[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High-Temperature Heat Contents of Na_2TiO_3, $Na_2Ti_2O_5$ and $Na_2Ti_3O_7$[1]

BY B. F. NAYLOR[2]

Investigation of the thermodynamic properties of metallurgically important titanium compounds has been part of the recent program of the Pacific Experiment Station. Smelting of titaniferous iron ores with sodium carbonate and carbon forms sodium titanates as part of the reaction products. The thermochemical data essential for studying the thermodynamics of this reaction do not exist in the literature. As partial fulfillment of this need, the present paper reports heat contents above 298.16°K. of three sodium titanates, from room temperature to about 1,600°K., from which specific heats, heats of fusion, and entropies above 298.16°K. have been calculated.

Method and Materials

The measurements were made by the "drop" method in an apparatus previously described.[3] The calorimeter was calibrated with electrical energy, measured in international joules, and the results were converted to the conventional calorie by the relation, 1 cal. = 4.1833 int. joules (NBS).[4] Thermocouple calibrations, made frequently in the manner described by Southard, were based on the melting points of gold and palladium.

During the measurements the samples were enclosed in platinum–rhodium alloy capsules, the necks of which were pinched off and sealed with platinum. The heat content of the empty capsules had been determined separately; a small correction for the platinum used in sealing was applied.

At about 800° in the case of the Na_2TiO_3, and at somewhat higher temperatures for the other titanates, small pin-holes began to appear in the capsule walls. During measurements in the liquid range some of the sample extruded through these holes. Simultaneously, a small increase in weight of the capsule was noted due to reaction of the sample with carbon dioxide and moisture. A close check was maintained and weight corrections were made. New capsules and fresh samples were substituted when the increase in sample weight amounted to more than 0.2%.

The titanates were prepared in this Laboratory by treating stoichiometric weights of Na_2CO_3, prepared from reagent-grade $NaHCO_3$, with J. T. Baker TiO_2, which analyzed 98.6% pure. The reaction mixtures were heated at 900 to 1,100° for several hours with constant pumping to remove carbon dioxide. Analyses for titanium and carbon dioxide were carried out on each compound. On the basis of the titanium analyses the Na_2TiO_3, $Na_2Ti_2O_5$ and $Na_2Ti_3O_7$ samples were judged 98.4, 98.9 and 98.6% pure, respectively. The carbon dioxide analyses, reported as Na_2CO_3, gave 0.5, 0.3 and 0.3%, respectively.

Results

Experimental results are presented in Table I and Fig. 1. The column labeled T, °K., lists the temperature of the sample immediately before dropping into the calorimeter and $H_T - H_{298.16}$, the heat liberated per gram molecular weight in cooling from T to 298.16°K. The values thought to involve premelting have been designated "(p)". The listing order is not necessarily the order in which measurements were made; however, determinations at lower temperatures generally preceded those at higher temperatures.

TABLE I

HEAT CONTENTS ABOVE 298.16°K. (CAL./MOLE)

Na_2TiO_3 (mol. wt. = 141.894)		$Na_2Ti_2O_5$ (mol. wt. = 221.794)		$Na_2Ti_3O_7$ (mol. wt. = 301.694)	
T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
388.7	2,925	362.8	3,078	374.3	4,725
513.4	7,220	474.3	8,530	478.6	11,400
531.3	7,890	573.4	13,640	624.4	21,300
555.0	8,940	705.7	20,650	738.8	29,260
589.7	10,390	814.0	26,580	843.5	36,700
638.0	12,120	924.9	32,510	962.7	45,310
765.6	16,990	996.2	36,480	1079.2	53,920
948.6	24,410	1034.4	38,680	1169.4	60,660
1056.9	28,970	1039.6	39,040	1198.9	63,040
1096.3	30,770	1109.1	43,450(p)	1260.7	68,240(p)
1414	62,360	1197.7	50,060(p)	1431	111,080
1536	68,090	1216.1	53,020(p)	1446	113,540
1584	72,320	1361	83,840	1484	121,750
		1381	86,380	1524	127,150
		1514	95,310	1606	134,870
		1579	99,650	1681	142,000

All molecular weights accord with the 1941 International Atomic Weights. Sample weights were corrected to vacuum using the experimentally determined densities: Na_2TiO_3, 3.19; $Na_2Ti_2O_5$, 3.40; $Na_2Ti_3O_7$, 3.44 g./cc. No correction of the heat contents was made for the minor impurities present.

