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High-Temperature Relative Enthalpies and Related Thermodynamic Properties of $\text{Na}_2\text{Ti}_6\text{O}_{13}$

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere	J	joule
cal	calorie	K	kelvin
cal/(mol·K)	calorie per mole per kelvin	kcal/mol	kilocalorie per mole
cm ³	cubic centimeter	μK	microkelvin
g	gram	μV	microvolt
g/cm ³	gram per cubic centimeter	ppm	part per million
h	hour	wt %	weight percent

HIGH-TEMPERATURE RELATIVE ENTHALPIES AND RELATED THERMODYNAMIC PROPERTIES OF $\text{Na}_2\text{Ti}_6\text{O}_{13}$

By M. J. Ferrante ¹

ABSTRACT

Relative enthalpies of high-purity disodium hexatitanate ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) were measured at the Bureau of Mines to provide new thermodynamic data needed to advance the technology of materials. Measurements from 298.15 to 1,478 K were made by drop calorimetry with a copper block. Tabulated values are listed for the standard relative enthalpy, heat capacity, entropy, and Gibbs energy function between 298.15 and 1,500 K. Enthalpy data are also given in equation form and are combined with thermodynamic data from the literature to derive values of standard enthalpies of formation, Gibbs energies of formation, and logarithms of the equilibrium constants of formation. Similar calculations were made for the reaction of Na_2O with TiO_2 .

INTRODUCTION

Relative enthalpies of disodium hexatitanate ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) were determined at the Bureau of Mines as part of a continuing program to investigate metallurgically important titanium compounds for the extraction of titanium from its ores. (Sodium titanates are formed when titaniferous iron ores are smelted under a slag containing sodium carbonate.) Because no high-temperature enthalpy data were available to study reactions involving $\text{Na}_2\text{Ti}_6\text{O}_{13}$, the present investigation was undertaken to supplement related studies conducted at the Bureau by Stuve (1),² Bennington (2), Shomate (3), and Naylor (4).

The measurements of relative enthalpies were made with a copper-block calorimeter capable of yielding highly reliable results. These results were combined with auxiliary data from the literature to derive complete thermodynamic properties at elevated temperatures for $\text{Na}_2\text{Ti}_6\text{O}_{13}$. Unless designated otherwise, $\text{Na}_2\text{Ti}_6\text{O}_{13}$ refers to the stable phase that exists between 0 and about 1,500 K and has a monoclinic crystal structure as shown on Powder Diffraction File (PDF) card 14-277.

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²Underlined numbers in parentheses refer to items in the list of references at the end of this report.

MATERIALS

Enthalpy measurements of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ were made with the same high-purity sample used by Stuve to determine low-temperature heat capacities and by Bennington to determine the enthalpy of formation at 298.15 K. The $\text{Na}_2\text{Ti}_6\text{O}_{13}$ was made by heating a stoichiometric mixture of titanium oxide (TiO_2) and sodium carbonate (Na_2CO_3) at 1,273 K for 3 h, 1,143 K for 17 h, and 1,323 K for 2 h. After an adjustment for a slight deficiency of sodium, the pulverized sample was

heated at 1,023 K for 15 h and finally at 1,323 K for 2 h. Chemical analyses of the powdered product showed 88.55 wt % TiO_2 and 11.43 wt % Na_2O , compared with the stoichiometric composition of 88.55 and 11.45 wt %, respectively. Less than 100 ppm metallic impurities were detected by optical emission spectroscopy. X-ray powder diffraction analysis showed that the pattern matched that listed in PDF card 14-277.

EXPERIMENTAL WORK AND RESULTS

Enthalpies relative to 298.15 K were measured with a drop calorimeter in an isothermal jacket. In this method, an encapsulated sample was heated in a furnace to a known temperature and dropped into the copper block. In order to provide a nearly isothermal region for heating the sample, one furnace with a cylindrical heat sink of silver was used to 1,200 K, and another furnace with a cylindrical heat sink of platinum was used between 1,200 and 1,800 K. The temperature of the sample in both furnaces was measured with platinum versus platinum-10 wt % rhodium thermocouples, which were frequently calibrated against the melting point of gold. The temperature of the calorimeter was measured with a resistance thermometer of the transposed bridge type that is wound around the copper block, which provides a significantly greater temperature sensitivity than a single winding. The use of the resistance thermometer in conjunction with a six-dial potentiometer and nanovolt null detector can resolve changes equivalent to $\pm 50 \mu\text{K}$ or $\pm 0.02 \mu\text{V}$. Before and after a series of enthalpy determinations for each substance, the calorimeter is calibrated electrically, and its constancy serves as a check on the precision of measurements. The average deviation of the electrical calibrations was 0.02%. The enthalpy of periclase (MgO) was also measured before and after a series of

