The heats of vaporization calculated from equation (6) are compared with the measurements of Fiock, Ginnings and Holton in Table I.

For water the data of Smith, Keyes and Gerry[9] for the vapor pressure, and the values of Osborn and Meyers[10] for the rate of change of the vapor pressure, have been used. The heats of vaporization calculated from equation (3) are compared with the values given by Osborn, Stimson and Ginnings[11] in Table II.

<div align="center">TABLE II</div>

<div align="center">HEAT OF VAPORIZATION OF WATER</div>

T, °C.	L, g. cal./g. O.S.G.	cal./g. eq. (3)	T, °C.	L, g. cal./g. O.S.G.	cal./g. eq. (3)	T, °C.	L, g. cal./g. O.S.G.	cal./g. eq. (3)
0	596.5	596.7	140	512.0	515.6	280	368.2	372.2
20	585.6	586.5	160	497.1	500.9	300	335.1	338.7
40	574.5	575.8	180	480.9	485.3	320	295.5	298.1
60	563.1	564.7	200	463.1	467.5	340	245.1	245.5
80	551.2	553.3	220	443.5	448.0	350	212.8	211.4
100	538.9	541.5	240	421.5	425.9	360	171.3	166.5
120	525.9	529.0	260	396.6	400.9	370	107.0	93.3
						374.11	0	0

Heats of vaporization may also be determined from equation (3) in the absence of an analytic correlation of the vapor pressure data. Given a sufficient number of experimental points an

(9) Smith, Keyes and Gerry, *Proc. Am. Acad. Arts Sci.*, **69**, 137 (1934).

(10) Osborn and Meyers, *J. Research Natl. Bur. Standards*, **1**, 1 (1934).

(11) Osborn, Stimson and Ginnings, *Mech. Eng.*, **57**, 162 (1935).

approximation for dp/dT is obtained from

$$\left|\frac{dP}{dT}\right|_{T_2} \cong \left|\frac{\Delta P}{\Delta T}\right|_{T_2} = \frac{P_3 - P_1}{T_3 - T_1}$$

where, geometrically, the slope of the chord between the points p_1, T_1 and p_3, T_3 is taken for the slope of the tangent line at p_2, T_2. The accuracy of the method, clearly, depends upon the narrowness of the spacing of the experimental points. A very useful method of evaluating dp/dT has been proposed by Rutledge.[12] His formulations permit simple application but require equal intervals of either p or T. Both methods are suitable for calculating the rate of change of the vapor pressure since in its entire range the vapor pressure curve is devoid of abrupt directional changes and points of inflection.

Summary

A function of pressure and temperature is derived for the heat of vaporization.

The equation is applicable to all substances whose critical pressure and critical temperature are known and for which vapor pressure data are available.

(12) Rutledge, *Phys. Rev.*, **40**, 262 (1932), and Margenau and Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., New York, N. Y., 1943, p. 456.

Heat Capacities at Low Temperatures of Na₂TiO₃, Na₂Ti₂O₅ and Na₂Ti₃O₇[1]

BY C. HOWARD SHOMATE[2]

The thermodynamic properties of certain titanates are of interest in connection with experimental studies of methods of treatment and utilization of titaniferous iron ores. Data for the sodium titanates are particularly pertinent to the smelting of such ores under a slag rich in sodium carbonate.

A recent paper[3] from the Pacific Experiment Station of the Bureau of Mines presented low temperature heat capacity and entropy data for ferrous, calcium, and magnesium metatitanates. This paper reports similar data for three titanates of sodium. No previous low-temperature values exist for these substances, but Naylor[4] has determined their high-temperature heat contents.

Materials

The titanates were prepared in this Laboratory by R. J. O'Dea[2] by repeated heating of stoichio-

metric amounts of sodium carbonate and titanium dioxide at 900 to 1,100° for several hours with continuous pumping to remove carbon dioxide.

