

Thermodynamic studies of zeolites: analcime and dehydrated analcime¹

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Abstract

The purpose of this investigation was to obtain accurate and precise thermodynamic quantities for well-characterized specimens of analcime and dehydrated analcime, and to relate the results to processes of geochemical interest. Calorimetric measurements have been carried out on a pure specimen of analcime whose composition was $\text{Na}_{0.96}\text{Al}_{0.96}\text{Si}_{2.04}\text{O}_6 \cdot \text{H}_2\text{O}$ and on the corresponding anhydride. The low-temperature heat capacity, standard enthalpy of formation (298.15 K), and high-temperature enthalpy increments have been determined by adiabatic, solution, and drop-calorimetric techniques, respectively. Thermodynamic functions have been calculated for analcime (to 600 K) and for dehydrated analcime (to 1000 K). The following values at $T = 298.15$ K and at a pressure of 1 bar have been obtained:

	$\Delta H_f^\circ(T)$ kJ/mol	$C_p^\circ(T)$ J/(mol·K)	$S^\circ(T)$ J/(mol·K)	$\Delta G_f^\circ(T)$ kJ/mol
analcime	-3296.9 ± 3.3	211.53 ± 0.21	226.75 ± 0.23	-3077.2 ± 3.3
dehydrated analcime	-2970.2 ± 3.5	163.59 ± 0.16	171.71 ± 0.17	-2803.7 ± 3.5

An examination of the thermodynamics of the following reactions has been carried out in the light of the results obtained in the present study:



Introduction

Most reactions involving zeolites take place at low temperatures (*ca.* 200° C) and with small entropy and volume changes. This combination of factors, along with the possibility that some zeolites may be metastable phases, makes equilibrium studies by the usual hydrothermal techniques difficult or impossible. As an alternative approach to the study of the stability (or metastability) of zeolite minerals, we have launched a program to determine by calorimetric techniques the thermodynamic properties of

important members of this group. In this paper we report calorimetric measurements of the heat capacity, enthalpy of formation, high-temperature enthalpy increments, and the derived thermodynamic properties for analcime and its anhydride.

Inasmuch as it occurs both as a low-temperature, diagenetic mineral phase in sediments and cavities of basaltic rocks and as a feldspathoid in igneous rocks, analcime has held a great deal of mineralogical interest. Furthermore, because of its relatively simple composition it is commonly encountered in studies of sodium aluminum silicates. For these reasons and others, much experimental attention has been focused on analcime.

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The most recently compiled thermodynamic properties of analcime (Robie, Hemingway, and Fisher, 1978; Helgeson, Delany, Nesbitt, and Bird, 1978) are not in agreement, because some of the data come from different literature sources.

Heat capacities (C_p°)² for analcime were measured from 51 to 298 K by King (1955) and he extrapolated the curve from 51 to 0 K in order to derive the entropy value (S°) at 298.15 K which is listed in both of the above compilations. The high-temperature heat capacities of analcime had not been measured, but those for fully dehydrated analcime were available to 1000 K (Pankratz, 1968). Helgeson *et al.* (1978) noted that between 250 and 300 K the difference between the heat capacities for analcime and dehydrated analcime was approximately constant; therefore, they extended the C_p° for analcime to 1000 K along a curve parallel to that for the dehydrated analcime.

The Gibbs energy of formation (ΔG_f°) for analcime at 298.15 K, -3091.73 kJ/mol, listed by Robie *et al.* (1978) was calculated from the enthalpy of formation (ΔH_f°) measured by Barany (1962) and corrected by Hemingway and Robie (1977) for assumed errors in the auxiliary thermochemical values used by Barany. The ΔG_f° value, -3088.05 kJ/mol, of Helgeson *et al.* (1978) was derived from solubility data obtained by J. J. Hemley (unpublished results) using the estimated C_p° curve and S° from King's paper.

The derivation of an internally consistent set of Gibbs energy values from experimental phase equilibrium data for analcime is made difficult by two composition variables, namely, the Si/Al ratio and the water content. The purpose of the present investigation was to obtain accurate and precise thermodynamic quantities for well-characterized specimens of analcime and dehydrated analcime, and to relate the results to processes of geochemical interest.

Materials

Analcime and dehydrated analcime

Many of the earlier workers used an analcime sample from Table Mountain, Colorado (King, 1955; King and Weller, 1961; Barany, 1962; Hemley, unpublished; and Yoder and Weir, 1960). The analcime used in the present study is from Skookumchuck Dam, Thursten County, Washington,

and has a composition that is virtually identical with that from Table Mountain. For a description of the locality and the zeolites found there, see Tschernich (1972).

Our sample came from a mass of clear to milky crystals up to 2 cm in diameter. The large crystals were easily hand picked from the matrix. A stock of about 20 grams was prepared for the calorimetric measurements by crushing selected crystals to about 0.5 mm size. A sample of 40 grains taken from this stock was analyzed by the usual electron microprobe methods to determine the average composition and compositional variations within the sample. The elements commonly found in zeolites—Na, Al, Si, Mg, K, Ca, Fe, Sr, and Ba—were sought, but only the first three were above detection limits. The water content was determined by heating a dried sample to 600° C for 24 hours and measuring the weight loss. The analytical results and the statistical variations thereof are given in Table 1.

The average of the forty individual analyses gives a close, but not perfect, charge balance between the number of Al atoms substituted for Si and the number of Na ions. For purposes of balancing chemical reactions and thermochemical cycles, the composition was taken to be $\text{Na}_{0.96}\text{Al}_{0.96}\text{Si}_{2.04}\text{O}_6 \cdot 1.00\text{H}_2\text{O}$. Based on this idealized composition and the refined cell dimension ($a = 13.700 \pm 0.003 \text{ \AA}$), the calculated density is 2.265 g/cm^3 , which compares well with the measured density ($2.26 \pm 0.01 \text{ g/cm}^3$). Analcime was dehydrated by heating in air at 600° C for about 18 h.

Table 1. Composition of analcime from Skookumchuck Dam, Washington

	Analytical Results ^a (mass per cent)	Calculated Results ^b (mass per cent)
SiO ₂	55.86 ± 0.48	55.90
Al ₂ O ₃	22.06 ± 0.38	22.32
Na ₂ O	13.81 ± 0.23	13.57
H ₂ O	8.20 ± 0.05	8.21
	99.93 ± 0.65	100.00
Molecular Proportions		
Na	0.975	0.96
Al	0.951	0.96
Si	2.042	2.04
O	6.00	6.00
H ₂ O	1.00	1.00

^aAverage of 40 individual analyses of separate analcime fragments.

