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

High-Temperature Heat Contents of the Metatitanates of Calcium, Iron and Magnesium[1]

BY B. F. NAYLOR[2] AND O. A. COOK[3]

Determination of thermodynamic properties of titanium compounds has been, for some time, one of the activities of the Pacific Experiment Station of the Bureau of Mines. At the beginning of the work, there were available only a few scattered thermal data, in most instances too incomplete for satisfactory free energy calculations. This situation has been improved appreciably by previous papers of this Station which dealt with low-temperature heat capacities and entropies of titanium metal and titanium carbide,[4] low-temperature heat capacities and entropies of three of the titanium oxides and titanium nitride,[5] high-temperature heat contents of three sodium titanates,[6] and high-temperature heat contents of titanium carbide and titanium nitride.[7]

The present paper reports additional high-temperature heat-content data. The substances investigated were the metatitanates of calcium, iron and magnesium. Ferrous titanate (ilmenite) is a major mineralogical constituent of titaniferous iron ores, and all three substances are of importance in studies of possible metallurgical use of such ores.

Method and Materials

The apparatus used in the high-temperature heat-content measurements was described previously[8,9] and repetition appears unnecessary. Each sample was enclosed in a platinum–rhodium alloy capsule, pure platinum being used in welding shut the capsule neck. The heat capacity of the capsule was known from previous measurements.

Calcium metatitanate was prepared by heating an intimate, -100 mesh, stoichiometric mixture of pure calcium carbonate and titanium dioxide in vacuum for a total of forty-one hours at 1,300 to 1,350°. The material was cooled to room temperature and reground to -100 mesh twice during this process. The final product was tested for acid-soluble (0.1 *N* hydrochloric acid) calcium and for carbon dioxide. The acid-soluble calcium was, at most, 0.69 per cent. (as CaO) and only 0.05 per cent. carbon dioxide was detected. X-ray examination[10] showed the presence of no material other than perovskite; the pattern checked that in the A.S.T.M. catalog.

Ferrous metatitanate was prepared from pure titanium dioxide, sponge iron and magnetite according to the reaction $Fe + Fe_3O_4 + 4TiO_2 = 4FeTiO_3$. The ingredients were ground to -200 mesh, intimately mixed in stoichiometric proportions, and heated in vacuum for thirty hours at temperatures ranging from 1,165 to 1,300°, the last eight hours being at 1,300°. The reacted mass was a dense, sintered, uniform material. It was crushed to -50 mesh and tested magnetically for unreacted iron and magnetite which were found to be absent. Oxidation tests indicated absence of unreacted ferrous oxide. Analyses for both iron and titanium indicated a purity of 99.4 per cent. The remaining 0.6 per cent. was mostly silica and could be accounted for on the basis of the analyses of the original ingredients. The X-ray diffraction pattern checked available data for ilmenite to within 0.5 per cent. No evidence of other ingredients was found.

Magnesium metatitanate was made by heating an intimate, -200 mesh, stoichiometric mixture of pure magnesium oxide and titanium dioxide for a total of eleven hours at 1,300 to 1,350°. The product was cooled to room temperature and reground to -200 mesh once during this process. The final material was uniform and white. Tests for acid-soluble (0.3 *N* hydrochloric acid) magnesium gave at most 0.45 per cent. (as MgO). Analyses for total magnesium and for titanium indicated a purity of at least 99 %. X-Ray examination showed no evidence of substances other than magnesium metatitanate; the pattern agreed with that given in the A.S.T.M. catalog.

Heat Contents

The experimentally determined heat contents, expressed in defined calories[11] (1 cal. = 4.1833 int. joules), are listed in Tables I, II and III, and shown graphically in Figs. 1 and 2.

Calcium metatitanate undergoes a transition at 1,530°K., the heat absorption being 550 cal. per mole. The heat capacities of the low- and high-temperature forms are about the same near the transition point, as evidenced by the slopes of the heat-content curves.

