percent, unaffected by the increasing size and mass of the cation. The activation energy for viscous flow is also nearly constant. (b) Viscosities and activation energies increase from $MgCl_2$ to $BaCl_2$. (c) Equivalent conductances decrease and activation energies increase from LiCl to CsCl. (d) There is a maximum in the conductance curve for the alkaline-earth chlorides at $CaCl_2$, caused by a relatively low value for $MgCl_2$. The activation energy is nearly constant (cf. below for data reliability).

These features conflict with chemical intuition: where one group behaves "ideally" in the sense that the property under consideration changes in a more or less regular fashion as one descends the ladder of the periodic system, the other property does not, and the property that has this ideal aspect in one group is the one that shows anomalies in the other group. Furthermore, anomalies for LiCl and $MgCl_2$ could reasonably be expected—almost demanded. They are remarkably absent except for the low conductance of $MgCl_2$, which is not dramatically low (30% under that of $BaCl_2$).

The conductance of $MgCl_2$ has been taken as evidence of covalent bonding. This leaves the problem of explaining a viscosity that by the same line of reasoning is quite normal. Neither do the activation energy curves in Figure 2 reflect this proposed structural different from the other group 2 chlorides. The low conductance of $MgCl_2$ is the *only* sign of covalency, and no more spectacular than some other features in Figure 2. We are aware that there is considerable evidence for the complex-forming ability of the Mg^{2+} cation in mixtures with other chlorides. The point that we wish to reiterate here is that macroscopic transport properties are not easily predicted even for relatively simple liquids.

Different authors disagree on the activation energies of electrical transport to an extent that makes details in the corresponding curves in Figure 2 uninteresting. If only MSDC-recommended values are considered, for example, then the weak minimum for $CaCl_2$ disappears completely. It might also be noted that the activation energy for viscous flow is slightly temperature dependent for $CaCl_2$, $SrCl_2$, and $BaCl_2$ according to Table II.

Plotting against the size or mass of the cations is no more illuminating than the row number selected in Figure 2. Interestingly, the lanthanide contraction in the radii of the alkaline earths is not usually met with a corresponding reduction in the transport properties, which causes several artificial-looking maxima and minima to emerge if the radius is chosen as the plotting parameter.

All pure salts hitherto examined by our latest viscometer (alkali-metal chlorides (*4*) and NaF (*7*)) have had one characteristic in common—they follow the Arrhenius (or Kelvin) temperature rule within 0.1% over the entire experimental range of temperatures. So do salt mixtures in which there is little evidence of shifting chemical equilibria (*2*, *7*, *6*, *10*). In the opposite case, the curves have always been nonlinear, and without exception concave upwards. Aluminum chloride is in a special class, since the Arrhenius plot for the pure compound is concave downwards (*2*). However, this is exactly what must be expected for a liquid that approaches its critical point. Although the validity of the Arrhenius rule has been questioned for constant-pressure transport processes, and a number of other temperature functions have been proposed, we arrived at the tentative conclusion that deviations are essentially associated with a liquid structure in which several species coexist in concentrations that depend on the temperature. This assumption worked well in several models for complex-forming liquids (*2*, *7*, *6*, *10*). The slight, but significant, deviations exhibited by $CaCl_2$, $SrCl_2$, and probably $BaCl_2$ are therefore disturbing to us. Almost as puzzling is the fact that the single salt which does not deviate is precisely that which was expected to do so, namely, $MgCl_2$. More data of accuracy and precision similar to the present are needed to determine what the typical temperature response—if any—of the group 1 and 2 halides is.

Acknowledgment

We thank Mrs. G. Urdahl and Mr. Th. Tharaldsen for experimental assistance.

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Received for review January 27, 1982. Accepted July 12, 1982. Financial support from "Norges teknisk-naturvitenskapelige forskningsråd" is gratefully acknowledged.

Low-Temperature Heat Capacities of Sodium Hexatitanate

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Low-temperature heat capacities of sodium hexatitanate, $Na_2Ti_6O_{13}(c)$, were measured at the U.S. Bureau of Mines over the nominal range 5.5–308 K by using precision adiabatic calorimetry. The standard entropy, $S^\circ_{298.15}$, of 95.27 ± 0.3 cal K^{-1} mol^{-1} was derived assuming $S^\circ = 0$ at 0 K.

Introduction

This investigation is part of a Bureau of Mines program to provide basic thermodynamic data useful to the mineral and chemical industries. Previous Bureau studies (*1*, *2*) have determined formation enthalpies and entropies of several closely related sodium titanates. The present study provides low-tem-