^bCalculated composition for idealized cell contents.

²Except where otherwise stated, thermodynamic properties refer to a pressure of 1 bar.

Gibbsite

The gibbsite, $\text{Al}(\text{OH})_3$, used in the enthalpy of reaction measurements was Fisher Reagent $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ which had been heated for approximately 6 h at 150°C 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 $\Delta H_f^\circ[\text{Al}(\text{OH})_3]$.

Sodium fluoride

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

α -Quartz

The α -quartz sample was a portion of National Bureau of Standards Standard Reference Material 1654 which passed through $44\ \mu\text{m}$ size mesh but was retained on a $37\ \mu\text{m}$ mesh.

Hydrofluoric acid

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

Apparatus, experimental procedures, and results

As stated in the introduction, three separate types of measurement were performed as part of the present investigation. Each of the techniques used, along with the results obtained, will be discussed under separate headings.

Heat capacity measurements (5 to 350 K)

The calorimeter (laboratory designation, 6-GS-1) was constructed from oxygen-free, high-conductivity copper, and it had an internal volume of $5.976\ \text{cm}^3$ at 298.15 K. Both analcime and dehydrated analcime were loaded into the calorimeter in a glovebox filled with dry helium. After removal from the glovebox, the analcime specimen was found to have been reduced in mass by approximately 0.08%; this was attributed solely to loss of adsorbed water. To promote rapid thermal equilibration, a small amount of helium, about $7 \times 10^{-6}\ \text{mol}$, was left in the calorimeter. Before measurements of the heat capacity of the loaded calorimeter were begun, separate experiments were performed to determine the heat capacity of the empty calorimeter.

Only a brief description of the apparatus and measuring technique will be given here, as this information has been published in detail elsewhere (Osborne *et al.*, 1972). The temperature of the adiabatic shields surrounding the calorimeter was controlled automatically so that it was close ($\pm 0.001\ \text{K}$) 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 within 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 made by observing the steady-state drift of the temperature both before and after the calorimeter was heated. While the calorimeter was being heated, the current and the 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 capacities of analcime and dehydrated analcime, $C_p^\circ(T)$, were 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 for 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

Experimental heat capacity results in order of ascending mean temperatures, $\langle T \rangle$, are given for analcime in Table 2 and dehydrated analcime in Table 3. The temperature increment, ΔT , 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, $\Delta T \approx 10\ \text{K}$. 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 each fitted by two polynomials in T using a weighted, least-squares 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 1.8 and 2.2% for analcime and dehydrated analcime, respectively. Above 20 K, the standard deviations were 0.14 and 0.22% for analcime and dehydrated analcime, respectively. Based on these polynomials, $C_p^{\circ}(T)$ values have been calculated at selected temperatures and are given in Tables 4 and 5.

The heat capacities below 13 K (see Tables 2 and 3) were used to construct plots of C_p°/T against T^2 for both analcime and dehydrated analcime. Smooth curves could be drawn through these points and also that at $T = 0$ K. In the case of analcime, this

Table 2. Experimental heat capacities of analcime

$\langle T \rangle$ K	$C_p^{\circ}(T)$ J/(mol·K)	$\langle T \rangle$ K	$C_p^{\circ}(T)$ J/(mol·K)	$\langle T \rangle$ K	$C_p^{\circ}(T)$ J/(mol·K)
5.63	0.164	26.51	13.01	155.66	134.76
5.65	0.149	29.28	16.04	165.66	141.42
7.67	0.396	32.37	19.51	175.70	148.15
7.80	0.410	35.79	23.43	185.72	154.46
9.40	0.737	39.57	27.80	190.49	157.81
9.70	0.805	43.75	32.62	200.41	163.76
11.37	1.350	47.82	37.40	210.41	169.43
11.61	1.439	48.42	37.93	220.37	175.96
13.40	2.269	53.49	43.73	230.35	181.53
13.59	2.364	59.47	50.37	240.38	186.57
15.41	3.412	65.77	57.25	250.39	191.30
15.63	3.556	72.78	64.64	260.18	195.63
17.43	4.780	80.23	72.08	270.17	200.76
17.67	4.961	86.17	78.01	280.18	204.93
19.53	6.433	88.47	80.28	290.19	208.71
19.70	6.575	95.47	86.41	300.21	212.02
21.71	8.311	105.60	95.10	310.23	214.78
21.76	8.365	115.64	103.79	320.26	216.80
23.98	10.44	125.61	112.13	330.30	218.09
23.98	10.45	135.65	120.20	340.27	220.23
26.49	13.00	145.67	127.74	347.59	223.38

Table 3. Experimental heat capacities of dehydrated analcime

$\langle T \rangle$ K	$C_p^{\circ}(T)$ J/(mol·K)	$\langle T \rangle$ K	$C_p^{\circ}(T)$ J/(mol·K)	$\langle T \rangle$ K	$C_p^{\circ}(T)$ J/(mol·K)
5.75	0.104	33.14	15.55	177.07	113.57
5.79	0.096	36.65	18.35	187.07	118.97
7.77	0.344	40.56	21.54	197.10	123.70
7.84	0.351	44.88	25.03	207.04	128.44
9.66	0.730	49.42	28.73	217.05	132.60
9.72	0.749	51.58	30.51	227.06	136.88
11.62	1.343	56.97	34.92	237.08	140.85
13.64	2.155	63.00	39.71	247.08	145.27
13.65	2.176	69.66	45.04	257.11	148.83
15.69	3.193	76.99	50.70	267.11	152.62
15.74	3.214	84.95	56.79	277.12	156.34
17.75	4.396	87.37	58.41	287.12	160.18
17.80	4.421	93.67	63.19	297.11	163.19
19.77	5.637	97.11	65.27	307.14	166.23
19.86	5.704	107.29	72.03	317.17	169.79
21.91	7.056	117.17	78.64	327.18	172.87
22.01	7.130	127.04	85.21	335.20	175.18
24.25	8.575	137.00	91.43	341.21	177.65
24.46	8.797	147.01	97.32	347.11	178.65
27.10	10.80	157.05	102.95		
29.97	13.04	167.07	108.36		

curve was essentially linear below 8 K. The heat capacities and other thermodynamic functions of analcime at 8 K (Table 4) and of dehydrated analcime at 9 K (Table 5) were derived from these curves. At $T = 10$ 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 in this part of the investigation. The 100 cm³ 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. The ampoules used to contain the calorimetric samples, with the exception of α -quartz, were constructed of KEL-F (a chlorotrifluoroethylene polymer) as described previously (Johnson *et al.*, 1973). The α -quartz samples were contained in Teflon ampoules with Teflon windows attached with wax.

