value for the compound is only 0.6% greater than for the constituents. This difference becomes progressively larger at lower temperatures, reaching 3.1% at 100°K. and an indicated 15.7% at 50°K. Although the designation of this substance as a compound (rather than as a solid solution of calcium oxide in calcium metatitanate) is justified by the work of Coughanour, Roth and DeProsse,[11] the present results offer further support in that these lower temperature differences appear too large to be ascribed to a solid solution.

Entropies at 298.16°K.—The entropies were calculated in the usual manner. The measured portions, between 51 and 298.16°K., were obtained by Simpson rule integrations of plots of C_p against log T. The extrapolated portions, between 0 and 51°K., were obtained from the following empirical sums of Debye and Einstein functions, which fit the measured heat capacities between 51 and 298.16°K. to within the maximum deviations indicated in parentheses.

Al_2TiO_5

$$D\left(\frac{276}{T}\right) + 4E\left(\frac{477}{T}\right) + 3E\left(\frac{1049}{T}\right)\ (1.8\%)$$

$Ca_3Ti_2O_7$

$$D\left(\frac{158}{T}\right) + 5E\left(\frac{300}{T}\right) + 5E\left(\frac{652}{T}\right) + E\left(\frac{781}{T}\right)\ (0.5\%)$$

Li_2TiO_3

$$D\left(\frac{299}{T}\right) + 3E\left(\frac{495}{T}\right) + E\left(\frac{676}{T}\right) + E\left(\frac{1023}{T}\right)\ (0.9\%)$$

Zn_2TiO_4

$$D\left(\frac{190}{T}\right) + 2E\left(\frac{284}{T}\right) + 2E\left(\frac{584}{T}\right) + 2E\left(\frac{754}{T}\right)\ (0.6\%)$$

The results of the entropy calculations are in Table II. It is noted that the measured portions constitute 93.7 to 96.9% of the totals for 298.16°K.

TABLE II

ENTROPIES AT 298.16° (CAL./DEG. MOLE)

Substance	$S^0_{51} - S^0_0$ (extrap.)	$S^0_{298.16} - S^0_{51}$ (meas.)	$S^0_{298.16}$
Al_2TiO_5	0.83	25.33	26.2 ± 0.2
$Ca_3Ti_2O_7$	3.02	53.08	56.1 ± .4
Li_2TiO_3	0.68	21.25	21.9 ± .1
Zn_2TiO_4	2.07	30.75	32.8 ± .2

Zinc–titanium spinel requires further consideration. This substance is a spinel of the variate class.[16] One-half of the zinc atoms occupy metal sites that are tetrahedrally coördinated with oxygen. The other half of the zinc atoms and the titanium atoms occupy metal sites that are octahedrally coördinated with oxygen, being irregularly arranged among these sites. The disorder of arrangement of the zinc and titanium atoms should lead to a zero-point entropy. However, the degree of disorder is not known and is not ascertainable by X-ray diffraction. If the arrangement is completely random, then the addition of $2R \ln 2 = 2.75$ cal./deg. mole to the $S^0_{298.16}$-value in Table II would be required, making $S^0_{298.16} = 35.6$, which is the maximum possible value. As there is a tendency for localized electrical neutralization in crystals, it may well be, for example, that each ZnO_4^{-6} group is neutralized. This would require an equal number of Ti^{+4} and Zn^{+2} nearest neighbors, and calculation gives an entropy increment of $R \ln 3/2 = 0.81$, making $S^0_{298.16} = 33.6$, which probably is about the minimum possible value. A more definite entropy assignment is not feasible at this time.

[16] R. W. G. Wyckoff, "Crystal Structures," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1951, p. 43.

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[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High Temperature Heat Contents of Some Titanates of Aluminum, Iron and Zinc

BY K. R. BONNICKSON

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Measurements of heat contents above 298°K. were conducted for aluminum titanate, ferric titanate, titanomagnetite and zinc–titanium spinel to temperatures of 1803, 1739, 1513 and 1798°K., respectively. Normal behavior was observed, except for titanomagnetite which shows an unusual upward trend in heat content beginning about 1200°K. A table of smooth matching values of heat content and entropy increments was constructed and heat content equations were derived.

