for  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 1.94\text{H}_2\text{O}$

$\langle T \rangle$	$C_p^0(T)$	$\langle T \rangle$	$C_p^0(T)$	$\langle T \rangle$	$C_p^0(T)$
K	J/(mol·K)	K	J/(mol·K)	K	J/(mol·K)
6.02	0.090	33.80	24.98	175.97	247.29
6.13	0.094	37.36	31.24	185.95	258.70
8.38	0.236	41.27	38.35	195.98	269.62
8.46	0.231	45.58	46.38	206.01	279.97
10.41	0.519	50.09	55.02	216.04	289.73
10.45	0.512	53.53	61.72	226.04	299.51
12.40	1.019	59.27	72.79	235.83	308.84
12.46	1.023	65.51	84.80	245.82	317.77
14.42	1.775	72.45	97.64	255.85	325.96
14.47	1.808	80.10	111.33	265.81	334.48
16.45	2.890	86.91	123.34	275.73	342.59
16.48	2.915	88.53	126.25	285.73	350.24
18.47	4.394	96.32	138.71	295.75	357.71
18.49	4.395	105.88	153.27	305.74	364.52
20.52	6.238	116.09	168.95	315.73	371.65
20.55	6.282	126.06	183.41	325.71	378.79
22.68	8.541	136.01	197.50	333.93	383.50
25.04	11.42	146.07	210.93	340.42	387.65
27.69	15.15	156.06	223.58	346.86	391.45
30.59	19.66	166.01	235.42		

procedure. One polynomial covered the region below 40 K, and the other the region above 20 K. Below 40 K, the standard deviations of the experimental heat capacities from the curves were 2.0 and 2.2% for natrolite and scolecite, respectively. Above 20 K, the corresponding standard deviations were 0.14 and 0.22%. Based on these polynomials,  $C_p^0(T)$  values have been calculated at selected temperatures and are given in Tables 4 and 5. At 298.15 K the heat capacities of natrolite and scolecite are  $359.23 \pm 0.72$  and  $382.81 \pm 0.77$  J/(mol·K), respectively.

The heat capacities below 13 K (see Tables 2 and 3) were used to construct plots of  $C_p^0/T$  against  $T^2$  for both natrolite and scolecite. Smooth curves could be drawn through these points and also that at  $C_p^0 = 0$  as  $T \rightarrow 0$ . These curves were essentially linear below 7 K (natrolite) and 6 K (scolecite). The heat capacities and other thermodynamic functions of natrolite at 7 K (Table 4) and scolecite at 6 K (Table 5) were derived from these curves. For  $T = 10$  K and above, the thermodynamic functions in Tables 4 and 5 were computed from appropriate integrals of the polynomials referred to in the preceding paragraph.

#### Enthalpy of reaction measurements at 298.15 K

An LKB-8700 precision calorimetric system was used for the enthalpy of solution and reaction measurements. The 100 cm<sup>3</sup> reaction vessel and stirrer were both constructed of 18-carat gold. The reaction vessel was modified for quartz-crystal

thermometry by the addition of a re-entry well, in which the sensor of a quartz-crystal thermometer (Hewlett-Packard Model 2801-A) was placed. For solution calorimetric work with HF(aq), we usually employ KEL-F (chlorotrifluoroethylene polymer) ampoules with windows made from thin KEL-F film (Johnson *et al.*, 1973). However, in experiments with natrolite, scolecite, and mesolite, it was found that the torn ampoule windows so inhibited the dispersal of zeolite into the acid that the reaction time became unacceptably long. In order to alleviate this problem, new all-Teflon ampoules were designed in which the windows were made of discs split across the diameter. The D-shaped halves were attached to each other and to the body of the ampoule with wax so that the entire assembly was leak-tight. When such an ampoule is brought into contact with the ampoule-breaker spike in the calorimeter, the windows are completely detached from the ampoule body, and the sample is immediately dispersed in the solution. In this way, the reaction time is shortened considerably.

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

Calorimetric measurements were made of the enthalpies of reaction of natrolite, scolecite, mesolite, gibbsite, and sodium fluoride with approximately 24.4 mass per cent HF(aq). For the reactions of scolecite and mesolite, it was assumed that the  $\text{CaF}_2$  precipitated quantitatively. In separate experiments, no enthalpy change was detected when pure  $\text{CaF}_2$  was introduced into an

Table 3. Experimental heat capacities for scolecite ( $\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$ )

$\langle T \rangle$	$C_p^0(T)$	$\langle T \rangle$	$C_p^0(T)$	$\langle T \rangle$	$C_p^0(T)$
K	J/(mol·K)	K	J/(mol·K)	K	J/(mol·K)
6.35	0.095	36.34	31.14	189.25	269.32
8.20	0.216	40.22	38.09	199.27	281.44
8.48	0.239	44.42	45.79	209.24	292.63
10.24	0.477	49.15	54.43	219.22	303.98
10.60	0.507	53.58	62.63	229.21	314.78
12.33	0.959	59.33	73.04	235.56	321.55
12.70	1.096	65.54	84.29	245.94	332.33
14.32	1.715	72.48	96.55	256.04	342.53
14.68	1.909	80.13	109.66	266.05	352.57
16.21	2.816	88.47	124.07	276.04	362.34
16.68	3.113	88.57	124.07	286.00	371.49
18.16	4.304	98.23	139.23	295.95	380.69
18.66	4.771	107.94	154.50	305.95	389.31
20.18	6.253	117.90	169.96	315.99	398.57
20.69	6.829	128.20	186.22	326.04	407.56
22.21	8.591	138.75	201.96	334.18	414.11
24.57	11.66	149.04	216.61	340.41	419.37
27.00	15.25	159.05	230.36	346.77	424.66
29.62	19.48	169.11	243.53		
32.80	24.87	179.19	256.77		

Table 4. Low-temperature thermodynamic functions for natrolite ( $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ )\*

$T$	$C_p^*(T)$	$S^*(T) - S^*(0)$	$H^*(T) - H^*(0)$	$-[G^*(T) - H^*(0)]/T$
K	J/(mol·K)	J/(mol·K)	J/mol	J/(mol·K)
7	(0.136)	(0.045)	(0.236)	(0.011)
10	0.434	0.134	1.009	0.033
20	5.700	1.608	25.17	0.350
30	18.69	6.155	141.7	1.432
40	36.01	13.84	413.1	3.513
60	74.16	35.60	1512	10.40
80	111.36	62.11	3373	19.95
100	144.49	90.59	5938	31.21
120	174.60	119.63	9132	43.53
140	202.82	148.69	12910	56.47
160	228.49	177.48	17228	69.81
180	251.82	205.76	22034	83.35
200	273.70	233.43	27291	96.98
220	293.95	260.48	32971	110.61
240	312.33	286.86	39036	124.21
260	329.68	312.55	45458	137.71
280	345.96	337.59	52217	151.10
300	360.53	361.96	59284	164.35
320	374.73	385.68	66636	177.44
340	387.25	408.79	74261	190.38
350	393.39	420.10	78163	196.78
273.15	340.57	329.08	49865	146.52
298.15	359.23	359.73	58618	163.12

\*Molecular mass of  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$  was taken to be 380.22 g/mol.

