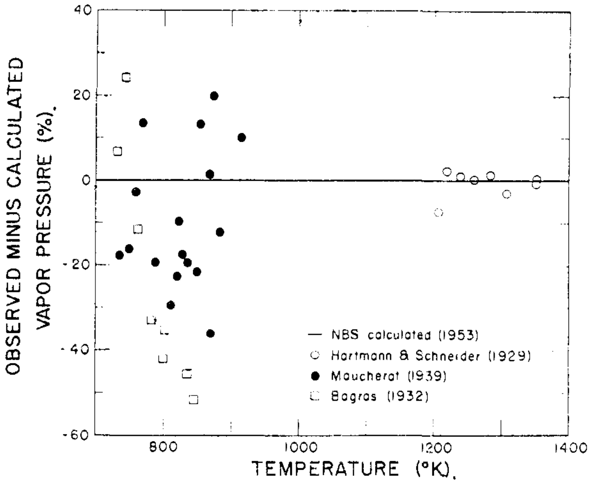

Fig. 4.—Observed and calculated vapor pressure of lithium.

than the heat of vaporization at 0°K., found above to be 37960 cal. g.-atom^{-1}, by the zero point energy of the crystal. An estimate of the latter may be made from the Debye theory, which gives (9/8)$R\theta_D$ per gram atom, where θ_D is the Debye characteristic temperature. The values of C_V of Simon and Swain,[14] corrected as described above, give values of θ_D showing no trend between 40 and 180°K. and averaging 393°K., which corresponds to a zero point energy of 880 cal. g.-atom^{-1}. The resulting "observed" cohesive energy of approximately 38800 cal. g.-atom^{-1} may be compared with that calculated independently of thermodynamic data by quantum-mechanical methods, which is 36200.[45] Seitz believed that the discrepancy is probably due largely to the use in the theoretical calculations of an approximate free-electron expression for the electronic correlation energy.

As shown in Figs. 2 and 3, the heat capacity of lithium increases rapidly with temperature just below the melting point and then decreases more gradually above. This fact may be associated with the unusually low entropy of fusion (0.8 R), and is analogous to the behavior of the alkali metals sodium[4] and potassium.[5]

Acknowledgments.—The authors wish to acknowledge the valuable help of several persons. L. P. Pepkowitz, R. J. Downer and their associates, of the Knolls Atomic Power Laboratory, performed the chemical analyses of the lithium. W. J. Youden, of the National Bureau of Standards, gave advice in the analytical formulation of the heat-content data.

(45) F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 365.

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

Low-Temperature Heat Capacities and Entropies at 298.16°K. of Some Titanates of Aluminum, Calcium, Lithium and Zinc

BY E. G. KING

RECEIVED NOVEMBER 3, 1954

Heat capacity measurements in the temperature range 51 to 298°K. were conducted for aluminum titanate, tricalcium dititanate, lithium metatitanate and zinc-titanium spinel. Regular behavior was observed for all four substances. The following entropy values (cal./deg. mole) at 298.16°K. were obtained: 26.2 ± 0.2 for aluminum titanate; 56.1 ± 0.4 for tricalcium dititanate; and 21.9 ± 0.1 for lithium metatitanate. The measurements and ordinary extrapolation for zinc-titanium spinel yield $S^{\circ}_{298.16} = 32.8 \pm 0.2$ cal./deg. mole. This value should be increased by an at present unknown amount to take account of randomness in the crystal structure.

Thermodynamic values for titanates are of importance in evaluating methods of treating titaniferous ores and of utilizing high titania slags. Titanates also are becoming increasingly important as ceramic constituents. Several[1-6] previous papers from this Laboratory have dealt with low-temperature heat capacities and entropies at 298.16°K. of titanates. The present paper is a continuation of this work, and presents data for aluminum titanate (Al_2TiO_5), tricalcium dititanate ($Ca_3Ti_2O_7$), lithium metatitanate (Li_2TiO_3), and zinc-titanium spinel (Zn_2TiO_4). No previous similar data are to be found in the literature for any of these substances.

