

Thermodynamic properties of zeolites: low-temperature heat capacities and thermodynamic functions for phillipsite and clinoptilolite. Estimates of the thermochemical properties of zeolitic water at low temperature

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Abstract

The heat capacities of phillipsite and clinoptilolite have been measured between 15 and 305 K. Smoothed values of the thermodynamic properties, heat capacity, entropy, enthalpy function and Gibbs energy function have been calculated from the measured heat capacities for the phillipsite composition $(\text{Na}_{1.08}\text{K}_{0.80})\text{Al}_{1.88}\text{Si}_{6.12}\text{O}_{16} \cdot 6\text{H}_2\text{O}$ and for the clinoptilolite composition $(\text{Na}_{0.56}\text{K}_{0.98}\text{Ca}_{1.50}\text{Mg}_{1.23})(\text{Al}_{6.7}\text{Fe}_{0.3})\text{Si}_{29}\text{O}_{72} \cdot 22\text{H}_2\text{O}$. At 298.15 K, $S_{298}^\circ - S_0^\circ$ is 771.9 ± 2.4 J/(mol · K) for phillipsite and 2872.3 ± 9.0 J/(mol · K) for clinoptilolite.

The heat capacities of the average H_2O in the natural zeolite samples are somewhat greater than the heat capacity of ice at 100 K and less than the heat capacity of pure water at 300 K. The H_2O component in phillipsite undergoes a glass transition at a transition temperature of about 175 K. The heat capacity of the H_2O component in clinoptilolite increases in a nearly linear fashion between 100 and 300 K.

Introduction

Zeolites are tectosilicates exhibiting an open three-dimensional structure containing cations needed to balance the electrostatic charge of the framework of silica and alumina tetrahedra and containing water. The open structure has led to the use of zeolites in many industrial processes (e.g., Barrer, 1978, 1981) that are well documented in the literature. The properties of zeolites also have been studied because of the deleterious effect the growth of zeolites has upon the porosity of rock through which fluids are extracted, in particular those rocks that have undergone hydrofracturing to increase the porosity (e.g., Hawkins, 1981). Recently, Bischoff et al. (1981) have proposed that the growth of the zeolite phillipsite together with manganese oxides represents a coupled chemical reaction that results in the growth of manganese nodules in the deep North Pacific.

Glaccum and Boström (1976) assumed that the alteration of basalt to phillipsite in the deep sea meant that phillipsite was thermodynamically stable. These authors estimated values for the Gibbs free energy of formation of the Na and K end-member phillipsite compositions based upon an assumed thermodynamic equilibrium reaction.

The evidence presented in most recent studies, however, confirms the metastable nature of most zeolites (e.g., Hawkins et al., 1978; Boles and Wise, 1978; Holler and Wirsching, 1978; Kastner and Stonecipher, 1978; Dibble

and Tiller, 1981; and Barrer, 1981). In laboratory (Holler and Wirsching, 1978) and field (e.g., Sheppard and Gude, 1968, 1973; Hawkins et al., 1978; Kastner and Stonecipher, 1978) studies of the alteration of volcanic glass, zeolites are formed as transitory phases that disappear with increasing alteration, following the Gay-Lussac-Ostward law of successive reactions (e.g., Barrer, 1981; Dibble and Tiller, 1981; and Hemingway, 1982). Because many zeolites are metastable, they are formed through irreversible reactions that do not attain thermodynamic equilibrium (e.g., Dibble and Tiller, 1981, and Hemingway, 1982). Therefore, typical equilibrium experimental procedures cannot completely define the thermodynamic properties of zeolites.

Zeolites can be expected to show disorder in the cations, water, and the aluminum and silicon tetrahedra in the framework. Therefore, traditional calorimetric procedures also will not be able to completely define the thermodynamic properties of zeolites.

The best estimates of the thermodynamic properties of zeolites will be obtained from a simultaneous analysis of synthesis and stability data, calorimetric data, and various metastable equilibrium measurements, each of which will place limits upon one or more of the thermodynamic properties of a given zeolite phase. Consequently, we have measured the heat capacity of natural samples of phillipsite and clinoptilolite between 15 and 305 K as a

preliminary step in our studies of the thermodynamic properties of zeolites.

Materials

The phillipsite and clinoptilolite were provided as cleaned and characterized samples of natural zeolites by A. J. Gude III. Phillipsite (T-49) was obtained from altered tuffs of Lake Tecopa, Inyo County, California. A description of the location and the chemical and physical properties of the phillipsite sample are given by Sheppard and Gude (1968). Clinoptilolite (W7-6B) was obtained from the altered tuffs of the Big Sandy Formation, Mohave County, Arizona. A description of the location and the chemical and physical properties of the clinoptilolite sample is given by Sheppard and Gude (1973).

Apparatus

The cryostat used for the low-temperature heat-capacity measurements has been described by Robie and Hemingway (1972). The calorimeter and data acquisition system used for our measurements have been described by Robie et al. (1976).

The differential scanning calorimeter was similar to that described by O'Neill (1966) and Fyans (1971). The procedures followed in data acquisition and analysis have been described by Krupka et al. (1979).