HF(aq) solution, and this lends strong support to the above assumption. Detailed results for the calorimetric reactions are given in Table 6.

### Standard enthalpies of formation at 298.15K

The reactions and enthalpy values necessary to derive the standard enthalpies of formation of natrolite, scolecite, and mesolite are given in Table 7. The molar enthalpies of reactions 2, 3, 5, 6, and 7 are based on the corresponding mean specific enthalpies of reaction in Table 6. For this conversion, the molar masses of  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ ,  $\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_{0.676}\text{Ca}_{0.657}\text{Al}_{1.99}\text{Si}_{3.01}\text{O}_{10} \cdot 2.647\text{H}_2\text{O}$ ,  $\text{Al}(\text{OH})_3$ , and  $\text{NaF}$  were taken to be 380.2235, 392.339, 387.784, 78.0034, and 41.9882 g/mol, respectively, based on the 1979 atomic weights (Holden, 1980). The enthalpy of reaction of  $\alpha$ -quartz with HF(aq), reaction 1, has been reported recently (Johnson *et al.*, 1982). Enthalpies of dilution of HF(aq) (reactions 8, 9, and 10) and the enthalpy of formation of  $\text{HF} \cdot 3.441\text{H}_2\text{O}$  (reaction 11) are based on an earlier study at this laboratory (Johnson *et al.*, 1973). For reactions 12, 13, 14, and 16 the standard enthalpies of formation of  $\text{H}_2\text{O}(l)$

(CODATA, 1978);  $\text{SiO}_2(\alpha)$  (Wise *et al.*, 1963);  $\text{Al}(\text{OH})_3(c)$  (Hemingway and Robie, 1977); and  $\text{CaF}_2$  (Robie *et al.*, 1978) were taken from the literature. The enthalpy of formation of NaF is based on  $\Delta H_f^\circ(\text{Na}^+, \text{aq})$ ,  $-240.300 \pm 0.065$  kJ/mol (CODATA, 1978);  $\Delta H_f^\circ(\text{F}^-, \text{aq})$ ,  $-335.64 \pm 0.29$  kJ/mol (Johnson *et al.*, 1973); and  $\Delta H_{\text{soln}}^\circ(\text{NaF}, c)$ ,  $937 \pm 36$  J/mol (Nuttall *et al.*, 1978).

The standard enthalpies of formation,  $\Delta H_f^\circ(298.15\text{K})$ , for natrolite,  $-5718.6 \pm 5.0$ , scolecite,  $-6049.0 \pm 5.0$ , and mesolite,  $-5947.1 \pm 5.4$ , are calculated as shown in Table 8, where the individual  $\Delta H$  values have been taken from Table 7. In the mesolite cycle, because of rounding-off errors, the solution that results from the sum of reactions 1, 2, 3, and 4 is not identical with solution [E]. The difference, however, is thermally insignificant and has been ignored.

### Enthalpy increment measurements

The drop calorimeter used for the enthalpy increment measurements on natrolite and scolecite has been described in detail (Fredrickson *et al.*, 1969). The system consisted essentially of a resistance-heated, molybdenum-core furnace and

Table 5. Low-temperature thermodynamic functions for scolecite ( $\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$ )\*

$T$	$C_p^*(T)$	$S^*(T) - S^*(0)$	$H^*(T) - H^*(0)$	$-[G^*(T) - H^*(0)]/T$
K	J/(mol·K)	J/(mol·K)	J/mol	J/(mol·K)
6	(0.080)	(0.027)	(0.120)	(0.007)
10	0.426	0.129	0.981	0.031
20	6.053	1.632	25.72	0.346
30	20.11	6.540	151.5	1.490
40	37.71	14.70	439.2	3.715
60	74.30	36.91	1560	10.92
80	109.54	63.17	3402	20.64
100	142.33	91.18	5925	31.93
120	173.38	119.89	9084	44.19
140	203.46	148.89	12854	57.08
160	231.86	177.94	17211	70.37
180	257.83	206.77	22112	83.93
200	281.91	235.19	27511	97.63
220	304.83	263.14	33381	111.41
240	326.35	290.60	39695	125.21
260	346.45	317.52	46425	138.97
280	365.87	343.91	53549	152.67
300	384.47	369.80	61054	166.28
320	401.81	395.17	68918	179.80
340	419.34	420.05	77130	193.20
350	427.13	432.32	81363	199.86
273.15	359.26	334.93	51065	147.98
298.15	382.81	367.42	60345	165.03

\*Molecular mass of scolecite was taken to be 392.34 g/mol.

Table 6. Enthalpies of reaction (298.15 K) with HF(aq) of natrolite, scolecite, mesolite, gibbsite, and sodium fluoride\*

