[Contribution from the Pacific Experiment Station, Bureau of Mines, United States Department of the Interior]

Heat Capacities at Low Temperatures of the Metatitanates of Iron, Calcium and Magnesium[1]

By C. Howard Shomate[2]

Thermodynamic properties of certain titanates are of interest in connection with studies of possible metallurgical processes for the treatment and utilization of titaniferous iron ores. The Pacific Experiment Station of the Bureau of Mines has undertaken, as part of a program of study, the determination of low-temperature heat capacities and entropies of several titanates of the more common elements. This paper presents such data for the metatitanates of iron, calcium and magnesium. No similar data for these or any other titanates have been published previously.

Materials

The metatitanates were prepared by prolonged heating in vacuum at approximately 1300° of intimately mixed, stoichiometric amounts of materials indicated by the following reactions

$$Fe + Fe_3O_4 + 4TiO_2 \longrightarrow 4FeTiO_3$$
$$CaCO_3 + TiO_2 \longrightarrow CaTiO_3 + CO_2$$
$$MgO + TiO_2 \longrightarrow MgTiO_3.$$

Details of the preparation procedures and of the examinations of the final products were reported by Naylor and Cook[3] and repetition appears unnecessary. It will suffice to state that the three materials gave X-ray diffraction patterns that agreed with previously reported structures and that no impurities were present in amounts large enough to be detected by X-ray examination.

Chemical analyses showed the ferrous metatitanate to be 99.4% pure, the remaining 0.6% being principally silica, which was introduced as an impurity in the titanium dioxide used in the preparation.

Chemical analysis of calcium metatitanate was difficult because of insolubility of the material even after fusion with the usual agents, and reliance had to be placed in the previously mentioned X-ray examination and in tests for impurities, which indicated less than 1% total impurities.

Analyses of magnesium metatitanate for both magnesium and titanium indicated a purity of at least 99%, the principal impurity being silica, probably present as magnesium metasilicate.

Heat Capacities

The method and apparatus used in the low-temperature heat capacity measurements have been described previously.[4,5] The experimental results, expressed in defined calories (1 calorie = 4.1833 int. joules),[6] are listed in Table I and shown graphically in Fig. 1. The values of the heat capacities at 298.16°K., obtained by extrapolation of a smooth curve through the experimental points, are also included in Table I. The molecular weights are in accordance with the 1941 International Atomic Weights. Corrections were made in the ferrous metatitanate results for 0.6% SiO_2 impurity, and in the magnesium titanate results for 0.8% $MgSiO_3$ impurity; no corrections for impurities were made in the results for calcium metatitanate.

Table I

Molal Heat Capacities

$FeTiO_3$ (Mol. wt. = 151.75)		$CaTiO_3$ (Mol. wt. = 135.98)		$MgTiO_3$ (Mol. wt. = 120.22)	
T, °K.	*Cp*, cal./deg.	*T*, °K.	*Cp*, cal./deg.	*T*, °K.	*Cp*, cal./deg.
51.6	7.014	52.5	2.791	52.6	1.378
52.6	7.365	56.4	3.253	56.5	1.675
54.0	7.920	60.7	3.781	60.3	1.973
55.3	8.544	65.0	4.325	64.5	2.333
56.6	8.643	69.6	4.914	69.8	2.834
56.8	8.989	73.9	5.477	74.0	3.248
58.6	6.482	78.2	6.033	78.3	3.690
59.8	5.911	84.6	6.837	85.8	4.485
61.4	5.806	94.8	8.122	94.7	5.492
63.4	5.863	104.5	9.339	104.3	6.590
67.4	6.161	116.3	10.76	114.9	7.827
69.3	6.336	125.7	11.82	125.2	9.005
71.5	6.552	135.0	12.84	135.2	10.12
75.8	6.991	145.6	13.92	145.8	11.28
80.0	7.436	155.6	14.87	155.6	12.27
84.9	7.958	165.5	15.78	165.5	13.25
95.1	9.092	175.6	16.65	175.5	14.20
104.7	10.16	185.5	17.40	185.5	15.05
115.1	11.30	195.8	18.13	195.8	15.88
125.2	12.36	205.8	18.83	205.8	16.66
135.3	13.38	216.2	19.49	216.3	17.44
145.7	14.37	226.3	20.07	226.2	18.08
155.5	15.26	235.7	20.59	235.8	18.68
165.7	16.15	246.0	21.10	246.3	19.32
175.8	17.00	256.0	21.65	256.0	19.91
185.7	17.73	266.1	22.07	266.2	20.50
196.0	18.46	276.3	22.48	276.1	20.97
206.1	19.16	286.1	22.88	286.1	21.40
215.9	19.78	296.3	23.27	296.2	21.88
226.1	20.38	(298.16)	(23.34)	(298.16)	(21.93)
235.8	20.89				
246.1	21.44				
256.1	21.98				
266.2	22.47				
276.2	22.93				
286.2	23.27				
296.4	23.73				
(298.16)	(23.78)				