enthalpy determinations for each substance, which served as an overall check of the entire equipment. Results of the MgO measurements agreed within 0.1% with the values derived by Pankratz (5) from studies conducted by Barron (6), Victor (7), and Pankratz (8). Detailed descriptions of the construction and operation of the drop calorimeter and furnaces are given by Ferrante (9).

Measurements of relative enthalpies were made with $\text{Na}_2\text{Ti}_6\text{O}_{13}$ sealed in a capsule of platinum-10 wt % rhodium (Pt-10 wt % Rh). The powdered $\text{Na}_2\text{Ti}_6\text{O}_{13}$ was loaded into the capsule in air. After the capsule was evacuated and backfilled with approximately 1 atm of ultra-high-purity helium, its neck was squeezed gastight. The neck of the capsule was then sealed by arc-welding with a non-consumable electrode under a stream of inert gases. A sample mass of 8.90843 g was sealed in 9.96850 g of Pt-10 wt % Rh. This amount of Pt-10 wt % Rh accounted for approximately 16% of the measured enthalpy. Enthalpies of the empty capsule were determined in separate tests. The mass of the capsule and sample was periodically checked for constancy by weighing between enthalpy measurements. All weighings were corrected to vacuum. A density of 3.51 g/cm^3 was used for $\text{Na}_2\text{Ti}_6\text{O}_{13}$, and the molecular weight of 541.25174 conforms to the 1981 Table of Atomic Weights (10).

TABLE 1. - Experimental measurements of relative enthalpies for $\text{Na}_2\text{Ti}_6\text{O}_{13}(\text{c})$

T, K	$\text{H}^\circ - \text{H}_{298}^\circ$, kcal/mol	Deviation, %	Run	T, K	$\text{H}^\circ - \text{H}_{298}^\circ$, kcal/mol	Deviation, %	Run
402.8	10.633	0.13	1	1,002.3	82.377	0.16	7
502.8	21.676	-.05	2	1,103.2	94.935	-.07	8
602.3	33.229	-.05	3	1,195.0	106.716	-.04	9
702.3	45.217	.01	4	² 1,265.7	116.005	.06	10
¹ 802.1	57.141	-.42	14	² 1,371.9	129.978	.03	11
802.1	57.383	.00	5	² 1,478.1	144.221	-.01	12
902.0	69.771	.07	6	^{1,2} 1,576.7	209.267	24.6	13

¹These runs were discarded; see "Discussion" section for reasons.

²Furnace with platinum heat sink used; other measurements used furnace with silver heat sink.

Relative enthalpies are expressed in terms of the thermochemical calorie where 1 cal = 4.1840 J. The results of enthalpy measurements were converted to kilocalories per mole and are listed in table 1 in order of increasing temperatures as standard enthalpies relative

to 298.15 K ($\text{H}^\circ - \text{H}_{298}^\circ$). The temperature (T) is in kelvin as defined by the International Temperature Scale of 1968 (11). Table 1 also shows the percent deviation between the experimental and smoothed values. The smoothed values are given in the "Discussion" section.

DISCUSSION

The relative enthalpies of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ were fitted with a smooth curve by a least squares technique. The fit was made with a polynomial function in terms of temperature by using a modified form of the computer program described by Justice (12). Care was taken during this fitting process to smoothly merge the high-temperature values with the low-temperature data between 250 and 298.15 K reported by Stuve (1). These low-temperature data were given more weight than the high-temperature enthalpy measurements near 400 K. The precision of measurements at this temperature is significantly less than it is above 500 K because of the small amount of heat measured. The polynomial giving the best fit to the experimental measurements was selected. The polynomial was then used to calculate smooth values of standard enthalpy ($\text{H}^\circ - \text{H}_{298}^\circ$) and related thermodynamic properties of heat capacity (C_p°), entropy (S°), and Gibbs energy function [$-(\text{G}^\circ - \text{H}_{298}^\circ)/\text{T}$]. These values

are listed in table 2 at selected temperature intervals above 298.15 K. A simplified standard equation, instead of the polynomial, is given later to represent the smoothed enthalpies because the polynomial can have up to 10 terms, with each term having 17 digits. Rounding of these numbers results in significant differences from the precise smooth values given in tabular form. The tabulated values are listed to three decimals to maintain internal consistency among the values, even though the experimental precision does not warrant this exactness.