The energy equivalent of the calorimetric system was obtained from electrical calibration experi-

Table 4. Low-temperature thermodynamic functions for analcime

T	$C_p^0(T)$	$S^0(T)$	$H^0(T) - H^0(0)$	$-[G^0(T) - H^0(0)]/T$
K	J/(mol·K)	J/(mol·K)	J/mol	J/(mol·K)
8	(0.444)	(0.148)	(0.890)	(0.037)
10	0.894	0.292	2.19	0.073
15	3.160	1.027	11.64	0.251
20	6.820	2.410	36.12	0.604
25	11.46	4.414	81.45	1.156
30	16.82	6.970	151.9	1.905
35	22.52	9.988	250.2	2.839
40	28.32	13.37	377.3	3.941
45	34.08	17.04	533.3	5.191
50	39.78	20.93	718.0	6.569
60	50.95	29.17	1172	9.642
70	61.77	37.85	1736	13.05
80	71.99	46.77	2405	16.70
90	81.49	55.80	3173	20.55
100	90.42	64.86	4033	24.52
110	99.02	73.88	4981	28.60
120	107.44	82.86	6013	32.75
130	115.64	91.78	7129	36.95
140	123.48	100.64	8325	41.18
150	130.86	109.42	9597	45.44
160	137.79	118.08	10940	49.71
170	144.39	126.64	12351	53.98
180	150.83	135.07	13828	58.25
190	157.21	143.40	15368	62.52
200	163.53	151.62	16972	66.77
210	169.69	159.75	18638	71.00
220	175.57	167.78	20364	75.22
230	181.11	175.71	22148	79.41
240	186.31	183.53	23985	83.59
250	191.22	191.24	25873	87.74
260	195.91	198.83	27809	91.87
270	200.42	206.31	29791	95.97
280	204.71	213.67	31817	100.04
290	208.68	220.93	33884	104.09
300	212.11	228.06	35989	108.10
310	214.75	235.06	38124	112.08
320	216.58	241.91	40281	116.03
330	218.09	248.60	42454	119.95
340	220.35	255.14	44645	123.83
350	223.70	261.57	46865	127.67
273.15	201.80	208.64	30424	97.26
298.15	211.53	226.75	35597	107.36
	±0.21	±0.23	±36	±0.11

^aMolecular mass of analcime was taken to be 219.278 g/mol.

Table 5. Low-temperature thermodynamic functions for dehydrated analcime

T	$C_p^0(T)$	$S^0(T)$	$H^0(T) - H^0(0)$	$-[G^0(T) - H^0(0)]/T$
K	J/(mol·K)	J/(mol·K)	J/mol	J/(mol·K)
9	(0.580)	(0.155)	(1.107)	(0.032)
10	0.834	0.229	1.810	0.048
15	2.814	0.901	10.44	0.206
20	5.812	2.104	31.70	0.519
25	9.169	3.759	69.09	0.995
30	13.05	5.769	124.5	1.619
35	17.06	8.081	199.8	2.374
40	21.09	10.62	295.2	3.244
45	25.12	13.34	410.7	4.213
50	29.18	16.20	546.4	5.268
60	37.34	22.24	879.0	7.587
70	45.37	28.60	1292	10.13
80	53.05	35.16	1785	12.85
90	60.33	41.84	2352	15.70
100	67.29	48.56	2991	18.65
110	74.05	55.29	3698	21.67
120	80.62	62.01	4471	24.75
130	86.99	68.72	5309	27.88
140	93.12	75.39	6210	31.03
150	98.99	82.02	7171	34.21
160	104.62	88.59	8189	37.41
170	110.02	95.09	9262	40.61
180	115.24	101.53	10389	43.81
190	120.25	107.90	11567	47.02
200	125.06	114.19	12793	50.22
210	129.63	120.40	14067	53.42
220	133.99	126.53	15385	56.60
230	138.15	132.58	16746	59.77
240	142.17	138.55	18148	62.93
250	146.11	144.43	19589	66.07
260	149.99	150.24	21070	69.20
270	153.80	155.97	22589	72.31
280	157.47	161.63	24145	75.40
290	160.93	167.22	25737	78.47
300	164.18	172.73	27363	81.52
310	167.31	178.16	29020	84.55
320	170.48	183.52	30709	87.56
330	173.79	188.82	32431	90.54
340	176.97	194.05	34185	93.51
350	179.40	199.22	35967	96.46
273.15	154.97	157.76	23075	73.28
298.15	163.59	171.71	27060	80.95
	±0.16	±0.17	±27	±0.08

^aMolecular mass of dehydrated analcime was taken to be 201.263 g/mol.

ments performed before and after each reaction experiment. These calibrations covered the same temperature range as the corresponding reaction experiments, and the mean temperature of all such experiments was 298.15 ± 0.01 K.

Calorimetric measurements were made of the enthalpies of reaction with HF(aq) of analcime, dehydrated analcime, gibbsite, sodium fluoride, and α -quartz. Detailed results for each of these reactions are given in Table 6. The column headings in Table 6 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 of the energy equivalent of the calorimetric system before and after the experiment; ΔH_{corr} , the combined correction for the thermal effects of opening the ampoule and for the vaporization of solvent into the free volume of the ampoule; and $\Delta H/M$, the specific enthalpy of reaction.