m g	$\Delta\theta_c$ K	$\epsilon(\text{calor})^{**}$ J/K	$\epsilon(\text{calor})(-\Delta\theta_c)$ J	$\Delta H_{\text{corr}}^\dagger$ J	$\Delta H/M$ J/g
Natrolite, $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$					
0.22211	1.25471	400.48	-502.49	0.0	-2261.9
0.22185	1.25103	400.98	-501.64	0.09	-2260.8
0.22383	1.26308	400.39	-505.72	0.09	-2259.0
0.22190	1.25142	400.34	-500.99	0.09	-2257.3
0.22117	1.24683	400.68	-499.58	0.09	-2258.4
0.22215	1.25414	400.55	-502.35	0.09	-2260.9
Average $\Delta H/M = -2259.7 \pm 0.7 \text{ J/g}^{\dagger\dagger}$					
Scolecite, $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$					
0.22912	1.28924	400.66	-516.55	0.09	2254.1
0.22812	1.28319	400.80	-514.30	0.09	-2254.1
0.22933	1.29011	400.31	-516.44	0.09	-2251.6
0.22932	1.28761	400.54	-515.74	0.09	-2248.6
0.22811	1.28036	400.82	-513.19	0.09	-2249.4
Average $\Delta H/M = -2251.6 \pm 1.1 \text{ J/g}^{\dagger\dagger}$					
Mesolite, $\text{Na}_{0.676}\text{Ca}_{0.657}\text{Al}_{1.990}\text{Si}_{3.010}\text{O}_{10}\cdot 2.647\text{H}_2\text{O}$					
0.22742	1.25478	402.24	-504.72	0.09	-2218.9
0.22715	1.23765	404.36	-500.46	0.09	-2202.8
0.22748	1.23909	404.55	-501.27	0.09	-2203.2
0.22396	1.22725	403.38	-495.05	0.09	-2210.0
0.22711	1.24410	403.31	-501.76	0.09	-2208.9
0.22791	1.26098	400.62	-505.17	0.09	-2216.1
Average $\Delta H/M = -2210.0 \pm 2.7 \text{ J/g}^{\dagger\dagger}$					
Gibbsite, $\text{Al}(\text{OH})_3$					
0.09060	0.47804	402.32	-192.33	0.52	-2117.1
0.09122	0.48249	402.10	-194.01	0.52	-2121.1
0.09106	0.48189	401.86	-193.65	0.52	-2120.9
0.09086	0.48172	402.14	-193.72	0.52	-2126.3
0.09086	0.48073	402.11	-193.31	0.52	-2121.8
Average $\Delta H/M = -2121.4 \pm 1.5 \text{ J/g}^{\dagger\dagger}$					

a copper-block calorimeter. Measurements of the furnace temperature were made with platinum-to-(platinum + 10% rhodium) thermocouples. The temperature of the calorimeter was determined with a quartz-crystal thermometer. The energy equivalent of the empty calorimeter was determined by electrical calibrations. For the present experiments, the calorimeter and furnace were filled with helium at a pressure of about 13 mbar, which substantially decreased equilibration times within the furnace and allowed measurements to be conducted at temperatures as low as 350 K. The performance of the calorimetric system was checked (Johnson *et al.*, 1980) by determining the enthalpy of synthetic sapphire (National Bureau

Table 6. (cont.)

m g	$\Delta\theta_c$ K	$\epsilon(\text{calor})^{**}$ J/K	$\epsilon(\text{calor})(-\Delta\theta_c)$ J	$\Delta H_{\text{corr}}^\dagger$ J	$\Delta H/M$ J/g
Sodium Fluoride, NaF					
0.04851	0.01143	402.31	-4.60	0.51	-84.3
0.04794	0.01136	402.31	-4.57	0.51	-84.7
0.04737	0.01159	402.31	-4.66	0.51	-87.6
0.04820	0.01076	402.31	-4.33	0.51	-79.3
0.04865	0.01199	402.31	-4.82	0.51	-88.6
Average $\Delta H/M = -84.9 \pm 1.6 \text{ J/g}^{\dagger\dagger}$					
*The column headings are m, the mass of the sample reacted; $\Delta\theta_c$ , the temperature change of the calorimeter corrected for heat exchange with the environment; $\epsilon(\text{calor})$ , the mean energy equivalent of the calorimetric system before and after the experiment; $\Delta H_{\text{corr}}$ , the combined correction for the thermal effects of opening the ampoule and of vaporizing the solvent into the free volume of the ampoule, and $\Delta H/M$ , the specific enthalpy of reaction.					
** $\epsilon(\text{calor})$ was not measured for the experiments with NaF but was taken to be the average of the values for the $\text{Al}(\text{OH})_3$ experiments plus 0.05 J for the heat capacity of NaF plus 0.15 J to allow for the difference in ampoule masses.					
$^\dagger\Delta H_{\text{corr}}$ includes the enthalpy effect of opening the ampoule, which was 0.10 J for all experiments except those for $\text{Al}(\text{OH})_3$ and NaF for which it was 0.53 J, as well as a correction for the vaporization of solvent into the free volume of the ampoule.					
$^\dagger\dagger$ The uncertainty is the standard deviation of the mean.					

of Standards Standard Reference Material 720) over the temperature range from 374 to 836 K.

The sample of natrolite (mass, 7.54511 g) was contained in a welded (platinum + 10 per cent rhodium) capsule (1.2 cm diameter, 4.8 cm long, 5.35 cm<sup>3</sup> internal volume, and 19.15696 g mass) which also included  $8.1 \times 10^{-5}$  mol of air. The sample of scolecite (mass, 7.46873 g) was contained in a similar capsule (mass, 19.13454 g) along with  $8.4 \times 10^{-5}$  mol of air.

### Enthalpy increment results

The results of the drop calorimetric experiments in order of increasing temperature are given in Table 9.

The energy equivalent of the calorimeter,  $\epsilon(\text{calor})$ , varies slightly as a function of  $\Delta\theta_c$ , from 4379.46 J/K for  $\Delta\theta_c \approx 0.5$  K to 4378.68 J/K for  $\Delta\theta_c \approx 1.5$  K. The enthalpy contribution of the capsule was determined in a separate series of experiments with an empty (platinum + 10% rhodium) capsule with dimensions and mass similar to those used for the present experiments. The measured enthalpy was corrected for the enthalpy of the air in the capsules, for the difference (usually less than 0.01 K) of the final calorimetric temperature from 298.15 K, and for the water vapor produced by thermal dehydration of the zeolites. The amount of water vapor produced was calculated from the  $\Delta H_T^\circ$  and  $S_{\text{wz}}^\circ$  results given in van Reeuwijk (1974):

$$\log P(\text{bar}) = -5373 T^{-1} + 7.864 \quad (1)$$

for natrolite and

$$\log P(\text{bar}) = -4240 T^{-1} + 7.822 \quad (2)$$

Table 7. Thermochemical equations used for the derivation of the standard enthalpies of formation at 298.15 K of natrolite, scolecite, and mesolite