Table 1. Experimental specific heats of natural phillipsite from Lake Tecopa, Inyo County, California

Temp. K	Specific heat J/(g·K)	Temp. K	Specific heat J/(g·K)	Temp. K	Specific heat J/(g·K)
Series 1		Series 5		Series 9	
53.42	0.2144	160.09	0.7093	169.46	0.7600
57.36	0.2352	165.67	0.7392	174.86	0.7883
63.57	0.2668	171.19	0.7684		
71.67	0.3070	176.65	0.7973	Series 10	
79.83	0.3469	182.14	0.8244	268.55	1.1366
				277.04	1.1592
Series 2		Series 6		285.41	1.1801
80.29	0.3493	180.18	0.8112	293.67	1.2011
85.19	0.3731	185.82	0.8419	301.82	1.2191
89.06	0.3921	191.52	0.8663	Series 11	
93.30	0.4122			300.58	1.2141
97.90	0.4336	Series 7		304.18	1.2204
103.14	0.4576	197.20	0.8897	307.80	1.2280
109.11	0.4843	202.85	0.9120	Series 12	
Series 3		208.56	0.9343	15.36	0.01771
115.29	0.5118	214.32	0.9567	16.76	0.02240
121.21	0.5375	Series 8		18.65	0.02937
Series 4		216.39	0.9639	20.47	0.03681
126.90	0.5619	222.26	0.9867	22.52	0.04602
132.40	0.5852	228.59	1.0089	25.04	0.05809
137.72	0.6076	235.58	1.0329	27.46	0.07047
126.43	0.5594	243.22	1.0587	29.91	0.08344
132.02	0.5832	251.45	1.0852	32.74	0.09906
137.52	0.6067	259.62	1.1102	35.98	0.1174
143.13	0.6309	267.65	1.1343	39.86	0.1391
148.75	0.6565	275.68	1.1557	44.33	0.1639
154.40	0.6811	283.60	1.1756	49.29	0.1910
				54.55	0.2198

Table 2. Experimental specific heats of natural clinoptilolite from the Big Sandy Formation, Mohave County, Arizona

Temp. K	Specific heat J/(g·K)	Temp. K	Specific heat J/(g·K)	Temp. K	Specific heat J/(g·K)
Series 1		Series 5		Series 7	
14.59	0.01295	69.96	0.2590	200.19	0.7973
16.03	0.01678	75.10	0.2829	206.22	0.8187
17.63	0.02142	80.55	0.3084	212.23	0.8387
19.41	0.02725	86.32	0.3349	218.21	0.8591
21.49	0.03462	92.28	0.3621	224.19	0.8787
23.95	0.04417	98.26	0.3887	230.17	0.8977
26.74	0.05581	104.26	0.4151	236.09	0.9178
29.70	0.06881	110.26	0.4411	242.04	0.9382
32.72	0.08278	116.24	0.4671	248.00	0.9554
35.92	0.09797	122.19	0.4930	253.95	0.9730
		128.05	0.5183	259.91	0.9905
Series 2		Series 6		265.94	1.0078
40.85	0.1214			Series 8	
44.86	0.1404	133.73	0.5446	271.05	1.0217
49.47	0.1623	139.48	0.5674	277.18	1.0400
54.21	0.1854	145.04	0.5900	283.21	1.0563
		150.45	0.6118	289.30	1.0729
Series 3		155.85	0.6327	295.49	1.0890
300.10	1.1019	161.25	0.6533		
304.25	1.1137	166.67	0.6744		
308.68	1.1232	172.12	0.6949		
		177.62	0.7161		
		183.20	0.7365		
Series 4		188.89	0.7573		
54.88	0.1889	194.67	0.7779		
60.66	0.2161				
66.41	0.2425				

Experimental results

Our experimental data for the low-temperature specific heats, J/(g · K), of phillipsite and clinoptilolite are given in Tables 1 and 2 in their chronological order of measurement. The data listed in Tables 1 and 2 have been corrected for curvature (e.g., Robie and Hemingway, 1972), but no corrections have been made for deviations from end-member stoichiometry.

Each sample was dry sieved to remove most of the material that would pass a 150 mesh sieve. The sample weights, corrected for buoyancy, were 32.8400 and 20.0043 grams, respectively, for phillipsite and clinoptilolite.

The phillipsite sample represented 45 percent of the measured heat capacity (i.e., the heat capacity of the calorimeter and the sample) at 100 K. The contribution of the phillipsite increased to 72% at 15 K and to 58% at 300 K. The clinoptilolite sample represented 31% of the measured heat capacity at 100 K and increased to 57% at 15K and to 43% percent at 300 K.