Standard enthalpies of formation at 298.15 K

The thermochemical cycle used to derive the enthalpies of formation of analcime and dehydrated

analcime is given in Table 7. The molar enthalpies of reactions 1, 2, 3, 4, and 11 are based on the mean specific enthalpies of reaction in Table 6. For this part of the calculation, the molar masses of $\text{Na}_{0.96}\text{Al}_{0.96}\text{Si}_{2.04}\text{O}_6 \cdot 1.00\text{H}_2\text{O}$, $\text{Na}_{0.96}\text{Al}_{0.96}\text{Si}_{2.04}\text{O}_6$, $\text{Al}(\text{OH})_3$, NaF , $\alpha\text{-SiO}_2$, and $\text{HF} \cdot 3.441\text{H}_2\text{O}$ were taken to be 219.278, 201.263, 78.0034, 41.9882, 60.0843, and 81.9966 g/mol, respectively, based on the 1979 atomic weights (Holden, 1980). Enthalpies of dilution of HF(aq) (reactions 5 and 12) and of formation of $\text{HF} \cdot 3.441\text{H}_2\text{O}$, -321.26 ± 0.40 kJ/mol (reaction 6) are based on an earlier study at this Laboratory (Johnson *et al.*, 1973). For reactions 7, 8, 9, and 13, the following standard enthalpies of formation (kJ/mol) were used: $\text{H}_2\text{O}(\text{l})$, -285.830 ± 0.042 (CODATA, 1978); $\text{SiO}_2(\alpha)$, -910.94 ± 1.42 (Wise *et al.*, 1963); and $\text{Al}(\text{OH})_3$, -1293.13 ± 1.19 (Hemingway and Robie, 1977). The enthalpy of formation of NaF , -576.88 ± 0.30 kJ/mol (reaction 10), is based on $\Delta H_f^\circ(\text{Na}^+, \text{aq})$, -240.300 ± 0.065 kJ/mol (CODATA, 1978); $\Delta H_f^\circ(\text{F}^-, \text{aq})$, -335.64 ± 0.29 kJ/mol (Johnson *et al.*, 1973); and $\Delta H_{\text{soln}}^\circ(\text{NaF}, \text{c})$, 937 ± 36 J/mol (Nuttall *et al.*,

Table 6. Enthalpies of reaction at 298.15 K of analcime, dehydrated analcime, α -quartz, $\text{Al}(\text{OH})_3$, and NaF with HF(aq) solutions. See text for explanation of column headings.

<i>m</i>	$\Delta\theta_c$	$\epsilon(\text{calor})^a$	$\epsilon(\text{calor})(-\Delta\theta_c)$	ΔH_{corr}^b	$\Delta H/M$
g	K	J/K	J	J	J/g
Analcime, $\text{Na}_{0.96}\text{Al}_{0.96}\text{Si}_{2.04}\text{O}_6 \cdot 1.00\text{H}_2\text{O}$					
0.19262	1.08135	405.56	-438.55	0.52	-2274.1
0.19157	1.07773	405.20	-436.70	0.52	-2276.9
0.19190	1.08515	404.10	-438.51	0.52	-2282.4
0.19284	1.09326	403.35	-440.97	0.52	-2284.0
0.19214	1.08673	403.47	-438.46	0.52	-2279.3
0.19279	1.09430	403.44	-441.48	0.52	-2287.3
Average $\Delta H/M = -2280.7 \pm 2.0$ J/g ^c					
Dehydrated analcime, $\text{Na}_{0.96}\text{Al}_{0.96}\text{Si}_{2.04}\text{O}_6$					
0.17468	1.16793	403.70	-471.49	0.51	-2696.2
0.17483	1.16609	403.78	-470.84	0.51	-2690.2
0.17493	1.16440	403.71	-470.08	0.51	-2684.3
0.17537	1.16785	403.14	-470.81	0.52	-2681.7
0.17534	1.16646	402.70	-469.73	0.52	-2676.0
Average $\Delta H/M = -2685.7 \pm 3.5$ J/g ^c					
α -Quartz, SiO_2					
0.10813	0.60906	400.92	-244.18	0.09	-2257.4
0.10722	0.60407	400.52	-241.94	0.09	-2255.6
0.10768	0.60863	400.82	-243.95	0.09	-2264.7
0.10784	0.60784	400.60	-243.50	0.09	-2257.1
0.10801	0.61012	400.24	-244.19	0.09	-2260.0

Table 6. (continued)

<i>m</i>	$\Delta\theta_c$	$\epsilon(\text{calor})^a$	$\epsilon(\text{calor})(-\Delta\theta_c)$	ΔH_{corr}^b	$\Delta H/M$
g	K	J/K	J	J	J/g
0.10831	0.60963	400.64	-244.24	0.09	-2254.2
0.10789	0.60624	401.02	-243.11	0.09	-2252.5
0.10747	0.60440	400.38	-241.99	0.09	-2250.9
Average $\Delta H/M = -2256.6 \pm 1.5$ J/g ^c					
Gibbsite, $\text{Al}(\text{OH})_3$					
0.06489	0.34189	402.40	-137.58	0.52	-2112.2
0.06474	0.34275	402.19	-137.85	0.52	-2121.3
0.06504	0.34331	402.41	-138.15	0.52	-2116.1
0.06464	0.34172	402.37	-137.50	0.52	-2119.1
0.06501	0.34375	402.34	-138.30	0.52	-2119.4
Average $\Delta H/M = -2117.6 \pm 1.6$ J/g ^c					
NaF					
0.03525	0.00968	402.38	-3.90	0.51	-96.2
0.03561	0.01004	402.38	-4.04	0.51	-99.1
0.03481	0.00996	402.38	-4.01	0.51	-100.5
0.03565	0.00942	402.38	-3.79	0.51	-92.0
0.03705	0.01004	402.38	-4.04	0.51	-95.3
Average $\Delta H/M = -96.6 \pm 1.5$ J/g ^c					

^a $\epsilon(\text{calor})$ for the experiments with NaF was not measured, but was taken to be the average of the values for the $\text{Al}(\text{OH})_3$ experiments plus 0.04 J for the heat capacity of NaF.

^b ΔH_{corr} includes the enthalpy effect of opening the ampoule, which was 0.53 J for all experiments except those for α -quartz for which it was 0.10 J, as well as a correction for the vaporization of solvent into the free volume of the ampoule.

^c The uncertainty is the standard deviation of the mean.