Reaction	$\Delta H^\circ$ (kJ/mol)
1. $\text{SiO}_2(\text{a}) + 755.57\text{HF} + 2602.2\text{H}_2\text{O} \rightarrow [\text{A}]^*$	$-135.59 \pm 0.18$
2. $\text{Al}(\text{OH})_3(\text{c}) + 3/2[\text{A}] \rightarrow [\text{B}]^{**}$	$-165.48 \pm 0.23$
3. $\text{NaF}(\text{c}) + [\text{B}] \rightarrow [\text{C}]^\dagger$	$-3.56 \pm 0.13$
4. $\text{CaF}_2(\text{c}) + 2[\text{B}] \rightarrow [\text{D}]^{\ddagger\dagger}$	$0.00 \pm 0.00$
5. $2[\text{C}]^\dagger \rightarrow \text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}(\text{c}) + 2268.7\text{HF} + 7806.6\text{H}_2\text{O}$	$859.19 \pm 0.53$
6. $[\text{D}]^{\ddagger\dagger} + \text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}(\text{c}) + 2268.7\text{HF} + 7805.6\text{H}_2\text{O}$	$883.39 \pm 0.86$
7. $[\text{E}]^{\ddagger\dagger\dagger} + \text{Na}_0.676\text{Ca}_0.657\text{Al}_1.99\text{Si}_3.01\text{O}_{10} \cdot 2.647\text{H}_2\text{O}(\text{c}) + 2276.29\text{HF} + 7831.943\text{H}_2\text{O}$	$857.0 \pm 2.1$
8. $2266.7\text{HF} + 7799.7\text{H}_2\text{O} + 6.88\text{H}_2\text{O}(\text{l}) \rightarrow 2266.7\text{HF} + 7806.6\text{H}_2\text{O}$	$-2.79 \pm 0.10$
9. $2266.7\text{HF} + 7798.7\text{H}_2\text{O} + 7.88\text{H}_2\text{O}(\text{l}) \rightarrow 2266.7\text{HF} + 7806.6\text{H}_2\text{O}$	$-3.20 \pm 0.15$
10. $2274.3\text{HF} + 7825.096\text{H}_2\text{O} + 7.504\text{H}_2\text{O}(\text{l}) \rightarrow 2274.3\text{HF} + 7832.6\text{H}_2\text{O}$	$-3.04 \pm 0.15$
11. $\text{HF} + 3.441\text{H}_2\text{O} \rightarrow 1/2\text{H}_2(\text{g}) + 1/2\text{F}_2(\text{g}) + 3.441\text{H}_2\text{O}(\text{l})$	$321.25 \pm 0.40$
12. $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	$-285.83 \pm 0.04$
13. $\text{Si}(\text{c}) + \text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{a})$	$-910.9 \pm 1.4$
14. $\text{Al}(\text{c}) + 3/2\text{H}_2(\text{g}) + 3/2\text{O}_2(\text{g}) \rightarrow \text{Al}(\text{OH})_3(\text{c})$	$-1293.1 \pm 1.2$
15. $\text{Na}(\text{c}) + 1/2\text{F}_2(\text{g}) \rightarrow \text{NaF}(\text{c})$	$-576.88 \pm 0.30$
16. $\text{Ca}(\text{c}) + \text{F}_2(\text{g}) \rightarrow \text{CaF}_2(\text{c})$	$-1229.26 \pm 0.42$

\*  $[\text{A}] = \text{H}_2\text{SiF}_6 \cdot 749.57\text{HF} \cdot 2604.2\text{H}_2\text{O}$ .

\*\*  $[\text{B}] = \text{AlF}_3 \cdot 1.5\text{H}_2\text{SiF}_6 \cdot 1121.36\text{HF} \cdot 3909.3\text{H}_2\text{O}$ .

†  $[\text{C}] = \text{NaF} \cdot \text{AlF}_3 \cdot 1.5\text{H}_2\text{SiF}_6 \cdot 1121.36\text{HF} \cdot 3909.3\text{H}_2\text{O}$ .

‡  $[\text{D}] = \text{CaF}_2 + 2\text{AlF}_3 \cdot 3\text{H}_2\text{SiF}_6 \cdot 2242.7\text{HF} \cdot 7818.6\text{H}_2\text{O}$ .

‡‡  $[\text{E}] = 0.657\text{CaF}_2 + 0.676\text{NaF} \cdot 1.99\text{AlF}_3 \cdot 3.01\text{H}_2\text{SiF}_6 \cdot 2250.27\text{HF} \cdot 7844.59\text{H}_2\text{O}$ .

for scolecite, where  $P$  is the equilibrium water-vapor pressure at  $T(\text{K})$ .

The natrolite experiments were not extended beyond 673 K because the bottom of the capsule began to bulge at this temperature. In the case of scolecite, experiments above 474 K gave enthalpy results that deviated significantly from a smooth curve. This deviation was attributed to irreversible decomposition of the sample, because results already obtained at lower temperatures could not subsequently be reproduced. The individual enthalpy results for scolecite, therefore, are reported to only 474 K.

The enthalpy increments for natrolite (Table 9) including those from the low-temperature study (Table 5) were fitted as a function of  $T$  over the range 298.15 to 675 K by the method of least squares, and the following equation was obtained:

$$H^\circ(T) - H^\circ(298.15 \text{ K}) = 4897565 T^{-1} - 123206.2 + 301.957 T + 0.188442 T^2 (\text{J/mol}) \quad (3)$$

This fit was constrained to give, at  $T = 298.15 \text{ K}$ ,  $H^\circ(T) - H^\circ(298.15 \text{ K}) = 0$  and  $C_p^\circ(T) = 359.12 \text{ J/(mol} \cdot \text{K)}$ . The root-mean-square deviation for equation (3) is 0.19 per cent.

The enthalpy increments for scolecite (Table 9) were similarly fitted between 298.15 K and 475 K, and the following equation was obtained:

$$H^\circ(T) - H^\circ(298.15 \text{ K}) = -77220.5 + 135.1876 T + 0.415265 T^2 (\text{J/mol}) \quad (4)$$

This fit was constrained as above, with  $C_p^\circ(T) = 382.81 \text{ J/(mol} \cdot \text{K)}$  at  $T = 298.15 \text{ K}$ . The root-mean-square deviation for equation (4) is 0.21 per cent.