The measured heat-capacity data for phillipsite (corrected for curvature and for the contribution of the empty calorimeter and the He exchange gas) were corrected to the formula $(\text{Na}_{1.08}\text{K}_{0.80})\text{Al}_{1.88}\text{Si}_{6.12}\text{O}_{16} \cdot 6\text{H}_2\text{O}$ by assuming that the sample contained 642.801 g of phillipsite (of the given formula), 3.354 g of hematite, 0.645 g of periclase, 2.080 g of NaOH, 0.799 of rutile, 0.085 g of P_2O_5 , 0.043 g of manganosite, and a deficiency of 5.963 g

of ice. The measured capacities of clinoptilolite were corrected to the formula $(\text{Na}_{0.56}\text{K}_{0.98}\text{Ca}_{1.50}\text{Mg}_{1.23})(\text{Al}_{6.7}\text{Fe}_{0.3})\text{Si}_{29}\text{O}_{72} \cdot 22\text{H}_2\text{O}$ by assuming that the sample contained 2701.524 g of clinoptilolite (of the given formula), 0.816 g of corundum, 15.171 g of hematite, 5.683 g of periclase, 1.907 g of lime, 3.803 g of BaO, 11.087 g of SrO, 0.080 g of NaOH, 0.337 g of KOH, 3.279 g of ice, 7.670 g of rutile, 0.852 g of P_2O_5 , and 2.554 g of manganosite. The corrections were made assuming simple additivity of the components. The difference between the uncorrected and the corrected specific heats of phillipsite were less than 1% above 130 K, less than 1.7% above 50 K, and less than 3.5% above 16 K and were less than 1.2% for all temperatures for the clinoptilolite sample. The impurity corrections should not introduce errors greater than 0.1% in the calculated entropy at 298.15 K (e.g., Robie et al., 1976).

Thermodynamic properties of phillipsite and clinoptilolite

Our measured heat-capacity data (corrected for chemical impurities) were extrapolated to 0 Kelvin using a plot of C_p/T versus T^2 . The data were smoothed analytically following the method of Westrum et al. (1968). The average deviation from the fitted curve above 20 K was less than 0.09% for phillipsite and 0.08% for clinoptilolite.

Smoothed values of the thermodynamic functions C_p , $S_T^\circ - S_0^\circ$, $(H_T^\circ - H_0^\circ)/T$, and $(G_T^\circ - H_0^\circ)/T$ are listed at integral temperatures in Tables 3 and 4 for phillipsite as $(\text{Na}_{1.08}\text{K}_{0.80})\text{Al}_{1.88}\text{Si}_{6.12}\text{O}_{16} \cdot 6\text{H}_2\text{O}$ and clinoptilolite as $(\text{Na}_{0.56}\text{K}_{0.98}\text{Ca}_{1.50}\text{Mg}_{1.23})(\text{Al}_{6.7}\text{Fe}_{0.3})\text{Si}_{29}\text{O}_{72} \cdot 22\text{H}_2\text{O}$, respectively. The tabulated values of the Gibbs energy function for the two zeolites do not include the contribution arising from the zero-point entropies. The contribution to the entropy, $S_{298}^\circ - S_0^\circ$, arising from the extrapolation of our data below 15 K was less than 0.5% for each zeolite.

Estimates of the configurational entropy of these natural zeolites have not been made because we lack specific site occupancy data for these samples. However, estimates of the configurational entropy for phillipsite may be made using the information provided by Rinaldi et al. (1974) for the crystal structure of a natural phillipsite from Casal Brunori, Rome, Italy and estimates of the configurational entropy of clinoptilolite may be made using the information provided by Barrer (1978, Chapter 2).

Estimates of the heat capacity of the H_2O component in phillipsite and clinoptilolite

The purpose of this section of the study is to review what is known about the manner in which H_2O affects the thermodynamic properties of zeolites and to discuss the limitations of our knowledge and the ramifications of assumptions made regarding thermodynamic properties of zeolites. Zeolites are commonly metastable phases. The literature of the synthesis of zeolites contains numerous examples of the precipitation of different zeolite

Table 3. Molar thermodynamic properties of phillipsite, $(\text{Na}_{1.08}\text{K}_{0.80})\text{Al}_{1.88}\text{Si}_{6.12}\text{O}_{16} \cdot 6\text{H}_2\text{O}$

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_p°	$(S_T^\circ - S_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
KELVIN		J/(mol·K)		
5	.445	.142	.105	.037
10	3.48	1.15	.860	.290
15	11.11	3.82	2.85	.970
20	23.08	8.57	6.33	2.240
25	38.20	15.29	11.15	4.140
30	55.15	23.74	17.06	6.685
35	73.14	33.58	23.77	9.810
40	91.61	44.56	31.10	13.46
45	110.0	56.41	38.84	17.56
50	127.8	68.93	46.85	22.07
60	162.0	95.23	63.23	32.06
70	194.9	122.7	79.70	43.04
80	226.7	150.9	96.10	54.75
90	257.7	179.4	112.3	67.01
100	288.0	208.1	128.4	79.68
110	317.5	236.9	144.3	92.67
120	345.9	265.8	159.9	105.9
130	373.2	294.5	175.2	119.3
140	400.4	323.2	190.4	132.8
150	429.2	351.8	205.3	146.5
160	460.8	380.5	220.3	160.2
170	494.3	409.4	235.4	174.0
180	527.3	438.6	250.7	187.9
190	557.6	467.9	266.1	201.9
200	584.6	497.2	281.3	215.9
210	609.7	526.4	296.4	230.0
220	634.1	555.3	311.2	244.1
230	657.9	584.0	325.7	258.3
240	680.4	612.5	340.1	272.4
250	701.2	640.7	354.1	286.6
260	721.4	668.6	367.8	300.8
270	740.6	696.2	381.3	314.9
280	757.4	723.4	394.4	329.0
290	773.4	750.3	407.2	343.1
300	788.4	776.8	419.7	357.1
273.15	746.2	704.8	385.5	319.4
298.15	786.2	771.9	417.4	354.5