The melting points are indicated by dotted lines in Fig. 1. Insufficient measurements were made near the melting points to allow independent determinations of the melting point temperatures. The temperatures used in this paper are those

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[2] Formerly chemist, Pacific Experiment Station, Bureau of Mines.

[3] J. C. Southard, THIS JOURNAL, **63**, 3142 (1941).

[4] E. F. Mueller and F. D. Rossini, *Am. J. Physics*, **12**, 1–7 (1944).

given by Washburn and Bunting.[5] By extrapolating the heat-content data to their reported temperatures, the heats of fusion per mole were calculated to be 16,810 cal. for Na_2TiO_3 at 1,303°K., 26,230 cal. for $Na_2Ti_2O_5$ at 1,258°K., and 37,100 cal. for $Na_2Ti_3O_7$ at 1,401°K. The metatitanate has a small transition at 560°K., the heat effect of which was computed to be 400 cal. per mole. However, the transition temperature was calculated from the experimental data and may be in error possibly by as much as 20°.

Heat-content equations, fitting the experimental data closely, were derived. They are given below, followed by the appropriate temperature range and, in the case of the solids, by the mean percentage deviation from the experimental results. The heat contents thought influenced by premelting were not used in computing the mean deviation. No mean deviation is given for the liquid range because it was possible to determine only a few experimental points in each instance and this precluded a significant calculation. (The equations were based upon the following smooth, molal heat content values: $Na_2TiO_3(\alpha)$ 3,300 at 400°K. and 6,750 at 500°K.; $Na_2TiO_3(\beta)$ 10,750 at 600°K., 18,320 at 800°K. and 30,950 at 1,100°K.; $Na_2TiO_3(l)$ 61,720 at 1,400°K. and 71,100 at 1,600°K.; $Na_2Ti_2O_5(s)$ 4,880 at 400°K., 20,350 at 700°K. and 36,750 at 1,000°K.; $Na_2Ti_2O_5(l)$ 87,400 at 1,400°K. and 101,100 at 1,600°K.; $Na_2Ti_3O_7(s)$ 6,360 at 400°K., 26,550 at 700°K. and 63,000 at 1,200°K.; $Na_2Ti_3O_7(l)$ 124,890 at 1,500°K. and 143,720 at 1,700°K.).

$$Na_2TiO_3(\alpha):\ H_T - H_{298.16} = 25.18T + 0.01036T^2 - 8429 \quad (298\text{-}560°\text{K.};\ 0.1\%)$$

$$Na_2TiO_3(\beta):\ H_T - H_{298.16} = 25.95T + 0.00850T^2 - 7880 \quad (560\text{-}1303°\text{K.};\ 0.1\%)$$

$$Na_2TiO_3(l):\ H_T - H_{298.16} = 46.9T - 3940 \quad (1303\text{-}1600°\text{K.})$$

$$Na_2Ti_2O_5(s):\ H_T - H_{298.16} = 49.32T + 0.00353T^2 + \frac{460,000}{T} - 16,560 \quad (298\text{-}1258°\text{K.};\ 0.3\%)$$

$$Na_2Ti_2O_5(l):\ H_T - H_{298.16} = 68.5T - 8500 \quad (1258\text{-}1600°\text{K.})$$

$$Na_2Ti_3O_7(s):\ H_T - H_{298.16} = 63.46T + 0.00532T^2 + \frac{564,000}{T} - 21,285 \quad (298\text{-}1401°\text{K.};\ 0.15\%)$$

$$Na_2Ti_3O_7(l):\ H_T - H_{298.16} = 94.15T - 16,335 \quad (1401\text{-}1700°\text{K.})$$

The corresponding specific heat equations are

$$Na_2TiO_3(\alpha):\ C_p = 25.18 + 0.02072T$$

$$Na_2TiO_3(\beta):\ C_p = 25.95 + 0.01700T$$

$$Na_2TiO_3(l):\ C_p = 46.9$$

$$Na_2Ti_2O(s):\ C_p = 49.32 + 0.00706T - \frac{460,000}{T^2}$$

$$Na_2Ti_3O_5(l):\ C_p = 68.5$$

$$Na_2Ti_2O_7(s):\ C_p = 63.46 + 0.01064T - \frac{564,000}{T^2}$$

$$Na_2Ti_3O_7(l):\ C_p = 94.15$$

Using the above equations, heat contents and entropies above 298.16°K. were computed at 100° intervals and the results are listed in Table II.