#### Derived heat capacities above 298.15 K

The first derivatives of equations (3) and (4) yielded the following expressions for the heat capacities above 298.15 K:

$$C_p^\circ(T)(\text{natrolite}) = -4897565 T^{-2} + 301.957 + 0.37688 T (\text{J/mol} \cdot \text{K}) \quad (5)$$

and

$$C_p^\circ(T)(\text{scolecite}) = 135.1876 + 0.83053 T (\text{J/mol} \cdot \text{K}) \quad (6)$$

#### Thermodynamic functions for natrolite and scolecite

Table 10 gives the thermodynamic functions of natrolite and scolecite at 20 K intervals and also at 298.15 K. Thermodynamic functions at intermediate temperatures can be reliably interpolated. The heat capacities and entropies up to and including 340 K have been taken from the low-temperature study. All the values for  $H^\circ(T) - H^\circ(298.15 \text{ K})$  have been calculated from equations (3) and (4), and the heat capacities above 340 K have been

Table 8. Calculation of  $\Delta H_f^\circ(298.15 \text{ K})^*$ 

1. $2\text{Na}(\text{c}) + 2\text{Al}(\text{c}) + 3\text{Si}(\text{c}) + 6\text{O}_2(\text{g}) + 2\text{H}_2(\text{g}) = \text{natrolite};$ $\Delta H_f^\circ(\text{natrolite}) = 3\Delta H_1 + 2\Delta H_2 + 2\Delta H_3 + \Delta H_5 + \Delta H_8 + 2\Delta H_{11} + 3\Delta H_{13} + 2\Delta H_{14} + 2\Delta H_{15} = -5718.6 \pm 5.0 \text{ kJ/mol}$
2. $\text{Ca}(\text{c}) + 2\text{Al}(\text{c}) + 3\text{Si}(\text{c}) + \frac{13}{2}\text{O}_2(\text{g}) + 3\text{H}_2(\text{g}) = \text{scolecite};$ $\Delta H_f^\circ(\text{scolecite}) = 3\Delta H_1 + 2\Delta H_2 + \Delta H_4 + \Delta H_6 + \Delta H_9 + 2\Delta H_{11} + \Delta H_{12} + 3\Delta H_{13} + 2\Delta H_{14} + \Delta H_{16} = -6049.0 \pm 5.0 \text{ kJ/mol}$
3. $0.676\text{Na}(\text{c}) + 0.657\text{Ca}(\text{c}) + 1.99\text{Al}(\text{c}) + 3.01\text{Si}(\text{c}) + 6.323502(\text{g}) + 2.647\text{H}_2(\text{g}) = \text{mesolite};$ $\Delta H_f^\circ(\text{mesolite}) = 3.01\Delta H_1 + 1.99\Delta H_2 + 0.676\Delta H_3 + 0.657\Delta H_4 + \Delta H_7 + \Delta H_{10} + 1.99\Delta H_{11} + 0.657\Delta H_{12} + 3.01\Delta H_{13} + 1.99\Delta H_{14} + 0.676\Delta H_{15} + 0.657\Delta H_{16} = -5947.1 \pm 5.4 \text{ kJ/mol}$

\* Individual  $\Delta H$  values are taken from Table 7.

calculated from equations (5) and (6). For both compounds,  $\Delta H_f^\circ$  at 298.15 K has been reported in the present paper; for the calculation of  $\Delta H_f^\circ(T)$  and  $\Delta G_f^\circ(T)$ , we used the heat capacities and standard entropies of Na, Ca, Al, Si, O<sub>2</sub>, and H<sub>2</sub> from the critical compilation of Robie *et al.* (1978).

At 298.15 K the standard entropy of formation,  $\Delta S_f^\circ$ , and Gibbs energy of formation,  $\Delta G_f^\circ$ , are  $-1348.2 \pm 0.8$  J/(mol · K) and  $-5316.6 \pm 5.0$  kJ/mol, respectively, for natrolite and  $-1512.9 \pm 0.9$  J/(mol · K) and  $-5597.9 \pm 5.0$  kJ/mol, respectively, for scolecite.

## Discussion

### Disorder in natrolite

Crystal structure refinements (Meier, 1960; Peacor, 1973) show that many natrolite samples have a fully ordered Si–Al distribution. Alberti and Vezzalini (1981) showed that partial disorder is reflected in the  $b - a$  difference. Fully ordered natrolite has  $b - a = 0.35 \text{ \AA}$ , and as the distribution approaches complete randomness in tetranatrolite,  $b - a$  approaches zero.

The effect on thermodynamic properties of disorder and non-stoichiometric Si–Al content can be partially deduced from the configurational entropy of the framework. In fully ordered natrolite one Si atom occupies the tetrahedral site, labeled Si(1) (Alberti and Vezzalini, 1981), and two atoms occupy the equivalent sites, labeled Si(2). The two Al atoms occupy the third tetrahedral site, labeled Al. The Al mixes evenly into the Si(1) and Si(2) sites as shown by the refinement of the partially disordered natrolite from Gulacs Hill, Topolca, Hungary (Alberti and Vezzalini, 1981). The configurational entropy,  $S_{\text{conf}}$ , is calculated from the mixing of Al into Si(1) and Si(2) and Si into Al:

$$S_{\text{conf}} = -3R(X_{\text{Al}} \ln X_{\text{Al}} + X_{\text{Si}} \ln X_{\text{Si}})_{\text{Si sites}} - 2R(X_{\text{Al}} \ln X_{\text{Al}} + X_{\text{Si}} \ln X_{\text{Si}})_{\text{Al sites}} \quad (7)$$

From equation (7) it can be calculated that fully disordered tetranatrolite with  $X_{\text{Al}} = 0.4$  in both Si and Al sites will have  $S_{\text{conf}} = 50.83$  J/(mol · K). Similarly, the 30 percent disordered natrolite from Gulacs Hills, Hungary, has  $X_{\text{Al}} = 0.11$  in Si sites and  $X_{\text{Al}} = 0.84$  in Al sites and, thus,  $S_{\text{conf}} = 15.96$  J/(mol · K). The cell dimensions of the Larne natrolite give a  $b - a$  value of  $0.31 \text{ \AA}$ , which indicates  $X_{\text{Al}} = 0.05$  in Si sites (see Alberti and Vezzalini, 1981, Fig. 4) and  $X_{\text{Al}} = 0.93$  in Al sites. The  $S_{\text{conf}}$  for this natrolite is  $9.17 \pm 3$  J/(mol · K). This partial randomness is expected to be present even at low temperatures, and at  $T \rightarrow 0$ ,  $S^\circ(T) - S^\circ(0)$  is not zero. Thus, approximately 9.2 J/(mol · K) should be added to our experimental values of  $S^\circ(T) - S^\circ(0)$  for natrolite (Table 4) to obtain the correct quantities for use in thermodynamic calculations.