phases from seemingly identical experimental conditions (e.g., Barrer, 1978, 1981). Thus the free energy differences between some of these zeolite phases or between solution components (e.g., Hemingway, 1982) that control the precipitating zeolite structure must be quite small. Therefore, the free energy contribution of the H_2O component in zeolites must be completely understood before we will be able to understand the chemistry of the zeolite systems.

Observations

Calorimetric studies of the heat capacity and differential heat of adsorption of water in zeolites (Kiselev et al., 1972; and Dzhigit et al., 1971) have shown a dependence upon the degree of filling of the zeolite cavity. Changes in the frequencies of infrared OH-stretching bands of water as a function of the sorbed water content have been correlated with the observed changes in the differential heat of adsorption of Kiselev et al. (1972). Kiselev et al. have concluded that the high differential heat of adsorption of water and the appearance of bands representing both free and perturbed hydroxyl groups in zeolites

Table 4. Molar thermodynamic properties of clinoptilolite, $(\text{Na}_{0.56}\text{K}_{0.98}\text{Ca}_{1.50}\text{Mg}_{1.23})(\text{Al}_{6.7}\text{Fe}_{0.3})\text{Si}_{29}\text{O}_{72} \cdot 22\text{H}_2\text{O}$

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_p^0	$(S_T^0 - S_0^0)$	$(H_T^0 - H_0^0)/T$	$-(G_T^0 - H_0^0)/T$
KELVIN		J/(mol·K)		
5	1.56	.506	.372	.134
10	12.03	4.006	2.990	1.016
15	38.20	13.21	9.85	3.36
20	79.86	29.58	21.85	7.73
25	132.4	52.88	38.55	14.33
30	191.4	82.14	59.02	23.12
35	254.6	116.4	82.42	33.94
40	320.0	154.6	108.0	46.60
45	385.9	196.1	135.2	60.88
50	451.1	240.2	163.6	76.59
60	579.4	333.8	222.2	111.6
70	706.8	432.7	282.3	150.3
80	833.6	535.3	343.3	192.0
90	957.7	640.7	404.7	236.0
100	1078.6	747.9	466.1	281.3
110	1197.9	856.3	527.2	329.1
120	1317.1	965.6	588.1	377.6
130	1435.3	1075.7	648.7	427.0
140	1550.3	1186.4	709.0	477.3
150	1660.4	1297.1	768.3	528.3
160	1766.2	1407.6	827.9	579.3
170	1869.8	1517.8	886.1	631.7
180	1972.2	1627.6	943.6	684.0
190	2072.8	1737.0	1000.4	736.6
200	2169.7	1845.8	1056.5	789.3
210	2263.0	1953.9	1111.7	842.2
220	2354.1	2061.3	1166.1	895.2
230	2444.9	2167.9	1219.7	948.2
240	2534.1	2273.9	1272.7	1001.2
250	2618.8	2379.1	1324.8	1054.2
260	2698.0	2483.3	1376.1	1107.2
270	2775.4	2586.6	1426.5	1160.1
280	2853.4	2688.9	1476.1	1212.9
290	2927.6	2790.4	1524.9	1265.5
300	3000.8	2890.8	1572.8	1318.0
273.15	2800.0	2613.9	1442.2	1176.7
298.15	2986.5	2872.3	1564.0	1308.3

having low water-filling factors indicated the formation of a hydrogen bond between the sorbed water and a negatively charged oxygen in the zeolite framework. At these low filling factors, the change in the position of the high-frequency OH-stretching band and the change in the heat of absorption of water with changes in the cation indicate either a direct or indirect (e.g., change in free volume of the cavity) interaction between the sorbed water and the cation. Bertsch and Habgood (1963) have suggested that the initial water molecule entering a zeolite cavity is bound simultaneously by an ion-dipole interaction with the exchangeable cation and through a hydrogen bond to an oxygen in the zeolite framework. Kiselev et al. concluded that additional water entering the cavities would continue to bond to lattice sites until the internal cavity sites were filled. Additional water entering the cavities would then begin to form weak hydrogen bonds with the other water molecules. As the water content of the cavity increases, the associated sorbed molecules are rearranged and begin to exhibit the properties of liquid water. Cruz et al. (1978) have shown a similar tendency for the sorbed water in the endellite (hydrous halloysite) interlay-

er to form strong hydrogen bonds between the water molecules and weak hydrogen bonds to the structural OH of the clay lattice.