Table I. Observed Heat Capacities of $Na_2Ti_6O_{13}(c)$

T, K	$C_p°$, cal K^{-1} mol^{-1}	T, K	$C_p°$, cal K^{-1} mol^{-1}
5.54	0.019	59.52	17.947
5.72	0.021	66.32	21.337
6.43	0.037	73.96	25.146
7.55	0.052	81.42	28.817
8.46	0.081	89.49	32.781
9.33	0.123	98.64	37.073
10.26	0.181	108.63	41.690
11.21	0.253	119.98	46.665
12.37	0.354	129.98	50.700
13.38	0.463	140.15	54.929
14.37	0.577	153.67	59.201
15.30	0.707	162.76	63.162
16.20	0.852	173.86	66.883
16.93	0.972	185.66	70.548
18.76	1.306	197.43	73.877
21.50	1.933	209.66	77.235
24.38	2.798	221.69	80.273
27.47	3.676	232.63	82.752
30.82	4.852	243.44	85.145
32.84	5.622	254.38	87.424
35.49	6.592	265.52	89.614
38.63	8.012	276.48	91.428
42.06	9.209	287.30	93.344
45.70	11.213	298.03	94.894
49.89	13.261	308.65	96.456
54.06	15.240		

perature heat capacities obtained by precision adiabatic calorimetry to evaluate the entropy of sodium hexatitanate, $Na_2Ti_6O_{13}(c)$. Measurements were accomplished in the temperature range 5.5–308.6 K. Smoothed values of heat capacity and related thermodynamic functions are tabulated within this range.

Materials and Apparatus

A single-phase, crystalline sample of high-purity $Na_2Ti_6O_{13}(c)$ was prepared by heating a stoichiometric mixture of sodium carbonate and titanium oxide for 3 h at 1273 K, followed by 17 h at 1143 K, and then finishing at 1323 K for 2 h. Chemical analysis of the resulting titanate gave 11.43 wt % Na_2O (theoretical = 11.45) and 88.55 wt % TiO_2 (theoretical = 88.55). The powder X-ray diffraction agreed with the ASTM catalog pattern for $Na_2Ti_6O_{13}(c)$. No significant metallic impurities were detected by emission spectrographic analysis.

Low-temperature measurements were made with a 0.229 34-mol (124.158-g) sample based on a calculated molecular weight of 541.372. An adiabatic calorimeter capable of measuring heat capacities of solids in the nominal temperature range of 4.6–310 K was used. A precision platinum resistance thermometer calibrated by the NBS to IPTS-68 was used for all calorimetric temperature measurements above 15 K. Temperatures below 15 K were obtained with a germanium resistance thermometer calibrated in the NBS Provisional Scale 2–20 K (1965). The high-resolution potentiometric technique of temperature measurement utilized was capable of resolving temperature differences of ±0.0001 K and absolute temperature with uncertainties of approximately ±0.005 K. Additional details of the experimental procedures and construction of the calorimeter are given elsewhere (*3*).

Results and Discussion

Measured heat capacities per mole of $Na_2Ti_6O_{13}(c)$ are listed in Table I. Energy units are in thermochemical calories (1 cal = 4.1840 J). No unusual thermal behavior was noted in the observed temperature range. These data were fitted with several overlapping orthogonal polynomial functions for the purpose of calculating heat capacities and deriving thermodynamic functions at selected temperature intervals. The results of this smoothing process and ancillary computations are given in Table II. The estimated uncertainties of the observed ata are approximately as follows: ±5%, 5–15 K; ±0.2%, 16–50 K; and ±0.1%, 50–300 K. Observed heat capacity data were extrapolated below 5.5 K to 0 at 0 K by using the function C_p/T vs. T^2, thus permitting evaluation of the heat capacity, the enthalpy, and the absolute entropy at 5 K. No other low-temperature heat capacity data for $Na_2Ti_6O_{13}(c)$ were found in the literature.

Table II. Thermodynamic Properties of $Na_2Ti_6O_{13}(c)$

T, K	$C_p°$, cal K^{-1} mol^{-1}	$S°$, cal K^{-1} mol^{-1}	$-(G° - H°_0)/T$, cal K^{-1} mol^{-1}	$H° - H°_0$, cal mol^{-1}
5	0.014	0.006	0.002	0.018
10	0.164	0.051	0.016	0.348
15	0.676	0.199	0.048	2.263
20	1.563	0.505	0.121	7.681
25	2.891	0.989	0.243	18.649
30	4.562	1.659	0.420	37.160
35	6.481	2.504	0.656	64.68
40	8.597	3.505	0.948	102.30
45	10.888	4.648	1.294	150.94
50	13.287	5.920	1.692	211.39
60	18.18	8.771	2.629	368.50
70	23.17	11.948	3.730	575.3
80	28.14	15.37	4.969	831.9
90	33.00	18.96	6.323	1137.7
100	37.73	22.69	7.772	1491.5
110	42.29	26.50	9.301	1891.7
120	46.67	30.37	10.895	2336.6
130	50.85	34.27	12.542	2824.4
140	54.84	38.18	14.234	3353.0
150	58.63	42.10	15.96	3920.5
160	62.22	46.00	17.72	4524.9
170	65.61	49.87	19.49	5164
180	68.80	53.71	21.29	5836
190	71.81	57.52	23.10	6540
200	74.64	61.27	24.91	7272
210	77.31	64.98	26.73	8032
220	79.82	68.63	28.55	8818
230	82.19	72.23	30.37	9628
240	84.42	75.78	32.19	10461
250	86.53	79.27	34.01	11316
260	88.52	82.70	35.81	12191
270	90.38	86.08	37.61	13086
273.15	90.93	87.13	38.18	13371
280	92.10	89.40	39.40	13998
290	93.71	92.66	41.18	14927
298.15	94.94	95.27	42.63	15696
300	95.21	95.86	42.95	15872

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Received for review December 24, 1981. Accepted May 17, 1982.