All weights were corrected to vacuum, using

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[3] Naylor and Cook, This Journal, **68**, 1003, (1946).

[4] Kelley, *ibid.*, **63**, 1137 (1941).

[5] Shomate and Kelley, *ibid.*, **66**, 1490 (1944).

[6] Mueller and Rossini, *Am. J. Phys.*, **12**, 1 (1944).

the following densities: ferrous metatitanate, 4.73; calcium metatitanate, 4.02; and magnesium metatitanate, 3.84 g./cc., respectively. Density determinations were made in this Laboratory by R. J. O'Dea.[2]

No anomalies appeared in the heat-capacity curves of the calcium and magnesium metatitanates; however, ferrous metatitanate has a marked "hump" in its heat-capacity curve, the peak being at 57°K. Anomalies such as this are not uncommon in ferrous iron compounds; similar "humps" have been reported in the heat capacity curves of ferrous oxide, ferrous chloride, ferrous silicate, and ferrous chromite. The "hump" in the ferrous silicate (Fe_2SiO_4) curve[7] is quite similar in temperature and magnitude to that in the ferrous metatitanate curve.

Entropies

The evaluation of the entropy at 298.16°K. is obtained by numerical integration of a plot of C_p against log T. This necessitates the extrapolation of the heat capacity curve from the temperature of the lowest measurement down to the absolute zero of temperature. It was found that the following function sums adequately represent all the measured heat capacities (within 1%), except in the region of the "hump" in the ferrous metatitanate curve

$$FeTiO_3\text{:}\quad 2D\left(\frac{272.3}{T}\right) + 3E\left(\frac{647}{T}\right)$$

$$CaTiO_3\text{:}\quad D\left(\frac{256}{T}\right) + 2E\left(\frac{375}{T}\right) + 2E\left(\frac{768}{T}\right)$$

$$MgTiO_3\text{:}\quad D\left(\frac{365}{T}\right) + E\left(\frac{383}{T}\right) + 3E\left(\frac{711}{T}\right)$$

The symbols D and E denote, respectively, Debye and Einstein functions. These functions were used for extrapolating to 0°K. the heat capacity curves of the calcium and magnesium metatitanates and the so-called "normal" heat capacity curve of ferrous metatitanate (broken-line curve in Fig. 1). The extrapolation of the actual ferrous metatitanate curve was effected by extending downward the curve determined by the four lowest-temperature runs, and smoothing this curve into the above-mentioned "normal" extrapolation curve at approximately 30°K.

The heat absorption in the region of the "hump" in ferrous metatitanate was obtained by summing the energies of five successive heat capacity determinations in the manner described by Shomate.[8] The total heat absorption between 50.42 and 65.27°K. is 102.9 calories/mole, and the increase in entropy is 1.802 E.U./mole. Unfortunately there is still some effect of the "hump" at the temperature of the lowest measurement, so that an estimate of the total energy and entropy in the "hump" itself would be less certain.