Introduction

Investigation of high temperature heat contents of interoxidic compounds of titanium has been a part of the recent program of thermodynamic measurements of this Laboratory. Previous papers dealt with the sodium titanates,[1] metatitanates of calcium, iron and magnesium,[2] titanates of magnesium,[3] and titanates of barium and strontium.[4] This paper reports results for aluminum titanate (Al_2TiO_5), ferric titanate (Fe_2TiO_5), titanomagnetite (a spinel, Fe_2TiO_4), and zinc–titanium spinel (Zn_2TiO_4). No previous similar data for any of these substances have appeared in the literature.

Materials.—The ferric titanate and titanomagnetite used in this work are portions of the samples described by Todd and King.[5] Likewise, the aluminum titanate and zinc–titanium spinel are portions of the samples described by King.[6] Their papers include the methods of preparation, the chemical analyses and the results of X-ray diffractions.

Measurements and Results

The measurements were conducted with previously described apparatus.[7] The samples were

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[1] B. F. Naylor, THIS JOURNAL, **67**, 2120 (1945).

[2] B. F. Naylor and O. A. Cook, *ibid.*, **68**, 1003 (1946).

[3] R. L. Orr and J. P. Coughlin, *ibid.*, **74**, 3186 (1952).

[4] J. P. Coughlin and R. L. Orr, *ibid.*, **75**, 530 (1953).

[5] S. S. Todd and E. G. King, *ibid.*, **75**, 4547 (1953).

[6] E. G. King, *ibid.*, **77**, 2150 (1955).

[7] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

enclosed in platinum–rhodium capsules, the heat contents of which were determined by separate experiments. The capsule containing the titanomagnetite was evacuated, filled with helium, and sealed by platinum welding. The necks of the other capsules were merely pinched shut. In all instances careful account was taken of the weights of the capsules and contents during the measurements to assure that no losses occurred. The furnace thermocouple was checked frequently against the melting point of pure gold.

The experimental heat content results are listed in Table I and plotted in Fig. 1. They are expressed in defined calories (1 cal. = 4.1840 abs. joules) per mole. Molecular weights are in accord with the 1953 International Atomic Weights.[8]

TABLE I

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

T, °K.	$H_T - H_{296.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
		Al_2TiO_5 (mol. wt., 181.86)			
411.0	4,030	1006.1	30,680	1517.3	56,190
509.9	8,050	1030.1	31,880	1527.5	56,760
594.7	11,660	1176.7	39,020	1553.5	58,070
608.7	12,350	1249.1	42,600	1610.7	60,870
708.8	16,800	1269.1	43,640	1703.1	66,110
724.1	17,560	1319.6	46,100	1736.8	67,340
806.8	21,260	1399.2	50,230	1744.1	67,700
847.1	23,220	1406.1	50,530	1803.2	71,300
848.4	23,280	1502.9	55,480		
		Fe_2TiO_5 (mol. wt., 239.60)			
410.2	4,650	908.6	28,470	1430.7	55,410
513.2	9,320	1017.8	33,780	1516.9	60,000
620.0	14,290	1122.8	39,410	1627.9	65,910
716.9	18,800	1232.5	44,890	1739.0	72,170
836.0	24,780	1322.6	49,720		
		Fe_2TiO_4 (mol. wt., 223.60)			
423.7	4,630	959.9	27,570	1279.7	43,140
517.6	8,150	994.3	29,140	1305.3	44,530
626.0	12,790	1041.0	31,330	1378.5	48,280
730.0	17,160	1130.7	35,850	1406.9	50,260
837.8	21,910	1213.9	39,940	1513.3	56,650
935.7	26,410				
		Zn_2TiO_4 (mol. wt., 242.66)			
402.2	3,660	1045.0	30,730	1507.9	52,320
513.5	7,740	1119.2	34,070	1610.4	57,210
596.4	11,120	1214.1	38,590	1701.6	61,520
716.3	16,120	1303.0	42,710	1759.6	64,300
793.8	19,470	1417.2	47,970	1798.2	66,490
925.0	25,250				