Direct calorimetric studies (e.g., Basler and Lechert, 1972, and Vucelic et al., 1976) of the heat capacity and entropy, and of the enthalpy of desorption of sorbate molecules in zeolites have been obtained by assuming that the difference observed between the properties determined for the zeolite free of sorbate and those of the zeolite and the sorbate can be attributed to the sorbate alone. Barrer and Bratt (1959) note that this procedure is an oversimplification as the intercalation of a sorbate molecule in a zeolite lattice should decrease the chemical potential of the host lattice (and therefore change the partial molal entropy), which results in an increase in the stability of the structure over the same structure without the sorbed molecule. In addition, complete removal of water from some zeolites produces irreversible structural changes that will be reflected in the thermal properties of the sorbant absent material.

Bearing in mind these limitations, let us examine the difference between heat capacity data for the natural phillipsite and clinoptilolite samples and estimates of the heat capacity of the anhydrous zeolite, and estimates of the heat capacity of water in zeolites determined in other studies. Hemingway and Robie (1984) have shown that the heat capacity of staurolite can be estimated by the principles of additivity to an average of $\pm 3\%$ in the temperature range 100–700 K through the proper choice of component groups. This procedure should provide an estimate of the heat capacity of the anhydrous zeolites of the same order of accuracy as would be obtained from direct measurements of the dehydrated zeolites. In this case, we have chosen to approximate the majority of the heat capacity of anhydrous phillipsite with feldspars, because Hoss and Roy (1960) have shown that phillipsite is irreversibly converted to a feldspar-like phase when completely dehydrated. For comparison, the heat capacity of dehydrated analcime was estimated as one mole of albite less one mole of quartz which yielded values which agreed with the measured heat capacities of dehydrated analcime (King and Weller, 1961) to better than 3% between 100 and 300 K.

The heat capacity of the anhydrous phillipsite was approximated by the heat capacity of 1.08 moles of albite, 0.80 moles of microcline and 0.48 moles of quartz and anhydrous clinoptilolite by 0.56 moles of albite, 0.98 moles of microcline, 1.50 moles of anorthite, 1.08 moles of corundum, 1.23 moles of periclase, 0.15 moles of hematite, and 21.38 moles of quartz.

In Figure 1 we present our estimate of the heat capacities (in the temperature range 100–300 K) of the "average" water contained in the phillipsite and clinoptilolite samples. Because the water molecules in zeolites are bonded to different sites, the thermal properties of the water molecules will vary. Thus, the difference calculation yields a value for the average water molecule. These

results may be compared with the heat capacities of the water in analcime, also shown in Figure 1, that were calculated as the difference between the heat capacities of analcime reported by King (1955) and of dehydrated analcime as given by King and Weller (1961). Similar results for the heat capacity of water in analcime are given by Johnson et al. (1982). For convenience, the H₂O component in these phases will be called water, regardless of the temperature or structural state.

The heat capacities of the "average" water in phillipsite, clinoptilolite, and analcime are somewhat greater than the heat capacity of ice at 100 K and are considerably lower than the heat capacity of water at 300 K. At 100 K, the estimated heat capacity of the water in the phillipsite sample is lower than the estimated value for the clinoptilolite and analcime samples. At 300 K, the heat capacity of the water in the phillipsite sample is considerably higher than the estimated values for clinoptilolite and analcime.

Our estimates of the heat capacities of water in the three zeolites are consistent with the results given by Basler and Lechert (1972) for a type X synthetic zeolite of the faujasite-type structure (e.g., Flanigen, 1977). Basler and Lechert determined the apparent molar heat capacity of the water for several concentrations of the sorbate from 46 to 293 mg/g of zeolite. The results of three of these experiments are presented schematically in Figure 1 for comparison.

Basler and Lechert (1972) found that the heat capacity of the water in the zeolite behaved more like ice at 100 K and more like water at 300 K as the amount of sorbate was increased from 46 to 293 mg/g of zeolite. Basler and Lechert concluded that the water in the holes of the zeolite exhibits no heat of melting, but instead undergoes a glass transition at a transition temperature of about 200 K.

Similar conclusions or results have been obtained in other studies of water in zeolite by Ducros (1960), in hydrated halloysite (endellite) by Cruz et al. (1978), and in the Wyodak coal and in porous alumina ceramic by Mraw and Naas-O'Rourke (1979). Ducros studied the mobility of water in chabazite using NMR and concluded there was no sharp melting point. Cruz et al. measured the heat capacity, the infrared spectra, and NMR (with hydration by H₂O and D₂O) spin-spin and spin-lattice relaxation times for endellite and found no evidence that the monolayer of sorbed water (e.g., Hendricks and Jefferson, 1938, for details for the crystal structure) behaved differently in endellite than the sorbed water in the zeolites. Mraw and Naas-O'Rourke found that below a threshold value of 220 mg of water per gram of dried subbituminous coal (Wyodak) and below 170 mg of water per gram of porous alumina the measured heat capacity of the sorbed water exhibited a similar increase to that observed in the type X zeolite of similar water content.