The selected polynomial was also used to calculate smooth values of relative enthalpies at the temperatures of the experimental measurements. These smooth enthalpies were compared with the measured enthalpies to derive the deviations shown in table 1. The standard deviation of the measured enthalpies from the smoothed values was 0.08%. The absolute uncertainty of the smoothed values was estimated to be $\pm 0.3\%$.

TABLE 2. - High-temperature thermodynamic properties of $\text{Na}_2\text{Ti}_6\text{O}_{13}(\text{c})$

T, K	cal/(mol·K)			$H^\circ - H_{298}^\circ$, kcal/mol
	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	
298.15	94.940	95.270	95.270	0
300	95.210	95.858	95.271	.176
400	106.690	124.963	99.162	10.320
500	113.708	149.585	106.850	21.368
600	118.103	170.736	115.777	32.975
700	120.888	189.167	124.974	44.935
800	122.751	205.438	134.035	57.122
900	124.197	219.981	142.791	69.472
1,000	125.593	233.138	151.178	81.960
1,100	127.183	245.181	159.184	94.597
1,200	129.106	256.327	166.820	107.408
1,300	131.388	266.749	174.110	120.430
1,400	133.954	276.578	181.082	133.695
1,500	(136.623)	(285.911)	(187.762)	(147.224)

NOTE.--Values in parentheses are extrapolations.

No enthalpy measurements for $\text{Na}_2\text{Ti}_6\text{O}_{13}$ were found in the literature. The relationship between the measured and smoothed enthalpies of the present investigation is shown graphically in figure 1 as the mean heat capacity, $(H^\circ - H_{298}^\circ)/(T - 298.15)$, versus T. Although

continuity was established down to 250 K during the merging of the high- and low-temperature data, the curve of figure 1 was extended down only to the low-temperature value of 300 K.

Enthalpy measurements were discontinued when it became apparent that the last valid experiment on the smooth curve was 1,478.1 K. The next measurement, at 1,576.7 K, showed by its high thermal effect, equivalent to 24.6% or 51.5 kcal/mol above the smooth curve, that a significant change in the $\text{Na}_2\text{Ti}_6\text{O}_{13}$ had occurred. The change was found to be irreversible when it was not possible to reproduce an enthalpy value previously obtained at a lower temperature. This measurement at 802.1 K was -0.42% or -0.239 kcal/mol below the smooth curve, which is about four times larger than the precision of the calorimeter. The average deviation of the 12 valid measurements from the smooth curve was 0.06%. A subsequent experiment at 1,627 K was aborted when the liquefied sample leaked from the capsule. X-ray powder diffraction analysis of the capsule contents after melting showed primary phases of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and disodium trititanate ($\text{Na}_2\text{Ti}_3\text{O}_7$) with a minor phase of rutile

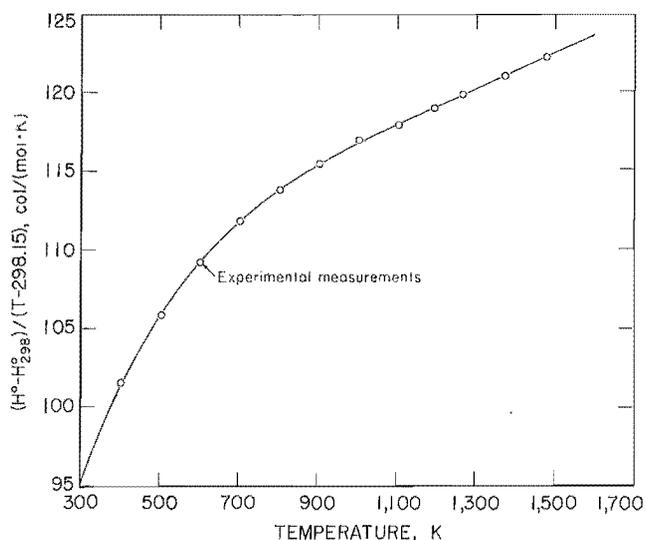


FIGURE 1. - Variation of mean heat capacity with temperature for $\text{Na}_2\text{Ti}_6\text{O}_{13}(\text{c})$.