Ferrous metatitanate melts at 1,640°K. Evaluation of the heat of fusion is made difficult by pre-

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(4) Kelley, *Ind. Eng. Chem.*, **36**, 865 (1944).

(5) Shomate, THIS JOURNAL, **68**, 310 (1946).

(6) Naylor, *ibid.*, **67**, 2120 (1945).

(7) Naylor, *ibid.*, **68**, 370 (1946).

(8) Southard, THIS JOURNAL, **63**, 3142 (1941).

(9) Kelley, Naylor and Shomate, Bureau of Mines Technical Paper, in press.

(10) The X-ray examinations mentioned in this paper were conducted by Dr. E. V. Potter, physicist, Salt Lake City Station, Bureau of Mines.

(11) Mueller and Rossini, *Am. J. Physics*, **12**, 1 (1944).

TABLE I

HIGH-TEMPERATURE HEAT CONTENTS OF $CaTiO_3$

Mol. wt. = 135.98

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
383.0	2,249	1486.9	35,900
484.3	4,978	1491.4	36,245
590.1	8,013	1507.0	36,675
680.4	10,655	1527.8	37,475
781.8	13,705	1548.8	38,330
881.8	16,765	1582.8	39,470
972.3	19,535	1629.4	41,075
1075.8	22,705	1678.2	42,525
1079.7	22,940	1689.2	43,010
1172.7	25,715	1707.1	43,560
1272.7	28,950	1753.7	44,925
1376.1	32,270	1793.9	46,185
1438.4	34,445		

TABLE II

HIGH-TEMPERATURE HEAT CONTENTS OF $FeTiO_3$

Mol. wt. = 151.75

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
375.5	1,934	1237.8	28,200
416.0	3,023	1341.6	31,860
528.7	6,145	1464.6	36,660(a)
641.5	9,415	1498.4	38,150(a)
748.6	12,580	1551.9	40,960(a)
835.1	15,250	1627.3	48,520(a)
980.7	19,790	1655.8	64,170
1058.0	22,220	1690.2	65,830
1148.6	25,140	1742.5	68,290
1215.7	27,480		

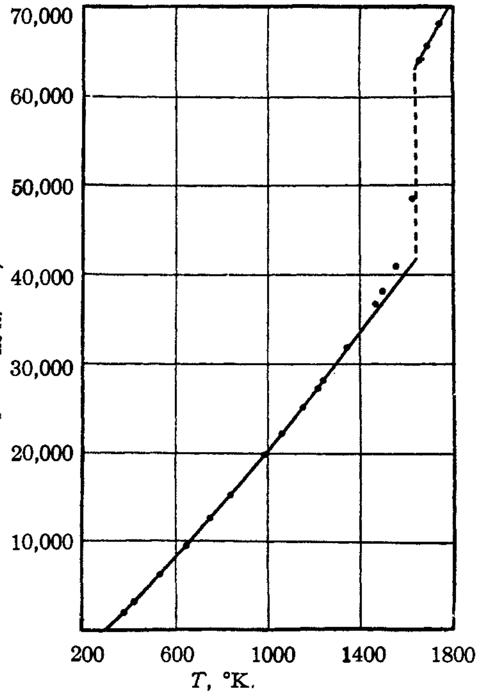

Fig. 1.—Heat content of $FeTiO_3$ above 298.16°K.

TABLE III

HIGH-TEMPERATURE HEAT CONTENTS OF $MgTiO_3$

Mol. wt = 120.22

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
402.2	2,552	1136.0	24,015
467.2	4,256	1225.4	26,800
574.6	7,237	1311.9	29,585
646.4	9,187	1408.3	32,810
784.4	12,240	1506.7	35,955
860.9	15,550	1612.6	39,460
952.0	18,330	1719.7	43,160
1047.6	21,290		

melting effects apparent in the four determinations marked "(a)" in Table II. The value chosen, in conformity with heat content equations given below, is 21,670 cal. per mole. The corresponding entropy of fusion is 13.21 cal. per deg. per mole.