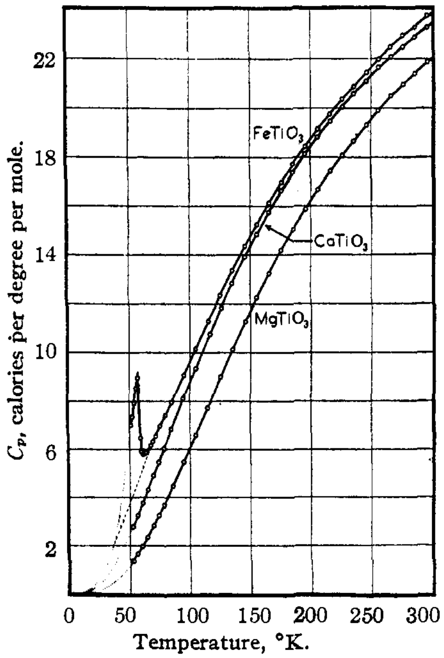

Fig. 1.—Heat capacities.

Table II summarizes the entropy calculations for the three substances. The entropy associated with the "hump" in ferrous metatitanate is calculated to be 0.95 E.U./mole. Similar examination of Kelley's data for ferrous silicate (Fe_2SiO_4)[7] shows that the "hump" in this substance contains 1.94 E.U./mole of excess entropy. Since the number of iron atoms per mole of the silicate is twice that of the metatitanate, it is not surprising that the entropies associated with the two "humps" have approximately this same ratio.

TABLE II

ENTROPIES AT 298.16°K. (E.U./MOLE)

	$FeTiO_3$ Actual	$FeTiO_3$ "Normal"	Entropy in "hump"
0–50.42°K. (extrapolated)	2.01	1.63	0.38
50.42–298.16°K. (measured)	23.31	22.74	.57
$S^0_{298.16}$	25.3 ± 0.3		.95
	$CaTiO_3$	$MgTiO_3$	
0–52.00°K. (extrapolated)	1.08	0.45	
52.00–298.16°K. (measured)	21.30	17.37	
$S^0_{298.16}$	22.4 ± 0.1	17.8 ± 0.1	

The entropies of formation of the metatitanates from the respective oxides and rutile (TiO_2) are listed in Table III. These values are obtained by a combination of the entropy data for the metatitanates with previously reported data for the oxides.[9]

TABLE III

ENTROPIES OF FORMATION

	$\Delta S_{298.16}$, E. U./mole
$FeO + TiO_2$ (rutile) → $FeTiO_3$	−0.4
$CaO + TiO_2$ (rutile) → $CaTiO_3$	+0.5
$MgO + TiO_2$ (rutile) → $MgTiO_3$	−1.1

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[7] Kelley. THIS JOURNAL, **63**, 2750 (1941).

[8] Shomate, *Ind. Eng. Chem.*, **36**, 910 (1944).

[9] Kelley, Bureau of Mines Bulletin 434 (1941).

Summary

The heat capacities of the metatitanates of iron, calcium, and magnesium were measured in the temperature range 52 to 298°K. Ferrous metatitanate has a marked "hump" in its heat-capacity curve, the maximum being at 57°K. There is approximately 0.95 unit of excess entropy in the "hump" above the "normal" curve.

The following molal entropies at 298.16°K. were computed: ferrous metatitanate, 25.3 ± 0.3; calcium metatitanate, 22.4 ± 0.1; and magnesium metatitanate, 17.8 ± 0.1 E.U.