The configurational entropy in the other zeolites is also

Table 9. Drop calorimetric results for natrolite and scolecite\*

Expt. No.	T K	$\Delta\theta_c$ K	$\epsilon(\text{calor})(\Delta\theta_c)$ J	$\Delta H(\text{capsule})$ J	$H^\circ(T) - H^\circ(298.15 \text{ K})^{**}$ J/mol
<u>Natrolite</u>					
1	373.81	0.17863	782.35	206.12	29054
3	374.05	0.17873	782.79	206.78	29024
2	423.25	0.30549	1337.93	343.37	50114
5	423.45	0.30519	1336.61	343.93	50012
4	473.80	0.43986	1926.37	485.17	72611
7	474.52	0.44141	1933.16	487.20	72854
16	485.97	0.47327	2072.68	519.49	78257
6	523.45	0.57732	2528.31	625.60	95876
9	523.51	0.57703	2527.04	625.77	95795
15	523.84	0.57858	2533.83	626.71	96089
8	573.53	0.72097	3157.33	768.21	120375
11	573.55	0.72076	3156.41	768.27	120318
14	623.07	0.86958	3808.03	910.11	145998
10	623.51	0.86967	3808.42	911.38	145957
13	673.15	1.02378	4483.18	1053.30	172764
<u>Scolecite</u>					
1	373.64	0.18225	798.20	205.41	31134
3	373.84	0.18314	802.10	205.96	31307
2	422.67	0.31343	1372.70	341.35	54167
5	422.91	0.31392	1374.84	342.02	54246
4	474.14	0.45962	2012.90	485.56	80193

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

\*\*Includes corrections for the enthalpy of the air in the capsule, for the difference between the final temperature of the experiment and 298.15 K, and for the water vapor in the capsule generated by the dehydration of the zeolites.

of concern. Order–disorder has not been studied in either mesolite or scolecite. However, because the Si(Al)–O chains are the same as those of natrolite, it is reasonable to expect at least similar amounts of disorder. Therefore, in exchange reactions such as those considered below, the configurational entropy contributions to the Gibbs free energies should tend to cancel. It should be noted that the thermodynamic quantities given in Table 10 and used throughout this paper have not been corrected to allow for the configurational entropy.

### Estimation of $C_P^\circ$ and $S^\circ$ for mesolite

Apart from the determination of  $\Delta H_f^\circ$ , no other experimental measurements on mesolite were performed in the present study because the composition of mesolite is intermediate between that of natrolite and scolecite and because of that its heat capacity and standard entropy



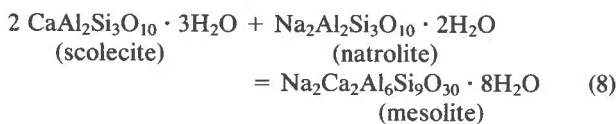
Table 10. Thermodynamic functions of natrolite and scolecite\*

$\frac{T}{K}$	$\frac{C_p^0(T)}{J/(mol \cdot K)}$	$\frac{[H^0(T)-H^0(298)]/T}{J/(mol \cdot K)}$	$\frac{-[G^0(T)-H^0(298 K)]/T}{J/(mol \cdot K)}$	$\frac{S^0(T)-S^0(0)}{J/(mol \cdot K)}$	$\frac{H^0(T)-H^0(298 K)}{(J/mol)}$	$\frac{\Delta H_f^0(T)}{(kJ/mol)}$	$\frac{\Delta G_f^0(T)}{(kJ/mol)}$
<u>Natrolite</u>							
298.15	359.23	0	359.73	359.73	0	-5718.6	-5316.6
300	360.61	2.22	359.74	361.96	666	-5718.6	-5314.1
320	374.73	25.07	360.62	385.69	8021	-5719.4	-5287.3
340	387.73	46.02	362.78	408.80	15648	-5719.9	-5260.3
360	399.85	65.35	365.96	431.31	23525	-5720.2	-5233.2
380	411.26	83.25	369.99	453.24	31637	-5725.6	-5205.9
400	422.10	99.93	374.68	474.61	39971	-5725.6	-5178.5
420	432.48	115.52	379.94	495.46	48518	-5725.5	-5151.2
440	442.49	130.15	385.66	515.81	57268	-5725.2	-5123.8
460	452.18	143.95	391.74	535.69	66215	-5724.8	-5096.5
480	461.60	156.99	398.15	555.14	75353	-5724.2	-5069.2
500	470.81	169.36	404.81	574.17	84678	-5723.4	-5041.9
520	479.82	181.12	411.69	592.81	94184	-5722.6	-5014.7
540	488.68	192.35	418.73	611.08	103870	-5721.5	-4987.4
560	497.40	203.09	425.92	629.01	113731	-5720.4	-4960.3
580	505.99	213.39	433.23	646.62	123765	-5719.1	-4933.2
600	514.48	223.28	440.64	663.92	133970	-5717.7	-4906.1
620	522.88	232.81	448.11	680.92	144343	-5716.1	-4879.0
640	531.21	242.01	455.65	697.66	154884	-5714.4	-4852.1
660	539.46	250.90	463.23	714.13	165591	-5712.6	-4825.2
680	(547.65)	(259.50)	(470.85)	(730.35)	(176462)	(-5710.7)	(-4798.7)
<u>Scolecite</u>							
298.15	382.81	0	367.42	367.42	0	-6049.0	-5597.9
300	384.47	2.37	367.43	369.80	710	-6049.1	-5595.2
320	401.81	26.76	368.41	395.17	8563	-6049.5	-5564.9
340	419.34	49.26	370.79	420.05	16748	-6049.6	-5534.6
360	434.18	70.18	374.09	444.27	25265	-6049.5	-5504.3
380	450.79	89.78	378.42	468.19	34115	-6049.1	-5474.0
400	467.40	108.24	383.49	491.74	43297	-6048.4	-5443.7
420	484.01	125.74	389.20	514.94	52811	-6047.5	-5413.5
440	500.62	142.40	395.44	537.84	62657	-6046.3	-5383.4
460	517.23	158.34	402.12	560.46	72836	-6044.8	-5353.3
470	525.54	166.06	405.61	571.68	78050	-6044.0	-5338.3

\*Values of the entropy have not been corrected for contributions due to disorder (see discussion in text).  
Values at 680 K have been estimated.

can, we believe, be reliably estimated. The estimation procedures used were as follows.

