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Heat capacity and entropy of rutile (TiO₂) and nepheline (NaAlSiO₄)

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Abstract From heat capacities measured adiabatically at low temperatures, the standard entropies at 298.15 K of synthetic rutile (TiO₂) and nepheline (NaAlSiO₄) have been determined to be 50.0 ± 0.1 and 122.8 ± 0.3 J mol⁻¹ K, respectively. These values agree with previous measurements and in particular confirm the higher entropy of nepheline with respect to that of the less dense NaAlSiO₄ polymorph carnegieite.

Keywords Rutile · Nepheline · Heat capacity
Entropy

Introduction

Rutile, the TiO₂ polymorph with a tetragonal symmetry, is a common accessory mineral in metamorphic and igneous rocks. Its importance also stems from the fact that it is isostructural to stishovite, a high-pressure polymorph of SiO₂. Although rutile has been selected as a key substance in thermochemistry (Cox et al. 1989), the reliability of available entropy information has been questioned from a thermodynamic analysis of ilmenite–rutile–iron equilibria (O'Neill et al. 1988). From adia-

batic heat-capacity measurements we have thus re-determined the standard entropy of a synthetic sample.

In this paper we also report on the thermodynamic properties of nepheline (NaAlSiO₄). This important mineral, found in a variety of alkaline igneous rocks, is stable up to 1550 K (Greig and Barth 1938), where it transforms into carnegieite, which melts congruently at 1799 K (Schairer and Bowen 1956). As is most generally observed, the high-temperature form, carnegieite, is less dense than the low-temperature polymorph, nepheline. At ambient temperatures, the unusual situation is that available low-temperature heat-capacity measurements indicate that carnegieite has a lower entropy than nepheline (Kelley et al. 1953; Richet et al. 1990). Because these measurements for nepheline extend down only to 54 K, we deemed that a new determination of the third-law entropy of this mineral should also be made.

Experimental methods

The rutile sample from Aldrich Chemical Company was labeled as 99.999% pure. It was heated at 600 °C for 3 h before the experiments. From 12 reflections observed in X-ray diffraction experiments, we determined the unit-cell parameters $a = 4.5936$ (10) and $c = 2.9587$ (2) Å, and the cell volume $V = 62.4327$ (32) Å³, in good agreement with the values $a = 4.5933$ and $c = 2.9592$ Å reported for rutile in the JCPDF file 21-1276.

The nepheline sample was investigated as a fine powder synthesized from a gel as described by Hamilton and Henderson (1968). A solution of aluminum nitrate, sodium carbonate, and tetraethyl orthosilicate, with the required amount of ethanol to ensure the miscibility of the TEOS, was gelled by addition of ammonia. The gel was left overnight, tightly sealed with parafilm in a PTFE vial, and then carefully dried at ca. 400 K for several days, quantitatively transferred in a tared clean silica container, and finally slowly fired to 970 K to decompose the nitrates. The final total weight (about 20 g) was checked against the expected amount. To synthesize nepheline, the gel was kept for 5 days under hydrothermal conditions in an internally heated vessel at 1080 K with initial and final pressures of 3140 and 2000 bar. The cell parameters, determined as described by Roux and Volfinger (1996) from eight reflections observed in the powder X-ray diffraction pattern, are $a = 9.9663$ (48) and $c = 8.3664$ (62) Å, and the cell volume $V = 718.82$ (66) Å³. These data are in good

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agreement with the results previously reported by Henderson and Roux (1977) for samples prepared under similar conditions.

The heat capacities were measured at equilibrium with the Mark XIII cryostat described by Westrum et al. (1968) and Westrum (1988). This is a computer-operated, intermittently heated, adiabatic system for measurements in the range 5–350 K, which has a gold-plated copper calorimeter with an axial entrant well for the heater/thermometer assembly and a gold gasketed screw-type closure. A capsule-type, platinum resistance thermometer calibrated at the National Bureau of Standards was used to determine the sample temperature against the NBS 1955 scale, below 90.18 K, and against the IPTS-48 scale at higher temperatures. Apiezon-T grease was used to enhance thermal contact between the calorimeter and the heater/thermometer assembly.