Materials.—Aluminum titanate was prepared[7] from pure hydrated alumina and pure titania. A stoichiometric mixture was pressed into pellets and heated five times for a total of 96 hours between 1400 and 1500° and 43 hours between 1500 and 1570°. After each heat the material was quenched to room temperature, to minimize residence time in the reported region of instability between 750 and 1300°.[8] Grinding, mixing, chemical analysis and adjustment of composition were conducted between heats. The final product analyzed 43.95% titania, as compared with the theoretical 43.93%. The principal impurity is 0.06% silica. The X-ray diffraction pattern agrees with those reported in the literature.[8,9]

Tricalcium dititanate was prepared[10] from reagent grade

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(1) C. H. Shomate, THIS JOURNAL, **68**, 964 (1946).

(2) C. H. Shomate, *ibid.*, **68**, 1634 (1946).

(3) S. S. Todd and R. E. Lorenson, *ibid.*, **74**, 2043 (1952).

(4) S. S. Todd and R. E. Lorenson, *ibid.*, **74**, 3764 (1952).

(5) S. S. Todd, *ibid.*, **74**, 4669 (1952).

(6) S. S. Todd and E. G. King, *ibid.*, **74**, 4547 (1953).

(7) This substance was prepared by C. J. O'Brien, Chemist, Minerals Thermodynamics Branch, Region III, Bureau of Mines.

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

(9) A. E. Austin and C. M. Schwartz, *Acta Cryst.*, **6**, 812 (1953).

(10) This substance was prepared by R. E. Lorenson, formerly Chemist, Minerals Thermodynamics Branch, Region III, Bureau of Mines.

calcium carbonate and pure titania. A stoichiometric mixture, pressed into pellets, was heated five times for a total of 12 hours at 1400 to 1500°, with intervening grinding, mixing, analysis and reforming into pellets. The final product analyzed 48.61% titania, as compared with the theoretical 48.71%. There has been some controversy as to whether the composition $Ca_3Ti_2O_7$ is a compound or a solid solution. The recent work of Coughanour, Roth and DeProsse[11] appears to have settled the matter and proved that a compound of this composition exists. They reported an X-ray diffraction pattern with which the present sample is in reasonably good agreement.

Lithium metatitanate was prepared[12] from reagent grade lithium carbonate and pure titania. A stoichiometric mixture was heated six times for a total of 70 hours at 1000 to 1050° and 30 hours at 1150°. Grinding, mixing, analysis and adjustment of composition were conducted between heats. The final product contained 72.70% titania, as compared with the theoretical 72.78%. Impurities are 0.03% silica and 0.06% nickel and platinum contamination from containers. The X-ray diffraction pattern agrees with that in the A. S. T. M. catalog, except for the presence of two additional lines. The latter are believed to be lines for lithium titanate as they do not correspond to any possible impurity.

TABLE I

HEAT CAPACITIES

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
Al_2TiO_5 (mol. wt., 181.86)					
52.74	2.230	114.75	11.21	216.20	25.28
56.55	2.633	124.74	12.80	226.10	26.36
60.98	3.163	135.93	14.55	236.04	27.37
65.50	3.759	145.50	16.03	245.67	28.28
70.22	4.392	155.96	17.56	256.22	29.25
75.04	5.059	165.82	18.99	266.21	30.13
80.73	5.875	175.83	20.35	276.27	30.99
85.01	6.523	185.70	21.67	286.46	31.79
94.82	8.032	195.95	22.93	296.39	32.47
105.13	9.648	206.12	24.11	298.16	(32.60)
$Ca_3Ti_2O_7$ (mol. wt., 328.04)					
52.63	7.253	114.31	26.38	216.18	48.08
56.50	8.339	124.38	29.19	226.70	49.55
61.10	9.763	135.58	32.13	236.29	50.83
65.60	11.24	146.01	34.78	245.74	51.97
69.86	12.61	155.76	37.04	256.21	53.15
74.28	13.98	165.69	39.17	266.17	54.14
80.15	15.87	176.52	41.28	276.05	55.20
84.36	17.22	186.67	43.26	286.53	56.14
93.53	20.11	196.44	44.88	296.87	57.03
103.69	23.20	206.18	46.50	298.16	(57.20)
Li_2TiO_3 (mol. wt., 109.78)					
54.58	2.043	114.33	9.445	216.33	21.26
60.12	2.534	124.30	10.86	226.09	22.07
64.35	2.958	135.84	12.43	235.82	22.77
68.29	3.377	145.54	13.72	245.67	23.50
72.14	3.805	155.80	15.02	256.13	24.21
76.04	4.269	165.68	16.19	266.50	24.84
81.62	4.977	175.81	17.36	276.20	25.38
86.23	5.569	185.77	18.39	286.44	25.95
94.65	6.696	196.16	19.42	295.94	26.42
104.80	8.111	206.09	20.35	298.16	(26.54)
Zn_2TiO_4 (mol. wt., 242.66)					
53.88	5.185	114.28	15.18	216.08	27.30
58.15	5.893	124.63	16.73	226.04	28.17
62.94	6.748	135.83	18.35	235.80	28.93
67.80	7.595	145.47	19.68	245.68	29.68
72.68	8.408	155.71	20.99	256.13	30.33
77.30	9.172	165.52	22.21	266.07	31.01
80.83	9.799	175.98	23.43	276.25	31.62
85.11	10.47	185.75	24.48	286.39	32.21
94.80	12.07	195.99	25.51	296.51	32.71
104.72	13.65	206.62	26.48	298.16	(32.82)