The data for magnesium metatitanate are regular, no change of state being observed in the temperature range 298 to 1,720°K.

There are no previous data for any of these substances with which to compare the present values.

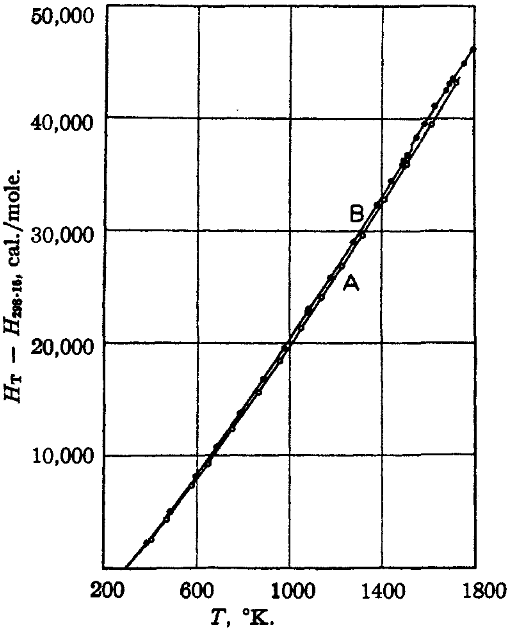

Fig. 2.—Heat contents of $CaTiO_3$ and $MgTiO_3$ above 298.16°K.: curve A, $MgTiO_3$; curve B, $CaTiO_3$.

The following heat-content relationships were derived for use by those who conduct thermodynamic calculations by means of algebraic equations. The temperature range of validity and the average deviation from the measured data are given in parentheses in each instance. The equations conform with measured true heat capacities[12] at 298.16°K.: 23.34 cal. per mole for $CaTiO_3$; 23.78 cal. per mole for $FeTiO_3$; and

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[12] Shomate, THIS JOURNAL, 68, 964 (1946).

21.93 cal. per mole for $MgTiO_3$. The constants in the equations were calculated by the graphical method described by Shomate,[13] which has the advantage of employing all the measured values rather than a selected few.

$CaTiO_3(\alpha)$: $H_T - H_{298.16} = 30.47T + 0.68 \times 10^{-3}T^2 + 6.690 \times 10^5T^{-1} - 11{,}389$ (0.6%; 298–1530°K.)

$CaTiO_3(\beta)$: $H_T - H_{298.16} = 32.03T - 11{,}197$ (0.2% 1530–1800°K.)

$FeTiO_3(s)$: $H_T - H_{298.16} = 27.87T + 2.18 \times 10^{-3}T^2 + 4.793 \times 10^5T^{-1} - 10{,}111$ (0.3%; 298–1640°K.)

$FeTiO_3(l)$: $H_T - H_{298.16} = 47.60T - 14{,}642$ (0.1%; 1640–1800°K.)

$MgTiO_3(s)$: $H_T - H_{298.16} = 28.29T + 1.64 \times 10^{-3}T^2 + 6.530 \times 10^5T^{-1} - 10{,}771$ (0.4%; 298–1800°K.)

The following, corresponding heat-capacity equations were obtained by differentiation.

$CaTiO_3(\alpha)$: $C_p = 30.47 + 1.36 \times 10^{-3}T - 6.690 \times 10^5T^{-2}$

$CaTiO_3(\beta)$: $C_p = 32.03$

$FeTiO_3(s)$: $C_p = 27.87 + 4.36 \times 10^{-3}T - 4.793 \times 10^5T^{-2}$

$FeTiO_3(l)$: $C_p = 47.60$

$MgTiO_3(s)$: $C_p = 28.29 + 3.28 \times 10^{-3}T - 6.530 \times 10^5T^{-2}$

Table IV contains values of the heat contents at even temperatures as read from smooth curves through the experimental data. The entropy increments above 298.16°K. also are included. The latter were obtained from the relationship

$$S_T - S_{298.16} = \frac{H_T - H_{298.16}}{T} + \int_{298.16}^{T} \frac{H_T - H_{298.16}}{T^2}\,dT$$

The last term was evaluated by numerical integration of a plot of $H_T - H_{298.16}/T$ against log T.