The heat capacity of the empty calorimeter was determined in a separate series of experiments, in which amounts of Apiezon-T grease and helium gas were used nearly identical to those in the present measurements. The reported data were obtained after subtraction of the heat capacity of the empty calorimeter, appropriate adjustment for the small differences in the amounts of grease and helium, and standard curvature corrections (Justice 1969). The sample weight was 35.3151 g for rutile and 16.3090 g for nepheline. After air had been pumped out of the apparatus, about 10^{-4} mol of helium was introduced to speed up thermal equilibrium. The heat capacity of the sample increased from about 50% at 70 K to 70% at 350 K of the total heat capacity of the calorimeter with the thermometer/heater assembly. Typically, the standard deviations of the reported data are lower than 10% below 15 K, 0.4% between 25 and 50 K, and 0.2% up to 350 K.

Results and discussion

Rutile

The new adiabatic heat capacities of rutile are listed in Table 1 and compared in Fig. 1 with available data. Experimental problems involving a helium leak precluded the planned extension of the measurements from 32 to 5 K. Given the higher error margins of measurements at very low temperatures, our data are consistent with the observations of Sandin and Keesom (1969) made between 4 and 20 K. Good agreement is also found with the adiabatic measurements of Shomate (1947), from 52 to 298 K. In contrast, the data of McDonald and Seltz (1939) are systematically higher than all other observations, for example by more than 3% near room temperature. Other measurements have been made at low temperatures by Dugdale et al. (1954), who also investigated the influence of the particle size, but they have been reported only graphically with the exception of a few fitted data between 20 and 50 K for an impure sample. Finally, measurements have been made above 80 K by laser flash calorimetry by Mitsunashi and Takahashi (1980), who unfortunately reported only fitted data, which agree closely with those of Shomate (1947).

Using the approach of Komada and Westrum (1997), we made a single fit to both our data and those of Sandin and Keesom (1969) to determine down to 5 K the thermodynamic functions of rutile of Table 2. The published standard entropies of rutile are summarized in Table 3. With the exception of the result of McDonald and Seltz (1969), the results are consistent, and indicate that sample or particle size differences do not strongly

Table 1 Experimental heat capacities of rutile (data in K and $\text{J mol}^{-1} \text{K}^{-1}$)

T	C_p	T	C_p	T	C_p
32.85	2.019	140.09	29.14	229.46	46.54
34.65	2.324	145.51	30.49	235.43	47.36
36.85	2.745	150.96	31.82	241.40	48.16
39.25	3.252	156.41	33.11	247.34	48.89
41.55	3.764	161.86	34.38	253.29	49.63
44.21	4.360	167.45	35.61	259.30	50.40
48.26	5.531	169.57	36.06	265.38	51.04
52.96	6.650	173.15	36.73	271.38	51.72
57.05	7.483	175.29	37.28	271.46	51.72
62.53	8.835	178.85	38.02	272.68	51.91
65.78	9.608	180.45	38.33	274.18	52.02
69.25	10.461	182.00	38.63	286.57	53.34
69.49	10.515	187.15	39.62	292.12	53.91
72.85	11.339	189.64	40.10	296.03	54.30
77.96	12.651	192.70	40.68	298.37	54.54
83.77	14.167	193.91	40.89	300.71	54.79
84.46	14.35	195.46	41.21	301.98	54.89
87.50	15.11	197.02	41.45	303.05	54.99
89.20	15.58	197.21	41.49	304.59	55.13
91.55	16.20	200.68	42.08	306.15	55.28
93.56	16.73	202.50	42.41	307.08	55.36
100.50	18.44	206.43	43.06	313.17	55.91
108.11	20.70	208.25	43.37	319.26	56.45
113.14	22.05	212.15	43.99	325.66	56.93
118.50	23.50	214.00	44.25	332.36	57.54
123.86	24.93	217.91	44.87	339.07	57.83
129.24	26.37	219.71	45.14	345.80	58.20
134.66	27.75	223.65	45.72		