Haly (1972) and Mraw and Naas-O'Rourke (1979) have shown that at higher water contents (above 233 mg of

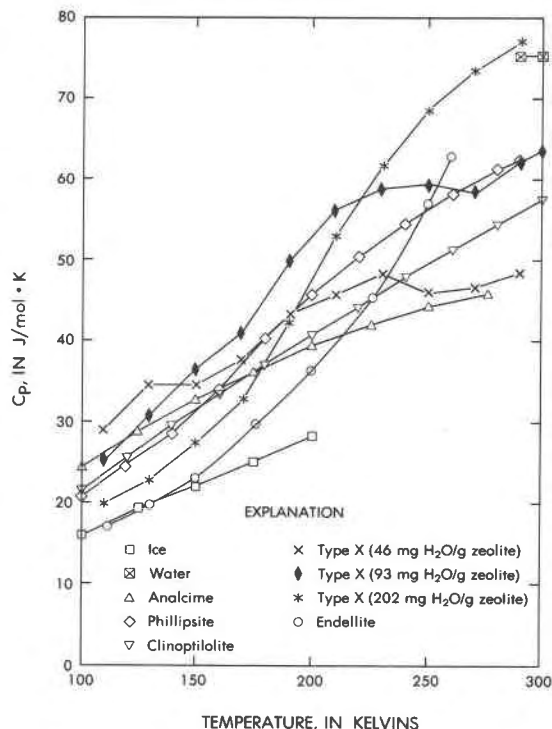


Fig. 1. Estimated values for the heat capacities of water in several zeolites and in endellite at low temperatures. The triangles were calculated from the data of King (1955) and King and Weller (1961), the open diamonds and inverted triangles are from this study (see text). The hexagons are the results of Cruz et al. (1978) and the filled diamonds, x, and * symbols represent the results reported by Basler and Lechert (1972).

water per gram of dried type Ca_{4.5}Na₃-A zeolite, 220 mg of water per gram of dried Wyodak coal, and 170 mg per gram of porous alumina) a broad peak centered at about 245 K is observed in the heat-capacity data that is ascribed to the sorbed water. This peak represents the melting of the sorbed water in the cavities of the zeolite and alumina and in the pores of the coal. Haly also observed a second peak, centered at about 270 K, which he interpreted to be the enthalpy of fusion of the water absorbed on the zeolite surface. A higher threshold of 280 mg of water per gram of the dried type A zeolite was required before the heat of melting of the surface water was observed. Barrer and Fender (1961) found that the properties (i.e., thermal entropies and expansivities) of sorbed water in chabazite and gmelinite approached the properties of liquid water (over the temperature range 303–353K) as the ratio of the amount of water sorbed in the zeolite to the amount of water necessary to saturate the zeolite cavities approached unity.

Numerous studies of the desorption of water from zeolites by differential scanning calorimetry (DSC), evolved gas analysis (EGA), differential thermal analysis (DTA) and/or thermogravimetric analysis (TG) appear in the literature (e.g., Barrer, 1978). Vucelic and coworkers

(1976, 1973) have examined the water loss from a series of ion-exchanged type A and X zeolites by both DSC and EGA techniques. Their findings show that the shape of the DSC trace is dependent upon the initial degree of filling of water in the zeolite cavity and upon the valence of the exchangeable cation. We have found that the pattern of the DSC trace obtained during the dehydration of a zeolite is also dependent upon the thermal history for a partially dehydrated zeolite.

Vučelić and coworkers (1976, 1974 and 1973) found three peaks in the DSC and EGA patterns obtained during the dehydration of zeolites with monovalent exchangeable cations. A fourth peak was observed for the same zeolites that had divalent exchangeable cations. The presence of a distinct fourth peak was dependent upon the amount of water estimated to be within the zeolite cavity. At low filling factors, the fourth peak was not observed. Similar results were obtained for type A and X zeolites.

In all cases Vučelić and coworkers (1976, 1974, and 1973) found that the lowest temperature peak could be correlated with the loss of water that exhibited the general properties of water (e.g., enthalpy of vaporization). The lowest temperature peak was centered from 370 to 390 K. The second peak was centered at about 430 K and the third at about 600 K; each was associated with correspondingly higher heats of absorption. The fourth peak was centered from 475 to 525 K depending upon the initial water filling factor for the sample, a dependence also observed in the first peak position and definition. The values of the enthalpies of desorption calculated by Vučelić and coworkers (assuming three or four peaks and a Gaussian or Lorentz distribution) from studies of the thermal dehydration of zeolites were similar to the results reported by Dzhigit et al. (1971) from measurements of the heat of adsorption at 300 K. Similar findings were reported by Barrer and Bratt (1959) for Na-faujasite.

McDaniel and Maher (1976) have shown that the thermal stability of X and Y type synthetic zeolites (faujasite-like phases) increases as the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ is increased. Sticher (1974) has shown that as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of synthetic K-G zeolites (chabazite-like phase) is varied, the pattern of water release is varied. When the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ is greater than 2.7, water is released smoothly and continuously from 350 to 600 K. At silica concentrations yielding a lower ratio than 2.7, X-ray evidence indicated that the cell collapses near 450 K resulting in a two-step dehydration process. Consequently, in addition to changes in the exchange cation and in the initial concentration of water in the zeolite cavity, DSC and DTA thermograms will reflect changes associated with any change in the framework of the zeolite.