Table 7. Thermochemical scheme for the derivation of the standard enthalpies of formation at 298.15 K of analcime and dehydrated analcime

Reaction	ΔH (kJ/mol)
1. $2.04\text{SiO}_2(\text{s}) + 1507.54\text{HF} \cdot 5190.82\text{H}_2\text{O} + [\text{A}]^{\text{a}}$	-276.60 ± 0.37
2. $0.96\text{Al}(\text{OH})_3(\text{c}) + [\text{A}]^{\text{a}} + [\text{B}]^{\text{b}}$	-158.57 ± 0.24
3. $0.96\text{NaF}(\text{c}) + [\text{B}]^{\text{b}} + [\text{C}]^{\text{c}}$	-3.90 ± 0.12
4. $[\text{C}]^{\text{c}} + \text{Na}_{0.96}\text{Al}_{0.96}\text{Si}_{2.04}\text{O}_{6.00} \cdot 1.00\text{H}_2\text{O} + 1508.50\text{HF} \cdot 5190.78\text{H}_2\text{O}$	500.11 ± 0.88
5. $1507.54\text{HF} \cdot 5187.477\text{H}_2\text{O} + 3.343\text{H}_2\text{O}(\text{l}) + 1507.54\text{HF} \cdot 5190.82\text{H}_2\text{O}$	-1.39 ± 0.14
6. $0.96\text{HF} \cdot 3.303\text{H}_2\text{O} + 0.48\text{H}_2(\text{g}) + 0.48\text{F}_2(\text{g}) + 3.303\text{H}_2\text{O}(\text{l})$	308.41 ± 0.38
7. $0.04\text{H}_2(\text{g}) + 0.02\text{O}_2(\text{g}) + 0.04\text{H}_2\text{O}(\text{l})$	-11.43 ± 0.00
8. $2.04\text{Si}(\text{c}) + 2.04\text{O}_2(\text{g}) + 2.04\text{SiO}_2(\text{s})$	-1858.32 ± 2.90
9. $0.96\text{Al}(\text{c}) + 1.44\text{O}_2(\text{g}) + 1.44\text{H}_2(\text{g}) + 0.96\text{Al}(\text{OH})_3(\text{c})$	-1241.40 ± 1.14
10. $0.96\text{Na}(\text{c}) + 0.48\text{F}_2(\text{g}) + 0.96\text{NaF}(\text{c})$	-553.80 ± 0.29
11. $[\text{C}]^{\text{c}} + \text{Na}_{0.96}\text{Al}_{0.96}\text{Si}_{2.04}\text{O}_6(\text{c}) + 1508.50\text{HF} \cdot 5191.78\text{H}_2\text{O}$	540.53 ± 1.41
12. $1507.54\text{HF} \cdot 5188.477\text{H}_2\text{O} + 2.343\text{H}_2\text{O}(\text{l}) + 1507.54\text{HF} \cdot 5190.82\text{H}_2\text{O}$	-0.95 ± 0.10
13. $0.96\text{H}_2\text{O}(\text{l}) + 0.96\text{H}_2(\text{g}) + 0.48\text{O}_2(\text{g})$	274.40 ± 0.04

^a[A] = $2.04\text{H}_2\text{SiF}_6 \cdot 1495.30\text{HF} \cdot 5194.90\text{H}_2\text{O}$.
^b[B] = $0.96\text{AlF}_3 \cdot 2.04\text{H}_2\text{SiF}_6 \cdot 1492.42\text{HF} \cdot 5197.78\text{H}_2\text{O}$.
^c[C] = $0.96\text{NaF} \cdot 0.96\text{AlF}_3 \cdot 2.04\text{H}_2\text{SiF}_6 \cdot 1492.42\text{HF} \cdot 5197.78\text{H}_2\text{O}$.

1978). Summation of the appropriate quantities in Table 7 yielded the following standard enthalpies of formation:

$$\Delta H_{\text{f}}^{\circ}(\text{Na}_{0.96}\text{Al}_{0.96}\text{Si}_{2.04}\text{O}_{6.00} \cdot 1.00\text{H}_2\text{O}, \text{c}, 298.15 \text{ K}) \\ = -3296.9 \pm 3.3 \text{ kJ/mol}$$

$$\Delta H_{\text{f}}^{\circ}(\text{Na}_{0.96}\text{Al}_{0.96}\text{Si}_{2.04}\text{O}_{6.00}, \text{c}, 298.15 \text{ K}) \\ = -2970.2 \pm 3.5 \text{ kJ/mol}$$

Enthalpy increment measurements (350 to 623 K)

The drop calorimeter used for the enthalpy increment measurements on analcime has been described in detail (Fredrickson *et al.*, 1969). The system consisted of a resistance-heated, molybdenum-core furnace and 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, and this substantially decreased equilibration times within the furnace and allowed measurements to be conducted at temperatures down to $T = 350 \text{ K}$. The performance of the calorimetric system was checked (Johnson *et al.*, 1980) by determining the enthalpy of synthetic sapphire (National Bureau of Standards Standard Reference Material 720) over the temperature range from 374 to 836 K. The average difference of an individual experimental

result from the certificate value was 0.13%, and this was deemed to be acceptable.

The sample of analcime (mass, 6.69709 g) was contained in a welded (platinum + 10% rhodium) capsule (1.2 cm diameter, 4.8 cm long, 5.35 cm³ internal volume, and mass, 18.83304 g) which was filled with 9.687×10^{-5} mol helium.

Enthalpy increment results

The results of the drop calorimetric experiments in order of increasing temperature are given in Table 8. The entries in this table are: T , the temperature of the furnace and sample; $\Delta\theta_c$, the change in temperature of the calorimeter corrected for energy 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.

The energy equivalent of the calorimeter, $\epsilon(\text{calor})$, varies slightly as a function of $\Delta\theta_c$, from 4379.46 J/K for $\Delta\theta_c \approx 0.5 \text{ K}$ to 4378.68 J/K for $\Delta\theta_c \approx 1.5 \text{ K}$. The enthalpy contribution of the capsule was determined in a separate series of experiments with an empty capsule (platinum + 10% rhodium) with dimensions and mass similar to those used for the experiments with analcime. The measured enthalpy was corrected for the enthalpy of the helium gas, for small deviations of the final calorimetric temperature from 298.15 K (usually less than 0.01 K), and for the water vapor in the free volume of the ampoule. The vapor pressure of water over analcime was calculated from the relationship (Van Reeuwijk, 1974):

$$\log P(\text{bar}) = -4371.2 T^{-1} + 7.6802 \quad (1)$$

This correction varied from 0.03 J at 450 K to 1.42 J at 550 K to 11.9 J at 623 K.