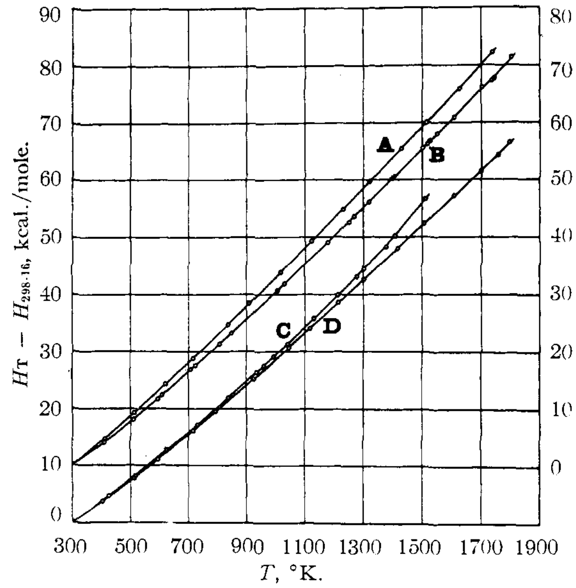

Fig. 1.—High temperature heat contents: curve A, Fe_2TiO_5; curve B, Al_2TiO_5; curve C, Fe_2TiO_4; curve D, Zn_2TiO_4. (Scale at left is for Fe_2TiO_4 and Zn_2TiO_4; scale at right is for Fe_2TiO_5 and Al_2TiO_5.)

Aluminum titanate has been reported as being unstable below 1570°K.[9] In the range 1000 to 1570°K. decomposition may occur at an appreciable rate. Consequently, in making the measurements care was taken to minimize the time in the furnace in this range, and to thoroughly heat the sample above 1570°K. between measurements to recombine any possible dissociated material. This procedure appears to have been effective as the results in Table I show no evidence of decomposition. Likewise, zinc–titanium spinel has been reported as unstable with respect to decomposition into a solid solution and free zinc oxide at temperatures below 1270°K.[10] The similar procedure of minimizing the furnacing time and thoroughly heating above 1270°K. between runs was adopted. Again, the heat content data show no evidence of decomposition of the sample.

The ferric and aluminum titanates give similar, very regular heat content curves. The heat content of ferric titanate averages about 11% higher than that of aluminum titanate at all temperatures between 500 and 1700°K.

Both titanomagnetite and zinc–titanium spinel belong to the variate class of spinels.[11] The titanium atoms and half of the iron atoms in the first instance, and the titanium atoms and half of the zinc atoms in the second, are irregularly arranged among the octahedral lattice sites. The remaining iron or zinc atoms are regularly arranged in tetrahedral sites. The heat content of the zinc compound follows a regular course throughout the temperature range studied. That of titanomagnetite follows a similar course to about 1200°K., but at higher temperatures the slope of the heat content curve increases in a rather unusual manner. The reason for this is not known. One possibility is that it may be related to increasing randomness in the arrangement of iron and titanium atoms in the crystal. Another possibility is that it is merely the result of additional electronic energy levels of the iron atoms (or preferably ions) coming into play at the higher temperatures. Magnetite itself does not show this behavior,[12] but does have a

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[8] E. Wichers, THIS JOURNAL, **76**, 2033 (1954).

[9] S. M. Lang, C. L. Fillmore and L. H. Maxwell, *J. Research Natl. Bur. Standards*, **48**, 298 (1952).

[10] S. S. Cole and W. K. Nelson, *J. Phys. Chem.*, **42**, 245 (1938).

[11] R. W. G. Wyckoff, "Crystal Structures," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1951, pp. 42–43.

[12] J. P. Coughlin, E. G. King and K. R. Bonnickson, THIS JOURNAL, **73**, 3891 (1951).

TABLE II

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

	Al_2TiO_5		Fe_2TiO_5		Fe_2TiO_4		Zn_2TiO_4	
T, °K.	$H_T - H_{298.15}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$
400	3,600	10.35	4,330	12.46	3,750	10.80	3,550	10.21
500	7,620	19.30	8,740	22.29	7,610	19.40	7,290	18.55
600	11,930	27.16	13,300	30.60	11,640	26.74	11,250	25.77
700	16,420	34.07	18,010	37.86	15,850	33.23	15,400	32.16
800	21,020	40.22	22,870	44.35	20,220	39.06	19,710	37.92
900	25,700	45.73	27,860	50.23	24,740	44.38	24,140	43.13
1000	30,450	50.73	32,960	55.60	29,400	49.29	28,660	47.89
1100	35,280	55.33	38,130	60.53	34,210	53.87	33,250	52.27
1200	40,180	59.59	43,330	65.05	39,180	58.20	37,890	56.30
1300	45,150	63.57	48,550	69.23	44,350	62.34	42,560	60.04
1400	50,180	67.30	53,800	73.12	49,160	66.35	47,250	63.52
1500	55,260	70.80	59,080	76.76	55,450	70.27	51,950	66.76
1600	60,370	74.10	64,400	80.20	61,460	74.15	56,680	69.81
1700	65,490	77.21	69,760	83.45			61,450	72.70
1800	70,620	80.14					66,270	75.46

magnetic inversion point at 900°K. which is absent for titanomagnetite.