Hoss and Roy (1960) examined the weight-loss patterns of natural and Ba-, Ca-, K-, and Na-exchanged phillipsite from 300 to 600 K and X-ray powder patterns made at several temperatures within this interval. Similar patterns were observed for each zeolite, with an exchangeable-

cation dependent structural change taking place between 360 and 420 K coincident with the loss of 50% of the water originally contained by the zeolite. Water loss continued, but at a reduced rate from 445 to 525 K accompanied by an increase in the crystallinity of the newly formed phase (called metaphillipsite by Hoss and Roy). The rate of water loss increased at temperatures above about 500 K.

Schematic examples of the DSC thermograms for Na-, K-, and Ca-exchanged type A zeolite from the work of Vučelić and others (1973 and 1976) are presented in Figure 2 with a DSC pattern which we obtained for the natural phillipsite studied in this paper. The curves are not normalized to a specific initial water content or zeolite weight and therefore should not be compared in terms of absolute energy differences. Instead, the relative energy distribution as a function of temperature shown by the K-Na natural phillipsite may be compared with that given for the Na-A and K-A type zeolites. The pattern shown for the natural phillipsite is obviously more complex than that indicated for the type A zeolites combining the heat effects of the desorption of water and the heat associated with the change in structure from phillipsite to metaphillipsite. Hoss and Roy (1960) observed a continuous increase in the crystallinity of the metaphillipsite phase heated in an X-ray furnace from 400 to 520 K, the

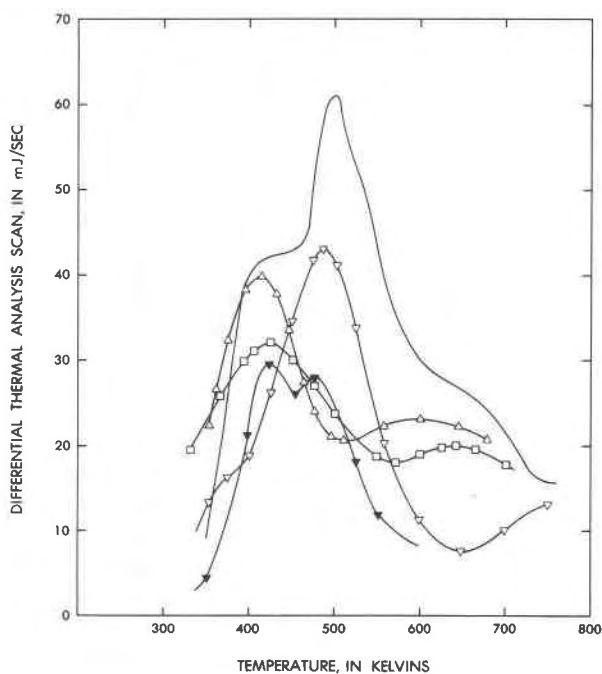


Fig. 2. A comparison of the differential scanning calorimeter thermogram (solid curve) for the natural phillipsite sample of this study with similar data for a type A zeolite. The triangles and squares are the data of Vučelić et al. (1976) for Na- and K-A, respectively. The inverted triangles are the data of Vučelić et al. (1973) for Ca-A where the filling factor is about 97% for the filled symbols and about 30% for the open symbols.

temperature range in which our heat capacity measurements show a broad anomalous peak.

The enthalpy of transition of phillipsite to metaphillipsite cannot be extracted from our experimental results because the heat of vaporization and the amount of water lost in the temperature interval 400–520 K are not known. Additional measurement under known water-pressure conditions will be required to make that determination. Possibly metaphillipsite forms only under conditions of reduced water fugacity. If this is true, one would expect the zeolites to behave differently in prograde and retrograde hydrothermal and metamorphic systems.

In addition, the zeolitic water may be expected to have a finite residual entropy arising from a possible frozen-in disordered state with respect to some degrees of freedom. Haida et al. (1974) have proposed the term "glassy crystal" for the non-equilibrium frozen-in state of a crystal that shows the classic behavior of a glass. The glassy state was discussed in terms of both short-range (hexagonal ice) and long-range ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) order. Haida et al. introduced the concept of the long-range-ordered glassy state that would appear applicable to the zeolitic water in natural zeolites. However, as noted earlier, the properties of zeolitic water vary with the degree of filling of the channels and cavities. Consequently, short-range order would be expected to be of increased importance as the water content of the cavities was increased or in natural zeolites in which the water is tightly bonded to the exchangeable cation.

Knowlton et al. (1981) have estimated average enthalpies of hydration for the three types of water bound in a natural clinoptilolite sample, from their DSC and TG experiments. These authors provide a fairly good discussion of the problems associated with the measurement of heat capacities or enthalpies of dehydration with the DSC technique. The dehydration curve obtained in this study was similar to that reported by Knowlton et al., and therefore, will not be discussed further.