Zinc–titanium spinel was prepared[7] from reagent grade zinc oxide and pure titania. A stoichiometric mixture, pressed into pellets, was heated four times for a total of 65 hours above 1000°. The product was quenched to room temperature after each heat, to minimize residence time in the region of instability reported by Cole and Nelson.[13] Grinding, mixing, analysis, adjustment of composition and reforming into pellets were conducted between heats. The final product contains 67.08% zinc oxide and 32.86% titania, as compared with the theoretical 67.07 and 32.93%. The principal impurity is 0.05% of hydrochloric acid insoluble matter. The X-ray diffraction pattern agrees with that in the A. S. T. M. catalog, except for one additional line that possibly is attributable to zinc oxide.

Measurements and Results

The measurements were conducted with previously described[14] apparatus. The masses of substances employed are: 192.74 g. of aluminum titanate, 165.45 g. of tricalcium dititanate, 200.18 g. of lithium titanate, and 310.44 g. of zinc–titanium spinel.

The experimental heat capacities, expressed in defined calories (1 cal. = 4.1840 abs. joules) per degree-mole, are in Table I and Fig. 1. Molecular weights accord with the 1953 International Atomic Weights.[15] All four substances show regular behavior.

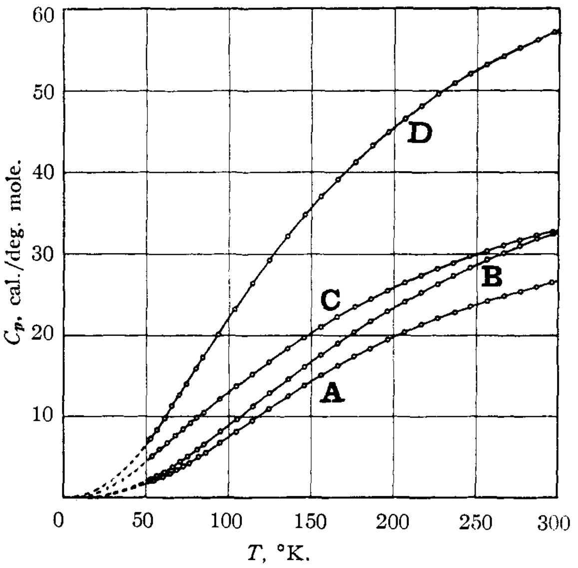

Fig. 1.—Heat capacities: curve A, Li_2TiO_3; curve B, Al_2TiO_5; curve C, Zn_2TiO_4; curve D, $Ca_3Ti_2O_7$.

It is of interest to compare the heat capacity of tricalcium dititanate with the sum of the heat capacities of 2 moles of calcium metatitanate and 1 mole of calcium oxide. At room temperature the

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[11] L. W. Coughanour, R. S. Roth and V. A. DeProsse, *J. Research Natl. Bur. Standards*, **52**, 37 (1954).

[12] This substance was prepared by K. C. Conway, Chemist, Minerals Thermodynamics Branch, Region III, Bureau of Mines.

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

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

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

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.

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[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

RECEIVED NOVEMBER 29, 1954

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).