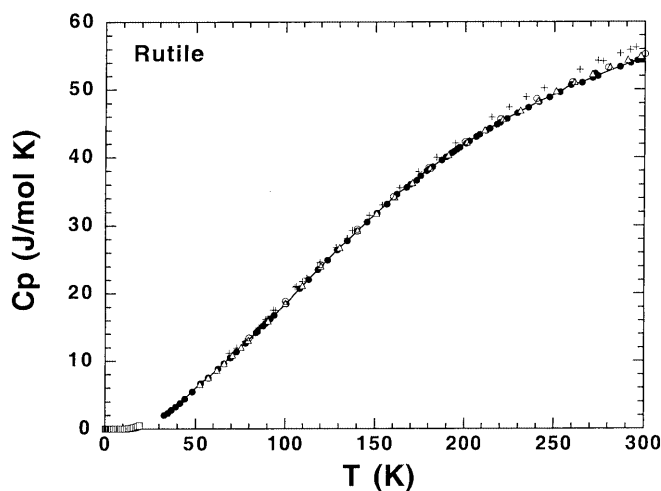


Fig. 1 Low-temperature heat capacity of rutile. Data of McDonald and Seitz (1939, crosses), Shomate (1947, open triangles), Sandin and Keesom (1968, open squares), Mitsunashi and Takahashi (1980, open circles), and this work (solid circles)

affect the entropy. The problems encountered in the thermodynamic analysis of ilmenite–rutile–iron equilibria by O'Neill et al. (1988), therefore, do not appear to originate in a misrepresentation of the actual low-temperature properties of rutile. New high-temperature measurements should prove useful, however, because available relative enthalpy data (Naylor 1946; Slyusar

Table 2 Smoothed heat-capacity and thermodynamic functions of rutile (data in K, J mol⁻¹ K and J mol⁻¹)

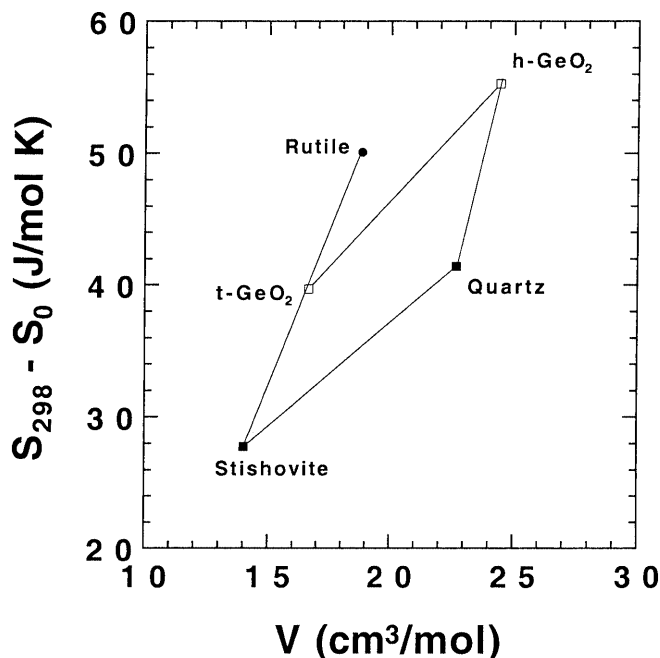
T	C_p	$S_T - S_0$	$H_T - H_0$	$-(G_T - H_0)/T$
0	0	0	0	0
5	0.002	0.000	0	0.000
10	0.018	0.005	0.036	0.001
15	0.132	0.028	0.364	0.005
20	0.493	0.109	1.789	0.019
25	1.011	0.274	5.541	0.052
30	1.564	0.505	11.918	0.108
35	2.395	0.805	21.701	0.185
40	3.438	1.191	36.231	0.286
45	4.565	1.661	56.214	0.412
50	5.740	2.202	81.963	0.563
60	8.164	3.462	151.42	0.938
70	10.65	4.906	245.43	1.400
80	13.18	6.493	364.53	1.936
90	15.79	8.196	509.35	2.536
100	18.46	9.997	680.55	3.191
110	21.16	11.88	878.63	3.895
120	23.87	13.84	1103.8	4.642
130	26.54	15.86	1356.0	5.426
140	29.14	17.92	1634.5	6.245
150	31.62	20.02	1938.3	7.093
160	33.97	22.13	2266.4	7.967
170	36.18	24.26	2617.3	8.863
180	38.24	26.39	2989.5	9.777
190	40.16	28.50	3381.2	10.707
200	42.03	30.61	3793.8	11.643
210	43.63	32.70	4220.4	12.603
220	45.18	34.76	4664.5	13.563
230	46.63	36.81	5123.7	14.529
240	47.98	38.82	5596.8	15.500
250	49.25	40.80	6083.1	16.472
260	50.44	42.76	6581.6	17.446
270	51.65	44.68	7091.6	18.419
280	52.64	46.58	7612.7	19.391
290	53.68	49.94	8144.4	20.361
298.15	54.50	50.28	8582.3	21.149
300	54.69	50.28	8686.3	21.328
325	56.93	54.75	10083	23.728
350	58.39	59.03	11526	26.098