Combination of the above entropies with related entropy data yields the following molal entropies of formation of the metatitanates from the respective oxides and rutile: ferrous metatitanate, −0.4; calcium metatitanate, +0.5; and magnesium metatitanate, −1.1 E.U.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of Acetic Acid in 50% Glycerol–Water Solution from 0 to 90°

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From electromotive force measurements of the cells, H_2 | HAc (m_1), NaAc (m_2), NaCl (m_3), Glycerol (X), H_2O (Y) | AgCl–Ag in which the solvent mixture was 50% by weight of glycerol, the ionization constant of acetic acid has been determined at 5° intervals from 0 to 90°. This is the widest temperature range over which measurements of this kind have been made.

Experimental Results

The measurements were carried on in cells and by the technique of Harned and Morrison.[2] Glycerol purified and analyzed by methods described by us in an earlier communication[3] was used. The stock buffer solution was prepared by neutralizing half the weight of acetic acid taken with sodium hydroxide. Water formed in the neutralization reaction was taken into consideration in computing its total weight in the cell solution. The concentrations were: $m_1 = 0.3947$, $m_2 = 0.3947$ and $m_3 = 0.3997$. The cell solutions were prepared from this solution.

Two series of cell measurements were made at given concentrations of cell electrolytes, one through a temperature range from 0 to 50° and another from 50 to 90°. After the temperature readings were recorded, the cell was brought to 25° for the low temperature series and to 50° for the high temperature series. Excellent recovery values were obtained at 25°. Recovery values at the higher temperatures were not so good but were considerably better for these cells containing a buffered solution than for those containing only hydrochloric acid.[3] Since the cells were run in triplicate at six concentrations, eighteen recovery checks at 50° were made. Of these four were within 0.1 mv. and sixteen within 0.3 mv. of the initial values at this temperature.

The experimental results obtained at nineteen temperatures have been expressed by the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (1)$$

The constants, a, b and the electromotive force, E_{25}, were obtained from the first order five degree differences in electromotive forces by the graphical method described by Harned and Nims.[4] These are given in Table I as well as the average and maximum deviations between the observed electromotive forces and those calculated by the equation. The average deviations are quite small and the maximum always occurs in the higher range of temperature. Although this shows that less reproducibility is obtained from 70 to 90°, the discrepancies are not large and we believe that considerable confidence may be placed in the results over the entire temperature range.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS, H_2|HAc(m_1), NaAc(m_2). NaCl(m_3), GLYCEROL (X), WATER (Y)|AgCl–Ag ACCORDING TO EQUATION $E = E_{25} + a(t - 25) + b(t - 25)^2$

Valid from 0 to 90°; $m_1 = 0.99992$, $m_2 = 0.98756\ m_3$; $\mu = m_2 + m_3 = 2.0125\ m_2 = 1.9876\ m_3$. Δ (av.) and Δ (max.) equal average and maximum deviations of calculated from observed electromotive forces. $X = Y =$ 50% by weight.

μ	E_{25}	$a \times 10^4$	$b \times 10^7$	Δ(av.)	Δ(max.)
0.02234	0.61131	6.55	−4.00	0.05	0.21[a]
.03805	.59756	6.06	−2.25	.10	.44[a]
.06878	.58231	5.50	−2.00	.05	.19[a]
.11281	.56972	5.04	−2.00	.05	.13[b]
.14211	.56393	4.82	−2.50	.04	.13[c]
.18439	.55727	4.59	−2.35	.05	.15[b]

[a] At 90°. [b] At 50°. [c] At 60°.

The Ionization Constant and Derived Thermodynamic Quantities

The ionization constant was determined by using the equation of the cell in the form[5]

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[1] This communication contains material from a dissertation presented by F. H. Max Nestler to the Graduate School of Yale University in partial fulfillment of the Degree of Doctor of Philosophy, June, 1943.

[2] Harned and Morrison, *Am. J. Sci.*, **33**, 161 (1937).

[3] Harned and Nestler, THIS JOURNAL, **68**, 665 (1946).

[4] Harned and Nims, *ibid.*, **54**, 423 (1932).

[5] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, p. 497.