The enthalpy increments for analcime, including those from the present low temperature study, were fitted as a function of T over the range 298.15–625 K by the method of least squares and the following equation was obtained:

$$\begin{aligned} H^\circ(T) - H^\circ(298.15 \text{ K}) = & -62042.7 + 237.6303 T \\ & - 0.237142 T^2 + 5.552207 \times 10^{-4} T^3 \\ & - 3.090050 \times 10^{-7} T^4 \text{ (J/mol)} \quad (2) \end{aligned}$$

This fit was constrained to give, at $T = 298.15 \text{ K}$, $H^\circ(T) - H^\circ(298.15 \text{ K}) = 0$ and $C_p^\circ(T) = 211.53 \text{ J/(mol}\cdot\text{K)}$ (see Table 4).

Table 8. Drop calorimetric results for analcime. See text for explanation of column headings.

Expt. No.	T	$\Delta\theta_c$	$\epsilon(\text{calor})(\Delta\theta_c)$	$\Delta H(\text{capsule})$	$H^\circ(T) - H^\circ(298.15 \text{ K})^a$
	K	K	J	J	J/mol
3	349.58	0.10891	477.00	137.21	11124
1	349.66	0.10914	478.01	137.43	11149
28	362.51	0.13729	601.29	172.29	14040
5	374.51	0.16350	716.08	204.95	16735
6	374.56	0.16369	716.92	205.09	16756
42	379.06	0.17398	761.98	217.36	17832
33	388.85	0.19522	855.00	244.10	20000
41	390.75	0.20079	879.40	249.30	20625
40	395.42	0.21090	923.67	262.08	21655
7	399.21	0.21885	958.49	272.46	22457
8	399.23	0.21855	957.18	272.51	22413
39	399.85	0.22137	969.53	274.21	22763
37	407.40	0.23797	1042.23	294.91	24470
27	411.80	0.24851	1088.39	306.99	25580
10	423.10	0.27317	1196.38	338.05	28099
9	423.20	0.27307	1195.95	338.33	28077
32	430.51	0.29151	1276.70	358.46	30063
29	435.47	0.30358	1329.56	372.13	31343
12	448.29	0.33255	1456.43	407.51	34339
11	448.36	0.33288	1457.87	407.70	34380
36	455.56	0.35001	1532.89	427.60	36183
34	461.18	0.36357	1592.28	443.14	37619
14	474.53	0.39542	1731.76	480.11	40973
13	474.56	0.39517	1730.66	480.20	40938
31	485.56	0.42217	1848.90	510.71	43803
25	486.34	0.42293	1852.23	512.87	43841
15	497.46	0.45165	1978.01	543.76	46943
16	523.25	0.51553	2257.74	615.52	53746
17	523.33	0.51608	2260.15	615.74	53814
30	534.95	0.54583	2390.43	648.14	57014
18	548.31	0.57901	2535.71	685.43	60530
19	573.24	0.64430	2821.62	755.11	67554
21	573.32	0.64361	2818.59	755.34	67444
20	597.95	0.70964	3107.72	824.32	74548
22	623.36	0.77734	3404.16	895.62	81734

^aIncludes corrections for the enthalpy of the He 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 analcime.

Enthalpy increments of dehydrated analcime were not measured because the published calorimetric results (Pankratz, 1968) were considered to be reliable. However, the composition of the calorimetric sample used in that work was, it is believed, somewhat different than had been originally assumed (Barany, 1962). The analytical results for the analcime from which Barany's dehydrated material was prepared indicated the following composition:

($\text{Na}_{0.949} \text{K}_{0.005} \text{Mg}_{0.001}$) ($\text{Fe}_{0.001} \text{Al}_{0.959}$) $\text{Si}_{2.041} \text{O}_{6.00} \cdot 0.99\text{H}_2\text{O}$. It was assumed by Barany (1962) that this material was a mixture of 96.5% $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, 3.3% silica, and 0.2% water. There was, however, no evidence to support the presence of such a large amount of free silica, and we note that Thompson (1971) found no free silica in analcime from the same locality (Table Mountain, Colorado). If one accepts the composition as given above and assumes that K and Mg substitute for Na and Fe for Al, all without significant thermal or structural effects, then the empirical formula, $\text{Na}_{0.96} \text{Al}_{0.96} \text{Si}_{2.04} \text{O}_{6.00} \cdot 0.99\text{H}_2\text{O}$, which is virtually identical to that found for our material, is obtained.

Accordingly, the calorimetric results (Pankratz, 1968) have been adjusted to refer to $\text{Na}_{0.96} \text{Al}_{0.96} \text{Si}_{2.04} \text{O}_{6.00}$. These recalculated enthalpy increments (400–1000 K) and those obtained in the present study by low-temperature calorimetry to 350 K fall on a smooth curve and have been fitted by a least-squares procedure to the following equation (298.15–1000 K):

$$H^\circ(T) - H^\circ(298.15 \text{ K}) = 1.58298 \times 10^6 T^{-1} - 49386.0 + 110.7986 T + 0.1358596 T^2 - 3.905086 \times 10^{-5} T^3 \text{ (J/mol)} \quad (3)$$

This fit was constrained to give, at $T = 298.15 \text{ K}$, $H^\circ(T) - H^\circ(298.15 \text{ K}) = 0$ and $C_p^\circ(T) = 163.59 \text{ J/(mol}\cdot\text{K)}$ (see Table 5).

Derived heat capacities above 298.15 K

The first derivatives of equations (2) and (3) yield the following expressions for the heat capacities above 298.15 K:

$$C_p^\circ(T)(\text{analcime}) = 237.6303 - 0.474284 T + 1.66566 \times 10^{-3} T^2 - 1.23602 \times 10^{-6} T^3 \text{ (J/K}\cdot\text{mol)} \quad (4)$$

$$C_p^\circ(T)(\text{dehydrated analcime}) = -1.58298 \times 10^6 T^{-2} + 110.799 + 0.27172 T - 1.17153 \times 10^{-4} T^2 \text{ (J/K}\cdot\text{mol)} \quad (5)$$

For later use in the present paper, it will be necessary to express heat capacities in the form:

$$C_p^\circ(T) = a + bT - cT^{-2} \text{ (J/K}\cdot\text{mol)} \quad (6)$$

For analcime, $a = 109.974$, $b = 293.4 \times 10^{-3}$, and $c = -12.514 \times 10^5$; for dehydrated analcime, $a = 168.469$, $b = 109.66 \times 10^{-3}$, and $c = 33.401 \times 10^5$.

Obviously, equation (6) does not represent the heat capacities as precisely as do equations (4) and (5).