Table 3 Reported standard entropies of rutile, nepheline, and carnegieite at 298.15 K (J mol⁻¹ K)

Rutile (TiO ₂)	
Shomate (1947)	50.24 ± 0.21
McDonald and Seltz (1939)	52.08 ± 0.42
Chase et al. (1985)	50.29
Cox et al. (1989) CODATA key value	50.62 ± 0.30
This work	50.0 ± 0.1
Nepheline (NaAlSi ₃ O ₈)	
Kelley et al. (1953)	124.3 ± 1.3
This work	122.8 ± 0.3
Carnegieite (NaAlSi ₃ O ₈)	
Richet et al. (1990)	118.7 ± 0.2

et al. 1973) show an unusual discrepancy of more than 5%.

Our results also confirm the difficulties of modeling accurately the heat capacity of rutile at low temperature, since they leave intact the discrepancies that range from -11% at 20 K to -3% at 240 K noted by Traylor et al. (1971) between their lattice dynamical calculations and

**Fig. 2** Standard entropy of rutile (this work), stishovite (Holm et al. 1967), quartz (Richet et al. 1982), and the hexagonal (King 1958) and tetragonal (Counsell and Martin 1967) forms of GeO₂, which are isostructural to quartz and rutile, respectively

the experimental values. This discrepancy has been assigned by Gervais and Kress (1983) to the fact that the anisotropy of the strong polarizability of oxygen in the presence of a transition metal ion is enhanced through hybridization between oxygen p states and titanium d states. As a result, rutile is an incipient ferroelectric showing soft modes associated with a markedly dependent dielectric constant. On the other hand, our data confirm the simple entropy-molar volume relationships for TO₂ oxides with quartz and rutile structures in which the cation T is either tetrahedrally or octahedrally coordinated by oxygen (Fig. 2). As noted by Richet et al. (1993), the standard entropy varies linearly with the molar volume for the three compounds with the rutile structure. This simple relationship supports the much-debated calorimetric standard entropy of 27.8 J mol⁻¹ K measured at 298.15 K by Holm et al. (1967) for a natural stishovite sample from Meteor Crater (Arizona).

Nepheline

For nepheline, the adiabatic measurements are listed in Table 4. The smoothed values are reported in Table 5 along with the derived thermodynamic functions. The comparison made in Fig. 3 with the measurements of Kelley et al. (1953), which begin at 54 K, shows very good agreement up to 200 K. Above this temperature, the data of Kelley et al. (1953) become slightly lower than the present results, but Kelley et al. (1953) derived a slightly higher standard entropy than the present value

Table 4 Experimental heat capacities of nepheline (data in K and $\text{J mol}^{-1} \text{K}$)