Measurements of titanomagnetite beyond 1513°K. were hampered because the substance began to attack the platinum–rhodium capsule. Higher temperature results are considered unsound and therefore are not reported.

Table II gives smooth values of heat content and entropy increments above 298.16°K. at even 100° intervals, for use of those who make thermodynamic calculations by the tabular method. The entropy increments were calculated to match the heat content values by the method of Kelley.[13]

The heat content data are represented by the following equations. The temperature range of validity and average deviation from the measured values are indicated in parentheses.

$Al_2TiO_5(c)$

$$H_T - H_{298.16} = 43.63T + 2.65 \times 10^{-3}T^2 + 11.21 \times 10^5T^{-1} - 17{,}004$$

(298–1800°K.; 0.4%)

$Fe_2TiO_5(c)$

$$H_T - H_{298.16} = 46.03T + 2.63 \times 10^{-3}T^2 + 7.41 \times 10^5T^{-1} - 16{,}443$$

(298–1700°K.; 0.4%)

$Fe_2TiO_4(c)$

$$H_T - H_{298.16} = 33.34T + 7.54 \times 10^{-3}T^2 + 3.40 \times 10^5T^{-1} - 11{,}751$$

(298–1600°K.; 0.7%)

$Zn_2TiO_4(c)$

$$H_T - H_{298.16} = 39.82T + 2.77 \times 10^{-3}T^2 + 7.69 \times 10^5T^{-1} - 14{,}698$$

(298–1800°K.; 0.8%)

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(13) K. K. Kelley, U. S. Bur. Mines Bull. 476 (1949).

[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Arsine. Vapor Pressure, Heat Capacity, Heats of Transition, Fusion and Vaporization. The Entropy from Calorimetric and from Molecular Data[1]

BY R. H. SHERMAN AND W. F. GIAUQUE

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The heat capacity of arsine has been measured from 13°K. to its boiling point, 210.68°K. The heat of vaporization at this temperature is 3988 cal. mole^{-1}. The heat of sublimation at the absolute zero is $\Delta H_0^0 = 5090$ cal. mole^{-1}. The heat of fusion is 285.7 cal. mole^{-1} at the triple point, 156.23°K. The melting point at 1 atm. total pressure is 156.28°K. The heat of transition at 105.55°K. is 131.0 cal. mole^{-1}. 0°C. is taken as 273.16°K. A gradual transition of the type characteristic of restricted rotation occurs near 32°K. The entropy obtained from the third law of thermodynamics is 53.15 cal. deg.$^{-1}$ mole^{-1} at 298.16°K. This is in excellent agreement with the value 53.18 cal. deg.$^{-1}$ mole^{-1} calculated from spectroscopic data. This latter is the value to be used in ordinary thermodynamic calculations. Considering the nuclear spin contribution the absolute entropy is 60.07 cal. deg.$^{-1}$ mole^{-1}. The vapor pressure of the liquid has been measured and represented by the equation $\log_{10}P$ (int. cm. Hg) $= -1403.32T - 9.45935 \log_{10}T + 0.008037T + 28.82835$. The vapor pressure of the solid has been tabulated from 40°K. to the triple point. The second virial coefficient of arsine gas has been determined by two different methods which agree well. The accepted equation of state for low pressures is $PV = RT + bp/T^2$, where $b = -4.3 \times 10^5$ cal. deg.^{2} atm.$^{-1}$ $= -1.8 \times 10^7$ cm.^{3} deg.^{2}. The thermodynamic properties of solid, liquid and gaseous arsine have been tabulated.

This paper reports a low temperature calorimetric investigation of arsine. Its primary purpose was the comparison of the entropy of arsine gas obtained by means of the third law of thermodynamics with the value calculable from existing molecular data. It was also of interest to compare its properties with those of phosphine which has been

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(1) This work was supported in part by the Office of Naval Research, United States Navy, and by the United States Atomic Energy Commission.