(TiO₂). Because the temperature at which the change in Na₂Ti₆O₁₃ takes place is not precisely known, the smoothed data of table 2 were extrapolated only from 1,478.1 to 1,500 K.

The smoothed enthalpies are given in a simplified algebraic form to better meet the needs of various users. The equation given below was derived from the smooth enthalpies of table 2 by Kelley's method (13). Because this equation contains a maximum of 4 terms, it gives less precise values than the tabulated values that were calculated from the polynomial; however, it is obviously more convenient to use a simplified equation that has 6 or fewer digits in a maximum of 4 terms rather than a polynomial with 17 digits in a maximum of 10 terms. The equation has been widely adopted as the standard form for the algebraic representation of high-temperature enthalpy values because it gives an adequate fit of the values without introducing undue complexity. The equation is given below with the temperature range of validity and the

average deviation from the smoothed data shown in parentheses.

$$\begin{aligned} H^\circ - H_{298}^\circ, \text{ kcal/mol} &= 115.444 \times 10^{-3} T \\ &+ 6.626 \times 10^{-6} T^2 + 21.739 \times 10^2 T^{-1} \\ &- 42.300 \end{aligned}$$

(298-1,500 K; 0.1%).

Standard enthalpies of formation (ΔH_f°), Gibbs energy of formation (ΔG_f°), and logarithms to the base 10 of the equilibrium constants of formation (log Kf) were derived as functions of temperature for Na₂Ti₆O₁₃ by combining relative enthalpies from the present investigation with supplementary data from other investigations. The results of these calculations are listed in table 3. Calculations were also made for the reaction of Na₂O(c) with TiO₂(c), and these are shown in table 4. For Na₂Ti₆O₁₃, S_{298}° was taken from Stuve (1) and ΔH_f° from Bennington (2). The remaining auxiliary data were obtained from Pankratz (5).

TABLE 3. - Formation data for 2Na(c,ℓ,g) + 6Ti(c) + 6.5 O₂(g) = Na₂Ti₆O₁₃(c)

T, K	kcal/mol		Log Kf	T, K	kcal/mol		Log Kf
	ΔH_f°	ΔG_f°			ΔH_f°	ΔG_f°	
298.15	-1,510.900	-1,423.906	1,043.738	1,000	-1,504.399	-1,221.318	266.915
300	-1,510.899	-1,423.358	1,036.903	1,100	-1,503.306	-1,193.103	237.045
¹ 371	-1,510.676	-1,402.658	826.272	² 1,156	-1,502.707	-1,177.297	222.573
371	-1,511.920	-1,402.658	826.272	1,156	-1,508.809	-1,177.297	222.573
400	-1,511.754	-1,394.124	761.704	³ 1,177	-1,508.452	-1,171.277	217.484
500	-1,510.797	-1,364.825	596.557	1,177	-1,555.022	-1,171.277	217.484
600	-1,509.524	-1,335.748	486.540	1,200	-1,554.539	-1,163.789	211.952
700	-1,508.167	-1,306.858	408.014	1,300	-1,552.398	-1,131.308	190.188
800	-1,506.835	-1,278.206	349.185	1,400	-1,550.190	-1,099.002	171.560
900	-1,505.583	-1,249.693	303.463	1,500	-1,547.870	-1,066.853	155.438

¹Melting point of Na. ² α - β transition of Ti. ³Boiling point of Na.

TABLE 4. - Thermodynamic data for Na₂O(c) + 6TiO₂(c)¹ = Na₂Ti₆O₁₃(c)

T, K	kcal		Log Kr	T, K	kcal		Log Kr
	ΔH_r°	ΔG_r°			ΔH_r°	ΔG_r°	
298.15	-57.180	-58.683	43.015	800	-57.907	-60.991	16.662
300	-57.179	-58.689	42.755	900	-58.187	-61.363	14.901
400	-57.207	-59.193	32.341	1,000	-58.509	-61.699	13.484
500	-57.272	-59.684	26.088	1,100	-58.939	-61.995	12.317
600	-57.424	-60.147	21.908	1,200	-59.595	-62.249	11.337
700	-57.651	-60.592	18.918	1,300	-60.655	-62.424	10.494

¹Rutile.

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³A title enclosed in parentheses is a translation from the language in which the work was published.