TABLE IV

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K.

	CaTiO₃		FeTiO₃		MgTiO₃	
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	2,680	7.73	2,595	7.46	2,500	7.21
500	5,430	13.86	5,330	13.56	5,130	13.07
600	8,300	19.09	8,200	18.78	7,900	18.12
700	11,260	23.65	11,120	23.28	10,790	22.57
800	14,270	27.67	14,150	27.33	13,740	26.51
900	17,310	31.25	17,250	30.97	16,750	30.05
1000	20,380	34.48	20,440	34.34	19,800	33.27
1100	23,490	37.44	23,650	37.38	22,900	36.22
1200	26,640	40.18	26,900	40.22	26,030	38.94
1300	29,820	42.73	30,200	42.87	29,190	41.47
1400	33,030	45.10	33,520	45.32	32,390	43.84
1500	36,270	47.34	36,920	47.67	35,660	46.09
1530	37,260(α)	47.99				
1530	37,810(β)	48.35				
1600	40,050	49.78	40,360	49.89	39,010	48.26
1640			41,750(s)	50.76		
1640			63,420(l)	63.97		
1700	43,250	51.72	66,280	65.68	42,450	50.34
1800	46,460	53.55	71,040	68.41	45,980	52.36

Summary

High-temperature heat contents of the metatitanates of calcium, iron, and magnesium were determined from 298° to temperatures near 1,800°K.

Calcium metatitanate has a transition at 1,530° K., the heat absorption being 550 cal. per mole.

Ferrous metatitanate melts at 1,640°K., the heat of fusion being 21,670 cal. per mole.

Heat-content and heat-capacity equations were derived for each titanate, and a table of smooth, even-temperature heat-content and entropy increment values was included.

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[13] Shomate, THIS JOURNAL, **66**, 928 (1944).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dipole Moment and Resonance in Vinyl Sulfide and Six Unsaturated Chlorohydrocarbons

BY N. BRUCE HANNAY AND CHARLES P. SMYTH

The large lowering of the dipole moment[1] of vinyl chloride and the shortening of the carbon–chlorine bond[2] below the normal single bond length have given evidence of double bond character in the carbon–chlorine bond as the result of resonance involving a structure with positive chlorine linked to the carbon by a double bond. It has seemed of interest, therefore, to investigate the polarities of the three different molecules in which one of the three hydrogens of vinyl chloride is replaced by a methyl group. In addition, three other molecules in which the chlorine is not adjacent to the double bond have been investigated. Analogy between the resonance in vinyl chloride and divinyl sulfide has led to the inclusion of work on the latter substance in this paper.

The dielectric constants of the vapors of these substances were measured with the apparatus and technique previously described and used to calculate the polarizations and dipole moments of the molecules.[3]

Materials

4-Chlorobutadiene-1,2.—Material kindly given us by the du Pont Company was regarded as pure. It was subjected to the usual double distillation required to introduce the vapor into the dielectric cell.

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[1] Hugill, Coop and Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938).

[2] Brockway, Beach and Pauling, THIS JOURNAL, **57**, 2693 (1935).

[3] McAlpine and Smyth, *ibid.*, **55**, 453 (1933); deBruyne and Smyth, *ibid.*, **57**, 1203 (1935); Wiswall and Smyth, *J. Chem. Phys.*, **9**, 352 (1941); Hurdis and Smyth, THIS JOURNAL, **64**, 2829 (1942).