The as-analyzed formula for mesolite is  $\text{Na}_{0.676}\text{Ca}_{0.657}\text{Al}_{1.99}\text{Si}_{3.01}\text{O}_{10} \cdot 2.647\text{H}_2\text{O}$ . Division by 0.33 of the stoichiometric coefficients gives the approximate formula  $\text{Na}_2\text{Ca}_2\text{Al}_6\text{Si}_9\text{O}_{30} \cdot 8\text{H}_2\text{O}$ . For the following equilibrium at 298.15 K:



it is assumed that  $\Delta C_p^\circ = 0$ . This assumption has proven to be valid for a number of silicate systems (Helgeson *et al.*, 1978). We take the  $C_p^\circ(298 \text{ K})$  values for scolecite and natrolite given in Table 10 and obtain  $C_p^\circ(\text{Na}_2\text{Ca}_2\text{Al}_6\text{Si}_9\text{O}_{30} \cdot 8\text{H}_2\text{O}, c, 298.15 \text{ K}) = 1125 \text{ J}/(\text{mol} \cdot \text{K})$ . For the as-analyzed composition,  $C_p^\circ(\text{Na}_{0.676}\text{Ca}_{0.657}\text{Al}_{1.99}\text{Si}_{3.01}\text{O}_{10} \cdot 2.647\text{H}_2\text{O}) = 371 \pm 2 \text{ J}/(\text{mol} \cdot \text{K})$ .

The standard entropy,  $S^\circ$ , of mesolite at 298.15 K has been estimated—again based on equilibrium (8)—by means of the equation (see Helgeson *et al.*, 1978):

$$S^\circ(\text{mesolite}) = A[B + V^\circ(\text{mesolite})]/2B \quad (9)$$

where  $A = 2S^\circ(\text{scolecite}) + S^\circ(\text{natrolite})$  and  $B = 2V^\circ(\text{scolecite}) + V^\circ(\text{natrolite})$

In the above equations,  $V^\circ$  denotes molar volume at 298.15 K with  $P = 1$  bar. The molar volumes ( $\text{cm}^3/\text{mol}$ ) are calculated from the molecular masses and the densities (Breck, 1974) and the requisite entropies are taken from Table 10. Thus, the following estimates have been made:

$$\begin{aligned} S^\circ(\text{Na}_2\text{Ca}_2\text{Al}_6\text{Si}_9\text{O}_{30} \cdot 8\text{H}_2\text{O}, c, 298.15 \text{ K}) \\ = 1099 \text{ J}/(\text{mol} \cdot \text{K}) \end{aligned}$$

and, for the as-analyzed composition,

$$\begin{aligned} S^\circ(\text{Na}_{0.676}\text{Ca}_{0.657}\text{Al}_{1.99}\text{Si}_{3.01}\text{O}_{10} \cdot 2.647\text{H}_2\text{O}) \\ = 363 \pm 2 \text{ J}/(\text{mol} \cdot \text{K}). \end{aligned}$$

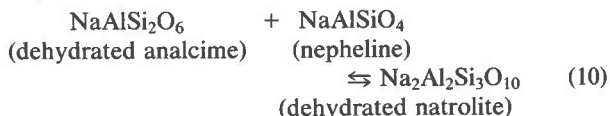
Thus for mesolite at 298.15 K we derive  $\Delta S_f^\circ = -1455.2 \pm 2.1 \text{ J}/(\text{mol} \cdot \text{K})$  and  $\Delta G_f^\circ = -5513.2 \pm 5.4 \text{ kJ}/\text{mol}$ .

#### Contribution of the zeolitic water to the entropies of natrolite and scolecite

Numerous experiments using such techniques as differential scanning calorimetry (van Reeuwijk, 1974) and thermogravimetric analysis (Peng, 1955) have shown that the dehydration of natrolite takes place in one sharp well-defined step, which is followed by an alteration of the zeolite framework. Because of this structural change, measurements on "dehydrated natrolite" would not be very meaningful. It is, however, interesting to estimate the entropy of hypothetical dehydrated natrolite and to compare the entropy difference for this system with values for other (zeolite + anhydrous zeolite) pairs.

The entropy of dehydrated natrolite could be estimated

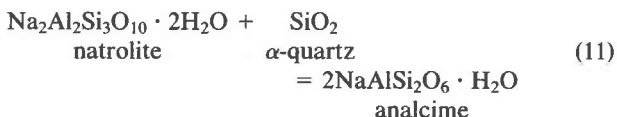
by means of a formula similar to that given in equation (9); however, the molar volume cannot be calculated. Thus, it is assumed that  $\Delta S^\circ = 0$  for the equilibrium:



For this reaction,  $S^\circ(\text{NaAlSi}_2\text{O}_6)$  is taken to be 171.7 J/(mol · K) (Johnson *et al.*, 1982) and  $S^\circ(\text{NaAlSiO}_4)$ , 124.3 J/(mol · K) (Helgeson *et al.*, 1978); thus  $S^\circ(\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}) = 296 \text{ J}/(\text{mol} \cdot \text{K})$ . It follows that  $S^\circ(\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}) - S^\circ(\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}) = 64 \text{ J}/(\text{mol} \cdot \text{K})$ . Each zeolitic water is, therefore, estimated to contribute an average of 32 J/(mol · K) to the entropy of natrolite.

Substitution of the  $\text{Ca}^{2+}$  ion for the two  $\text{Na}^+$  ions in dehydrated natrolite yields dehydrated scolecite. This substitution, by comparison with other such processes for which reliable entropy data are available, is expected to be accompanied by an entropy reduction of approximately 24 J/(mol · K); consequently,  $S^\circ(\text{CaAl}_2\text{Si}_3\text{O}_{10}) = 272 \text{ J}/(\text{mol} \cdot \text{K})$ , and  $S^\circ(\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}) - S^\circ(\text{CaAl}_2\text{Si}_3\text{O}_{10}) = 95 \text{ J}/(\text{mol} \cdot \text{K})$ . On average, therefore, each zeolitic water in scolecite contributes 32 J/(mol · K) to the entropy, exactly (but coincidentally) the same as the value estimated for the natrolite system. These estimates suggest that at 298 K the structure of the zeolitic water in both natrolite and scolecite is very much closer to that of ice, for which  $S^\circ = 38 \text{ J}/(\text{mol} \cdot \text{K})$ , than that of liquid water, for which  $S^\circ = 70 \text{ J}/(\text{mol} \cdot \text{K})$ . For the analcime system, on the other hand,  $S^\circ(\text{analcime}) - S^\circ(\text{dehydrated analcime}) = 55 \text{ J}/(\text{mol} \cdot \text{K})$  (Johnson *et al.*, 1982). Thus, the entropy of the zeolitic water is significantly greater in analcime than in natrolite and scolecite and is intermediate between that of ice and liquid water.