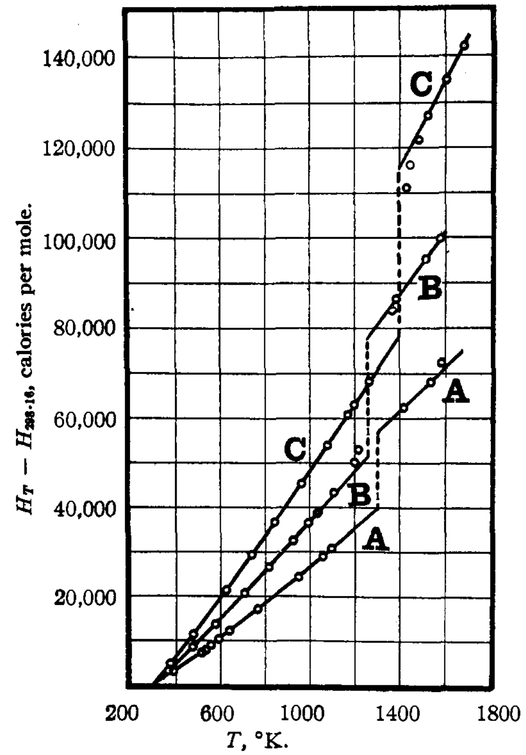

Fig. 1.—High temperature heat contents: A, Na_2TiO_3; B, $Na_2Ti_2O_5$; C, $Na_2Ti_3O_6$.

TABLE II

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K.

	Na_2TiO_3		$Na_2Ti_2O_5$		$Na_2Ti_3O_7$	
T, °K.	$H_T - H_{298.16}$ (cal./mole)	$S_T - S_{298.16}$ (cal./deg./mole)	$H_T - H_{298.16}$ (cal./mole)	$S_T - S_{298.16}$ (cal./deg./mole)	$H_T - H_{298.16}$ (cal./mole)	$S_T - S_{298.16}$ (cal./deg./mole)
400	3,300	9.51	4,880	14.06	6,360	18.32
500	6,750	17.20	9,900	25.26	12,900	32.91
560	8,920(α)	21.30				
560	9,320(β)	22.01				
600	10,750	24.48	15,070	34.67	19,650	45.20
700	14,450	30.18	20,350	42.81	26,550	55.84
800	18,320	35.34	25,730	49.99	33,590	65.24
900	22,360	40.10	31,200	56.43	40,760	73.69
1000	26,570	44.53	36,750	62.28	48,060	81.37
1100	30,950	48.71	42,380	67.65	55,470	88.44
1200	35,500	52.66	48,090	72.64	63,000	95.02
1258			51,440(s)	75.34		
1258			77,670(l)	96.19		
1300	40,220	56.44	80,550	98.44	70,640	101.10
1303	40,360(β)	56.55				
1303	57,170(l)	69.45				
1400	61,720	72.82	87,400	103.52	78,390	106.84
1401					78,470(s)	106.90
1401					115,570(l)	133.38
1500	66,410	76.06	94,250	108.24	124,890	139.81
1600	71,100	79.08	101,100	112.66	134,300	145.89
1700					143,720	151.59

Discussion

The heat contents above 298.16°K. of many substances can be calculated with fair accuracy by adding together the known heat contents of

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(5) E. W. Washburn and E. N. Bunting, *Bur. Standards J. Research*, 12, 239 (1934).

their constituents. Parks and Kelley[6] have shown this to be true for calcium and magnesium silicates, and later Kelley[7] based his calculation of the entropy and free energy of formation of sodium oxide upon the same principle.

Values for the heat content above 298.16°K. of Na_2O, obtained by subtracting the heat contents of one, two and three moles of TiO_2[8] from the heat contents of Na_2TiO_3,[9] $NaTi_2O_5$ and $Na_2Ti_3O_7$, respectively, have been listed in Table III. A similar extraction for Na_2O, also given in Table III, was computed using the heat contents of Na_2SiO_3 and $Na_2Si_2O_5$.[10] As SiO_2 exists in several forms, the heat content of SiO_2, used in this instance, was obtained by taking the difference between the heat contents of $Na_2Si_2O_5$ and Na_2SiO_3. The mean of the calculated heat contents is shown in a separate column in Table III. The following algebraic equations were derived and use of them in thermodynamic calculations is suggested pending actual measurements of Na_2O.