T	C_p	T	C_p	T	C_p
Series 1		Series 2		217.93	98.13
8.59	0.096	60.24	25.82	223.81	99.40
10.30	0.304	63.28	27.93	229.76	101.85
11.20	0.530	66.35	29.87	235.71	102.95
12.56	0.630	69.59	31.87	241.67	105.57
13.90	0.721	72.99	33.89	247.62	106.27
15.32	1.080	76.56	36.28	253.60	108.75
16.90	1.429	80.32	38.41	259.55	110.05
18.49	1.862	84.27	40.99	265.57	112.06
19.95	2.341	88.42	43.30	271.61	112.79
21.45	2.863	92.79	45.66	277.70	114.87
23.13	3.534	97.39	48.09	283.78	116.36
24.83	4.272	102.43	50.70	289.91	118.12
26.56	5.136	107.79	53.60	295.98	119.68
28.47	6.044	113.17	56.11	302.08	120.06
30.54	7.100	118.57	58.91	308.18	121.66
32.69	8.259	123.99	61.75	314.26	123.29
34.85	9.366	129.41	64.19	320.34	125.15
37.00	10.766	134.86	66.86	326.39	125.61
39.28	12.177	140.31	69.72		
41.63	13.672	145.78	71.79	Series 3	
44.03	15.22	151.26	74.53	285.21	117.02
46.45	16.90	156.74	76.49	290.14	117.41
48.90	18.39	162.24	79.18	296.24	119.26
51.55	20.14	167.74	81.03	302.33	120.48
54.39	22.06	173.35	83.20	308.42	122.18
57.26	23.90	179.07	85.27	314.51	123.13
60.15	25.86	184.79	87.57	320.60	125.28
63.05	27.70	190.51	89.38	326.68	125.49
		196.24	91.51	332.76	128.04
		201.98	92.84	338.83	128.05
		207.93	95.23	344.91	129.93
		213.66	96.84		

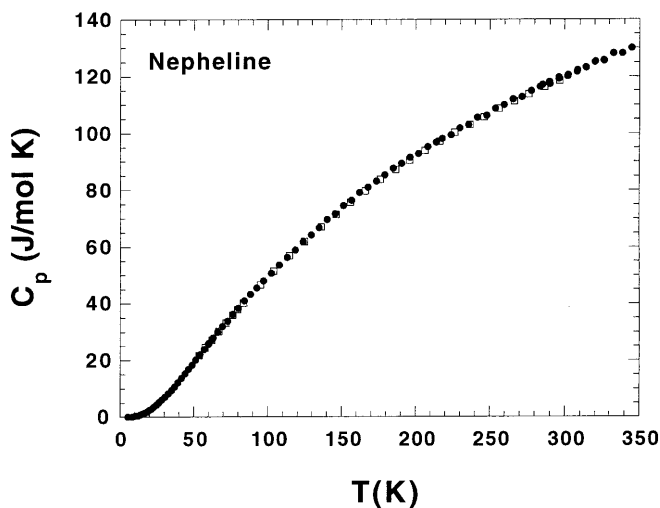
(Table 3), probably because their extrapolation down to 0 K overestimated the heat capacity. Both determinations are, nonetheless, consistent over the common regions of measurements.

Four different tetrahedral sites, which are occupied by Si and Al, exist in the nepheline structure (e.g., Gregorkiewitz 1984). The configurational entropy of nepheline was assumed to be zero by Kelley et al. (1953). That Si and Al actually have an ordered distribution has been demonstrated by structure determinations (Gregorkiewitz 1984) and ^{29}Si nuclear magnetic resonance spectroscopy (Stebbins et al. 1986). Using the calorimetric data of Kelley et al. (1953) for nepheline, and newly measured heat capacities and enthalpies of transition for the carnegieite and the glass and liquid phases of NaAlSiO_4 , Richet et al. (1990) found a very good consistency between the thermodynamic properties and phase equilibria information for these amorphous and crystalline phases of NaAlSiO_4 . We have not deemed necessary to update this dataset in view of the marginal difference between our new standard entropy for nepheline and the result of Kelley et al. (1953), and also because of the lack of a new determination of the high-temperature heat capacity of nepheline.