It is interesting to compare the experimental result for  $S^\circ(\text{natrolite})$  at 298.15 K with a recent estimate (Helgeson *et al.*, 1978) which was based on the equilibrium;



Using a formula similar to equation (9) and our result for  $S^\circ(\text{analcime})$  (Johnson *et al.*, 1982), the Helgeson *et al.* (1978) estimate for  $S^\circ(\text{natrolite})$  is recalculated to be 409 J/(mol · K). The published estimate is 425 J/(mol · K). Both values differ significantly from the experimental result, 359.7 J/(mol · K). Of course, implicit in the use of an equilibrium such as (11) to estimate entropies is the assumption that contributions from the zeolitic water on both sides of the equation are the same. Here such an assumption is not valid. Indeed, if a correction of  $2(55 - 32) = 46 \text{ J}/(\text{mol} \cdot \text{K})$  is made to allow for the difference in the entropies of the zeolitic water in analcime and natrolite, then the calculated  $S^\circ(\text{natrolite})$  becomes  $409 - 46 =$

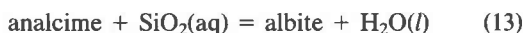
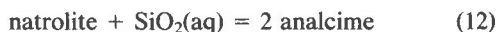
363 J/(mol · K), in reasonable agreement with the experimental result.

### Standard enthalpies of formation

A comprehensive literature search has failed to reveal any previous experimental determinations of the enthalpies of formation of the zeolites studied in the present work. Nor, as far as we are aware, have any equilibrium or solubility studies been performed from which  $\Delta H_f^\circ$  values could be retrieved.

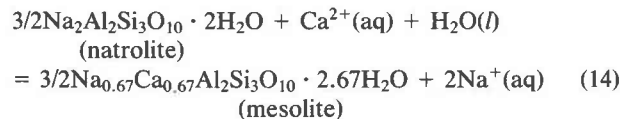
### Some geochemical interpretations

Natrolite occurs in association with analcime, but never with albite. Therefore, the two reactions

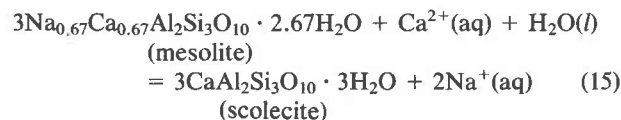


delimit the stability fields of each Na-silicate phase as a function of the activity of aqueous silica. Calculations using the available  $\Delta G_f^\circ$  data for these three phases (natrolite, this work; analcime, Johnson *et al.*, 1982; and albite, Robie *et al.*, 1978) do not produce a phase diagram consistent with the observations mentioned above. The reason lies with the Si–Al composition of the analcime. The Si/Al ratio in analcime in equilibrium with natrolite is very close to 2.0, while analcime in equilibrium with albite has a Si/Al ratio that approaches 3.0. A formalization of these relationships and the calculation of a phase diagram consistent with observations of natural occurrences are currently in progress.

Because each of the three zeolites studied here has such narrow compositional ranges with respect to the cations, it is of interest to define a phase diagram in terms of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  activities. The exchange reactions



and



have equilibrium constants expressed by

$$K = \frac{(a_{\text{Na}^+})^2}{(a_{\text{Ca}^{2+}})(a_{\text{H}_2\text{O}})} \quad (16)$$

By combining  $\Delta G_f^\circ(T)$  at  $T = 298.15$  K for the zeolites with the same quantities for water and the cations (Robie *et al.*, 1978) and assuming  $a_{\text{H}_2\text{O}} \approx 1.0$ , we obtain the following expressions for equilibria (14) and (15), respectively:

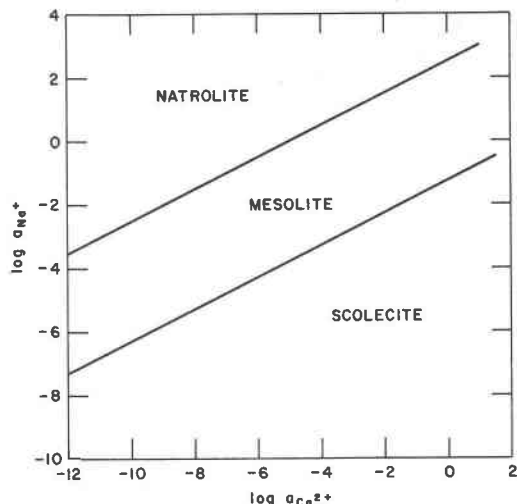


Fig. 1. A plot of  $\log a_{\text{Na}^+}$  against  $\log a_{\text{Ca}^{2+}}$  at  $T = 298.15$  K and  $P = 1$  bar which delineates the stability fields of natrolite, mesolite, and scolecite.

$$2 \log a_{\text{Na}^+} - \log a_{\text{Ca}^{2+}} = 5.07 \quad (17)$$

$$2 \log a_{\text{Na}^+} - \log a_{\text{Ca}^{2+}} = -2.55 \quad (18)$$

A plot of these lines (Fig. 1) emphasizes the observation that natrolite is stable only in solutions with very low  $\text{Ca}^{2+}$  activities. It is somewhat surprising that the width of the mesolite field is nearly 4 orders of magnitude in terms of  $\text{Na}^+$  activity. The above calculations, of course, apply to a mesolite of the given composition. There is a likelihood of ion exchange which would shift the phase boundaries. However, the composition range for mesolite is small (Alberti *et al.*, 1982) and thus this effect would be minimized. These calculations give quantitative results that are consistent with qualitative field observations. It should be reemphasized that by using the tabulated values for  $\Delta G_f^\circ(T)$  of the zeolites, we are making the implicit assumption that contributions to this function due to disorder tend to cancel out in each of the equilibria. Until detailed information on disorder in scolecite and mesolite becomes available, we are unable to do otherwise.

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