Complete thermodynamic functions for analcime and dehydrated analcime

The complete thermodynamic functions of analcime and dehydrated analcime are given in Table 9. For the calculation of ΔH_f° and ΔG_f° , enthalpy increments and standard entropies for Na, Al, Si, O_2 , and H_2 were the critically selected values (Robie, Hemingway, and Fisher, 1978). The ΔH_f° and ΔG_f° values are believed to be uncertain by approximately 4 kJ/mol.

Discussion

Comparison of present results with previous measurements

Low-temperature heat capacity measurements (53–296 K) on analcime have been reported previously (King, 1955). In the vicinity of 53 K, those measurements differ by about 3–4% from the present results; the agreement is better, close to 0.3% at about 280 K. If, however, the composition of the specimen of analcime (King, 1955) is revised as we have described previously, and the heat capacities recomputed, then the agreement is significantly improved and is no worse than about 1.8%. If the heat capacities for dehydrated analcime (King and Weller, 1961) are recalculated in the same way, the agreement is no worse than 0.8%. Our measurements cover a significantly wider temperature range than the earlier studies and are therefore preferred.

The standard enthalpies of formation at 298.15 K derived by us are: $\Delta H_f^\circ(\text{Na}_{0.96} \text{Al}_{0.96} \text{Si}_{2.04} \text{O}_{6.00} \cdot 1.00 \text{H}_2\text{O}, \text{c}, 298.15 \text{ K}) = -3296.9 \pm 3.3 \text{ kJ/mol}$ and $\Delta H_f^\circ(\text{Na}_{0.96} \text{Al}_{0.96} \text{Si}_{2.04} \text{O}_{6.00}, \text{c}, 298.15 \text{ K}) = -2970.2 \pm 3.5 \text{ kJ/mol}$, which differ significantly from those reported previously for the stoichiometric compositions $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ and $\text{NaAlSi}_2\text{O}_6$ (Barany, 1962). We have, however, recomputed his results so that they refer to the revised compositions given earlier. In this recalculation, the most recent $\Delta H_f^\circ(298.15 \text{ K})$ of α -quartz (Wise *et al.*, 1963) has been used, and the thermochemical cycle has been rewritten in terms of gibbsite rather than $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Hemingway, private communication). This latter change has been made because it is believed (Hemingway and Robie, 1977) that the enthalpies of solution of quartz and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Barany, 1962) are in error. A recalculation gives standard enthalpies of formation of -3298.4 ± 2.6 and $-2982.7 \pm 3.6 \text{ kJ/mol}$ for

Table 9. Thermodynamic quantities for analcime and dehydrated analcime

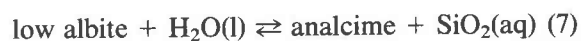
T	$C_p^\circ(T)$	$[H^\circ(T) - H^\circ(298\text{ K})]/T$	$-[G^\circ(T) - H^\circ(298\text{ K})]/T$	$S^\circ(T)$	$H^\circ(T) - H^\circ(298\text{ K})$	$\Delta H_f^\circ(T)$	$\Delta G_f^\circ(T)$
K	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	(kJ/mol)	(kJ/mol)	(kJ/mol)
$\text{Na}_{0.96}\text{Al}_{0.96}\text{Si}_{2.04}\text{O}_6 \cdot \text{H}_2\text{O}(c)$							
0	0	∞	∞	0	-35.60	-3276.5	-3276.5
298.15	211.53	0	226.75	226.75	0.00	-3296.9	-3077.2
300	211.88	1.31	226.75	228.06	0.39	-3296.9	-3075.9
400	235.32	56.73	235.32	292.05	22.69	-3300.0	-3001.8
500	262.40	95.15	252.31	347.47	47.58	-3299.0	-2927.4
600	285.72	125.08	272.41	397.48	75.05	-3295.9	-2853.3
$\text{Na}_{0.96}\text{Al}_{0.96}\text{Si}_{2.04}\text{O}_6(c)$							
0	0	∞	∞	0	-27.06	-2954.1	-2954.1
298.15	163.59	0	171.71	171.71	0.00	-2970.2	-2803.7
300	164.18	1.01	171.71	172.72	0.30	-2970.2	-2802.7
400	190.85	45.32	178.50	223.82	18.13	-2973.4	-2746.4
500	211.04	76.53	192.14	268.67	38.26	-2972.6	-2689.7
600	227.26	100.34	208.29	308.63	60.21	-2970.6	-2633.3
700	240.37	119.44	225.24	344.68	83.61	-2967.6	-2577.3
800	250.72	135.23	242.25	377.48	108.2	-2963.9	-2521.9
900	258.50	148.52	258.97	407.49	133.7	-2959.7	-2466.8
1000	263.78	159.80	275.21	435.01	159.8	-2965.5	-2411.5

analcime and dehydrated analcime, respectively, in good agreement with our results. Although we made a number of assumptions when correcting the measurements of Barany, it appears that his results support the enthalpies of formation obtained in the present work.

The recommended enthalpy of reaction of $\alpha\text{-SiO}_2$ with $\text{HF}(\text{aq})$ (Kilday and Prosen, 1973) continues to be a subject of controversy (Hemingway and Robie, 1977). Accordingly, we have remeasured this quantity (see Tables 6 and 7) and obtained a result about 0.8% less negative than the recommended value. Our value is used in the present study because it is strictly applicable to the conditions of temperature, concentration, and acid strength that prevailed in the calorimetric experiments.

Implications of the thermodynamic results

The concentration of aqueous quartz, $[\text{SiO}_2, \text{aq}]$, in the equilibrium mixture

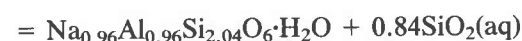


at a pressure of 1 kbar has been determined as a function of temperature by Hemley (private communication, 1973). These results (Table 10) have been used by Helgeson *et al.* (1978) to retrieve $\Delta G_f^\circ(T)$ and $\Delta H_f^\circ(T)$ values for analcime. Conversely, now that $\Delta G_f^\circ(T)$ has been established calorimetrically for analcime, the concentration of aqueous silica can be computed.