As already noted, carnegieite has a lower entropy than nepheline (Table 3). Because carnegieite is less

Table 5 Smoothed heat capacity and thermodynamic functions of nepheline (data in K, $\text{J mol}^{-1} \text{K}$ and J mol^{-1})

T	C_p	$S_T - S_0$	$H_T - H_0$	$-(G_T - H_0)/T$
0	0	0	0	0
5	0.039	0.013	0.049	0.003
10	0.305	0.103	0.769	0.026
15	1.006	0.341	3.825	0.086
20	2.329	0.795	11.872	0.201
25	4.362	1.520	28.315	0.387
30	6.913	2.536	56.37	0.657
35	9.578	3.802	97.59	1.014
40	12.625	5.278	153.03	1.452
45	15.83	6.949	224.12	1.969
50	19.12	8.786	311.46	2.557
60	25.71	12.855	535.60	3.928
70	32.11	17.30	824.90	5.516
80	38.23	21.99	1176.9	7.279
90	44.03	26.83	1588.4	9.181
100	49.55	31.76	2056.5	11.195
110	54.81	36.73	2578.5	13.289
120	59.85	41.72	3152.0	15.45
130	64.69	46.70	3774.9	17.66
140	69.31	51.67	4445	19.92
150	73.72	56.60	5160	22.20
160	77.92	61.49	5919	24.50
170	81.89	66.34	6718	26.82
180	85.65	71.12	7556	29.14
190	89.19	75.85	8430	31.48
200	92.55	80.51	9339	33.82
210	95.74	85.10	10281	36.14
220	98.8	89.63	11253	38.48
230	101.75	94.09	12256	40.80
240	104.61	98.48	13288	43.11
250	107.41	102.81	14348	45.42
260	110.13	107.07	15436	47.70
270	112.78	111.28	16551	49.98
280	115.34	115.43	17691	52.25
290	117.81	119.52	18857	54.50
298.15	119.73	122.81	19825	56.32
300	120.16	123.55	20047	56.73
325	125.64	133.39	23121	62.25
350	131.02	142.89	26328	67.67

**Fig. 3** Low-temperature heat capacity of nepheline. Data from Kelley et al. (1953, *open squares*) and this work (*solid circles*)

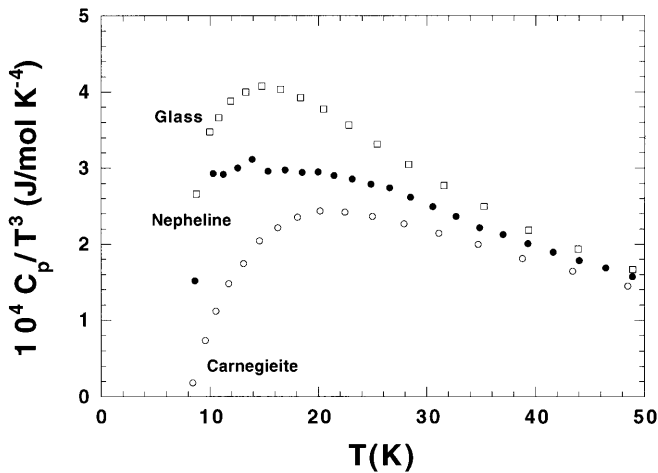


Fig. 4 Deviations of the heat capacities of nepheline, carnegieite and NaAlSiO_4 glass from Debye's laws. Data from Richet et al. (1990) for carnegieite (*open circles*) and NaAlSiO_4 glass (*open squares*) and this work for nepheline (*solid circles*)

dense than nepheline, this result seems to contradict the well-established empirical observation that the standard entropy of minerals increases with the molar volume (Robinson and Haas 1983; Holland 1989). In fact, this anomaly mainly stems from the premonitory effects of the α - β phase transition of nepheline that takes place near 450 K (Henderson and Thompson 1980). A second contribution to the entropy difference between nepheline and carnegieite is found below 50 K, where deviations from Debye's laws are higher for nepheline than for carnegieite (Fig. 4), but lower than for NaAlSiO_4 glass. In all three cases, a marked boson peak is apparent, with a maximum at about 20 K, as observed previously for other tectosilicates like anorthite and SiO_2 polymorphs (e.g., de Ligny et al. 1996). As reported for SiO_2 polymorphs (Buchenau et al. 1986), the excess C with respect to Debye's model should be due to coupled librations at THz frequencies of the corner-shared three-dimensional network of SiO_4 and AlO_4 tetrahedra. The C_p difference between nepheline and carnegieite would thus mean that the excess density of state of the former is either greater or shifted to frequencies lower than that of the latter.

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