TABLE III

CALCULATED HEAT CONTENTS ABOVE 298.16°K. OF Na_2O (CAL./MOLE)

T. °K.	(Na_2TiO_3-(α)-TiO_2) $H_T - H_{298.16}$	($Na_2Ti_2O_5$-2TiO_2) $H_T - H_{298.16}$	($Na_2Ti_3O_7$-3TiO_2) $H_T - H_{298.16}$	(Na_2SiO_3-SiO_2) $H_T - H_{298.16}$	(Mean) $H_T - H_{298.16}$
400	1,760	1,800	1,740	1,750	1,760
500	3,650	3,700	3,600	3,560	3,630
600	5,615	5,600	5,445	5,320	5,495
700	7,605	7,460	7,215	7,220	7,375
800	9,745	9,380	9,065	9,150	9,335
900	12,050	11,380	11,030	11,060	11,380
1000	14,510	13,430	13,080	13,080	13,520
1100	17,125	15,530	15,195	15,110	15,740

$$Na_2O\colon\ H_T - H_{298.16} = 15.9T + 0.0027T^2 - 4980 \quad (298\text{-}1100°\text{K.})$$

$$Na_2O\colon\ C_p = 15.9 + 0.0054T$$

Summary

High-temperature heat contents above 298.16° K. of Na_2TiO_3, $Na_2Ti_2O_5$ and $Na_2Ti_3O_7$ were determined to about 1,600°K. The heat of fusion of each compound and the heat of transition of Na_2TiO_3 at 560°K. were calculated from these data.

Heat-content and entropy increments above 298.16°K. have been tabulated at 100° intervals and algebraic heat content and specific equations fitting the experimental data were derived.

Estimated heat contents above 298.16°K. of Na_2O at 100° intervals to 1,100°K. and corresponding heat-content and specific-heat equations were suggested for use in thermodynamic calculations.

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(6) G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **30**, 1175 (1926).

(7) K. K. Kelley, THIS JOURNAL, **61**, 471 (1939).

(8) Unpublished heat content data for TiO_2.

(9) Heat contents used for Na_2TiO_3 above 560°K. were obtained by extrapolation of the α-curve.

(10) B. F. Naylor, THIS JOURNAL, **67**, 466 (1945).

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[CONTRIBUTION FROM WESTERN REGIONAL RESEARCH LABORATORY[1a]]

An X-Ray Diffraction Investigation of Sodium Pectate

BY K. J. PALMER AND MERLE B. HARTZOG

The occurrence of long chains in pectin was first suggested by Smolenski.[1b] In 1930 Meyer and Mark[2] proposed a structure for pectin consisting of a long straight chain of galacturonide units in the pyranose form linked together by 1:4 glycosidic bonds. The structural formula for pectic acid (completely demethylated pectin) proposed by them is shown in Fig. 1. The existence of long chains in pectin has since been confirmed by the work of Schneider and co-workers, Van Iterson and others. The results of these investigations and their bearing on the pectin problem have been well reviewed in Meyer's recent book.[3]

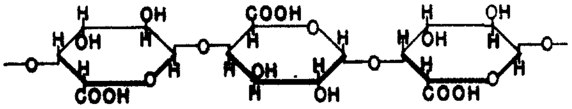

Fig. 1.—Structural formula of pectic acid as suggested by Meyer and Mark.

In addition to this evidence the more recent investigations of the flow birefringence,[4a,b] sedimentation and diffusion,[5a,b] and the viscosity studies[6] of pectin solutions are all in agreement with the concept that pectin is a long chain molecule.

It also has been shown recently[7] that pectin is composed essentially of α-*d*-galacturonide units in the pyranose form connected by 1:4 glycosidic linkages. Another aspect of the structure pro-

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(1a) Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

(1b) Smolenski, *C. A.*, **19**, 41 (1925).

(2) Meyer and Mark, "Der Aufbau der Hochpolymeren organischen Naturstoffe," Leipzig, 1930, p. 219.

(3) Meyer, "Natural and Synthetic High Polymers," Vol. 4, Interscience Publishers, Inc., New York, N. Y., 1942, p. 363.

(4) (a) Snellman and Saverborn, *Koll. Beihefte*, **52**, 467 (1941); (b) Boehm, *Arch. exptl. Zellforsch, Gewebezücht.*, **22**, 520 (1938–1939).

(5) (a) Saverborn, *Kolloid Z.*, **90**, 41 (1940); (b) Tiselius and Ingelmann, *Förh. Svenska Suckerfabriksdirigenternas Fören. Sammanträden*, 1942, II, 16 pp.; *C. A.*, **38**, 4465 (1944).

(6) Owens, Lotzkar, Merrill and Peterson, THIS JOURNAL, **66**, 1178 (1944).

(7) Morrell, Baur and Link, *J. Biol. Chem.*, **105**, 1 (1934); Luckett and Smith, *J. Chem. Soc.*, 1106 (1940); Hirst, *ibid.*, 70 (1942).