Assumptions and limitations

Zeolites, natural or synthetic, are largely metastable phases that precipitate from aqueous solutions (i.e., the transformation from one phase to another under hydrothermal conditions proceeds by the dissolution of the less stable phase and precipitation of the more stable phase, (see for example Barrer, 1981)). Unlike most of the phases of importance to geologists, the stability of zeolites cannot be completely determined from reversed phase equilibrium reactions because, in this system, the metastable equilibria can only be reached experimentally from conditions of supersaturation (e.g., Hemingway, 1982). Therefore, to model the zeolites in geologic processes, we must be able to ascertain the affect of variations in the exchangeable cations, the silicon/aluminum ratio of the framework, and the H_2O component upon the thermodynamic properties of the phases.

One limitation we face arises from the preparation of zeolites for studies like calorimetric measurements, chemical analysis, X-ray diffraction analysis, etc.; the phases must be removed from the solutions in which they grew and some moderate drying must be done. Some water present in the structure at the time the phase was crystallizing is necessarily lost in the processes. Presently, we must assume for the purposes of calculating thermodynamic properties for zeolites that the heat capacity, enthalpy of formation, entropy, and free energy of formation of H_2O lost in sample preparation does not differ significantly from our estimated correction for that component. Presently, our estimates for the H_2O component must be based upon the properties of pure H_2O or upon values calculated from models such as those discussed in the preceding section.

A related limitation arises from our need to be able to estimate the thermodynamic properties for a zeolite of a particular composition for a specific reaction or geologic process. We cannot, at present, make corrections to the measured thermodynamic properties of zeolites by corresponding states or additivity arguments because we cannot access the affect of, for example, a change in the exchangeable cation upon the thermodynamic properties of the H_2O component of the zeolite (similarly, changes of silicon/aluminum ratio cannot be evaluated).

In the preceding section we have seen that the thermodynamic properties of the H_2O component in zeolites vary with the type of exchangeable cation, the silicon/aluminum ratio, and the degree of filling of the cavities and channels within a particular zeolite structure type. We may also readily conclude that the thermodynamic properties of the H_2O component vary significantly between structure types, i.e., the H_2O component more closely represents the properties of pure H_2O in the faujasite (zeolite X) type structure than in the phillipsite type structure (see Fig. 1). Clinoptilolite and analcime (see Fig. 1) show even greater deviations from the properties of pure H_2O than phillipsite does. Thus, we may conclude that the thermodynamic properties of the H_2O component of a zeolite phase deviate more strongly from the thermodynamic properties of pure H_2O as the stability of the zeolite phase increases. We cannot, however, quantify the effect at this time. Therefore, systematic studies of several structure types in which the exchangeable cations and the silicon/aluminum ratios are varied will be necessary before adequate models of the thermodynamic properties of zeolites may be derived.

The process by which most zeolite phases are lost from mineral assemblages and replaced by more stable phases will vary with the fugacity of H_2O . At high H_2O fugacities, as noted above, the zeolite is removed by dissolution and some of the components are precipitated from the aqueous solution as the more stable phase. At low H_2O fugacities, the zeolite decomposes to an amorphous material that recrystallizes to form one or more phases (e.g., Breck, 1974, p. 494). The limiting values of H_2O fugaci-

ties are not known at this time. Therefore, kinetic studies will be required to determine the pressure and temperature limits for each type of process before models of geologic processes involving zeolites can be completely developed. Similarly, modelling of sites for disposal of radioactive wastes will require careful analysis of the affect of the thermal pulse if the sites contain zeolites.

Conclusion

Measurements of the heat capacities of natural phillipsite and clinoptilolite presented in this study represent initial results from an ongoing study of the thermodynamic properties of zeolites. From these measurements, we may calculate the entropy changes, $S_{298} - S_0$, as 772 ± 2.4 and 2872.3 ± 9.0 J/(mol · K), respectively, for the natural phillipsite and clinoptilolite samples described earlier in this study. However, no estimates of the configurational entropies have been made because of a lack of information, particularly that regarding the degree of order of the zeolitic water. Therefore, the entropy values reported in this study should be regarded as minimum.

The heat capacities of the average H₂O component in phillipsite show a clear glass transition in the region of 175 K. The H₂O component in clinoptilolite has a steadily increasing heat capacity with increasing temperature that is nearly linear between 100 and 300 K. The heat capacity of the average H₂O component in natural zeolites will be somewhat greater than the heat capacity of ice at 100 K and somewhat less than that for water at 300 K. The thermodynamic properties of the H₂O component in zeolites will increasingly deviate from those of pure H₂O as the stability of the zeolite phases increases.

Systematic studies in which the exchangeable cations and the silicon/aluminum ratios are varied will be necessary before we can derive adequate models for the thermodynamic properties of zeolites. In addition, kinetic studies will be required before we can determine the temperature and H₂O fugacity limits of the two processes that control the removal of most zeolites from natural mineral assemblages, and thereby model geologic processes or model containment sites for radioactive waste disposal.

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