In his experiments, Hemley (private communication, 1973) equilibrated Table Mountain analcime with albite; thus, the solution reaction should be written:



low albite



analcime

(8)

Table 10. Concentration of aqueous quartz in equilibrium with albite + analcime + H₂O at a pressure of 1 kbar

T/K	373.15	473.15	573.15	673.15
		-2.45 ± 0.04 ^a	-2.18 ± 0.04 ^a	-2.00 ± 0.04 ^a
log[SiO ₂ , aq]	-3.76 ± 0.86 ^b	-3.22 ± 0.69 ^b	-2.94 ± 0.56 ^b	-2.77 ± 0.48 ^b
		-3.21 ± 0.86 ^c	-2.57 ± 0.56 ^c	-2.46 ± 0.48 ^c

^aHemley (private communication).^bBased on Hemingway and Robie (1977) value for ΔH_f⁰(albite).^cBased on Helgeson *et al.* (1978) value for ΔH_f⁰(albite).

We take the equilibrium constant for reaction (8) to be [SiO₂, aq]^{0.84} and, therefore,

$$\ln[\text{SiO}_2, \text{aq}] = -\Delta G^\circ(P, T)/0.84RT \quad (9)$$

In this equation, ΔG°(P, T) is the standard Gibbs energy change for reaction (8) at pressure P and temperature T. For the purposes of this calculation, ΔG_f⁰(P, T), the apparent standard Gibbs energy of formation as a function of temperature and pressure, is needed for each of the four species in equation (8). Helgeson and Kirkham (1974) and Walther and Helgeson (1977) have tabulated ΔG_f⁰(P, T) for H₂O(l) and SiO₂(aq), respectively, and we have calculated this quantity for analcime and low albite by means of equations (14), (16), (19), (20), and (21) given by Helgeson *et al.* (1978). For analcime, we have used our new results, including equation (6). The situation with low albite is not straightforward, however, because two authoritative values for ΔH_f⁰ have appeared in the recent literature—one based upon a calorimetric determination by Hemingway and Robie (1977), and the other retrieved by Helgeson *et al.* (1978) from a consideration of equilibria involving low albite. Accordingly, we have computed two results for ΔG_f⁰(P, T) of low albite; the difference between them, 3.5 kJ/mol, is, of course, identical to that between the ΔH_f⁰ values. Two corresponding sets of solubilities are given in Table 10. It is clear that the calculated solubilities are in harmony with those obtained by Hemley; the agreement is somewhat better, however, when ΔH_f⁰ (low albite), as given by Helgeson *et al.* (1978), is used in the calculations.

For analcime, the Gibbs energy values extracted from hydrothermal experimental data obtained by Liou (1971), Thompson (1971), and Kim and Burley (1971) are several kilojoules more negative than that given in Table 9. Moreover, they are internally inconsistent (Thompson, 1973). As suggested by Helgeson *et al.* (1978), this may be due to the

unknown compositions of the phases involved, particularly analcime.

In Figure 1, ΔC_p⁰(T) = C_p⁰(T)(analcime) - C_p⁰(T)(dehydrated analcime) has been plotted as a function of temperature. The curve rises more or less regularly to a maximum at about 230 K, goes through a minimum at about 365 K, and then rises smoothly once again. The irregularity of this curve is attributed to internal structural changes in the analcime *vis-a-vis* the positions of the H₂O. The rearrangement of the H₂O is followed by a loss of water which begins at 373 K and continues to 673 K (Balgard and Roy, 1973). A plot of the entropy difference is also given. The entropy change associated with the H₂O rearrangement is evidently quite small, as we are unable to distinguish between the curves for the initial and rearranged states of the zeolite.

A differential scanning calorimetric (DSC) technique has been used (Van Reeuwijk, 1974) for the determination of thermodynamic quantities for the dehydration of analcime. These results are compared in Table 11 along with the same quantities deduced from the data in Table 9. In this table, S_{wz}⁰ denotes the entropy of the zeolitic water which is defined (Van Reeuwijk, 1974) as the difference between the standard entropies of analcime and dehydrated analcime. There is excellent agreement between the two sets of enthalpy values, and at T = 660 K there is little discrepancy between the entropies.

It is also interesting to compare the equilibrium

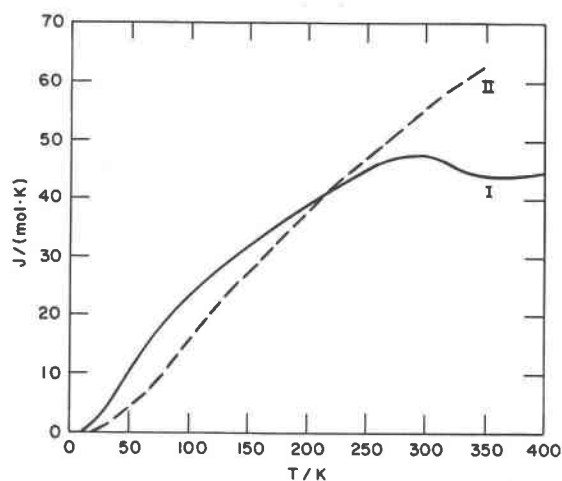


Fig. 1. Curve I gives ΔC_p⁰(T) = C_p⁰(T)(analcime) - C_p⁰(T)(dehydrated analcime). Curve II gives ΔS⁰(T) = S⁰(T)(analcime) - S⁰(T)(dehydrated analcime)

Table 11. Thermodynamic quantities for the reaction: analcime = dehydrated analcime + H₂O (g, 1 bar)

	T (K)	ΔH (kJ/mol)	S_{wz}^0 (J/K \cdot mol)
Van Reeuwijk (1974)	569.0	83.7 \pm 4	97.9 \pm 4.9
	660.0	86.6 \pm 4	
Present work	569.0	80.7 \pm 4	85.8 \pm 0.9
	660.0	79.8 \pm 4	97.2 \pm 0.9
	298.15	84.9 \pm 4	55.1 \pm 0.5

vapor pressures as a function of temperature (Van Reeuwijk, 1974) with those calculated from the results in Table 9. At 660 K, the equilibrium vapor pressure from the DSC study is about 1 bar; the thermodynamic data predict 1.3 bar. However, at 500 K the agreement is not nearly so good, as the DSC technique gave 5×10^{-2} bar, while our results predict 1×10^{-2} bar. It should be pointed out that two vapor pressure curves are given by Van Reeuwijk (1974) to allow for two different types of zeolitic water. However, if no such difference is assumed, then $P(\text{H}_2\text{O})$ from the DSC studies is 5×10^{-3} bar; with this assumption, the agreement is clearly improved.

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