Analyses of the final products for titanium and carbon dioxide, and the known silica impurity of the original titanium dioxide, indicated the following proximate compositions: 98.4% Na_2TiO_3, 1.1% Na_2SiO_3 and 0.5% Na_2CO_3; 98.7% $Na_2Ti_2O_5$, 1.0% Na_2SiO_3 and 0.3% Na_2CO_3; 98.6% $Na_2Ti_3O_7$, 1.1% Na_2SiO_3 and 0.3% Na_2CO_3.

X-Ray examinations of the samples were made by Dr. E. V. Potter.[5] The crystalline character of the substances was proved, but there were no previous data with which to check the diffraction patterns.

Heat Capacities

The method and apparatus used in the low-temperature heat capacity measurements were described previously.[6,7] The experimental results, expressed in defined calories (1 calorie =

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(2) Chemist, Pacific Experiment Station, Bureau of Mines.

(3) Shomate, THIS JOURNAL, **68**, 964 (1946).

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

(5) Physicist, Salt Lake City Station, Bureau of Mines.

(6) Kelley, THIS JOURNAL, **63**, 1137 (1941).

(7) Shomate and Kelley, *ibid.*, **66**, 1490 (1944).

4.1833 int. joules),[8] are listed in Table I and shown graphically in Fig. 1. The values of the heat capacities at 298.16°K., read from 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 heat capacity results for the impurities mentioned above.

All weights were corrected to vacuum, using the following densities: Na_2TiO_3, 3.19; $Na_2Ti_2O_5$, 3.40 and $Na_2Ti_3O_7$, 3.44 g./cc., respectively. These values were determined in this Laboratory by R. J. O'Dea.[2]

TABLE I

MOLAL HEAT CAPACITIES

Na_2TiO_3 Mol. wt. = 141.89		$Na_2Ti_2O_5$ Mol. wt. = 221.79		$Na_2Ti_3O_7$ Mol. wt. = 301.69	
T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
52.9	3.726	52.7	5.773	52.6	8.306
56.9	4.352	56.9	6.699	56.8	9.517
61.0	5.026	60.9	7.608	61.1	10.78
68.0	6.199	65.3	8.601	65.4	12.08
71.9	6.889	69.6	9.623	69.7	13.39
76.1	7.616	74.0	10.66	73.8	14.65
80.4	8.354	78.4	11.69	78.1	15.96
84.5	9.037	84.7	13.15	84.9	17.97
94.6	10.72	94.9	15.42	94.9	20.85
106.7	12.68	104.7	17.60	104.5	23.54
116.5	14.17	115.1	19.77	115.0	26.38
125.2	15.45	125.3	21.78	125.0	28.90
135.0	16.79	135.0	23.62	135.0	31.32
145.7	18.15	145.7	25.44	145.6	33.67
155.4	19.30	155.5	27.07	155.5	35.72
165.5	20.43	165.8	28.64	165.5	37.75
175.4	21.48	175.6	30.07	175.6	39.63
185.5	22.44	185.6	31.38	185.6	41.32
195.8	23.32	196.0	32.61	195.9	42.95
205.8	24.20	205.9	33.81	205.8	44.49
216.1	25.04	216.2	34.91	216.1	45.88
225.9	25.76	226.7	35.94	226.0	47.16
235.7	26.38	235.9	36.77	235.7	48.34
246.2	27.07	246.0	37.66	246.1	49.53
256.0	27.71	256.1	38.58	256.2	50.78
266.0	28.24	266.1	39.39	266.3	51.84
276.0	28.87	276.1	40.18	276.1	52.70
286.0	29.40	286.0	40.83	286.1	53.80
296.2	29.91	296.3	41.54	296.4	54.72
(298.16)	(30.02)	(298.16)	(41.68)	(298.16)	(54.85)

The three sodium titanates exhibited normal behavior, there being no thermal anomalies in the temperature range studied.

Entropies

Evaluation of the entropies 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 the measured heat capacities (within 1%) in the regions indicated

$$Na_2TiO_3: \quad D\left(\frac{234}{T}\right) + 2E\left(\frac{315}{T}\right) + 3E\left(\frac{617}{T}\right) \quad (52-255°K.)$$

$$Na_2Ti_2O_5: \quad D\left(\frac{175.6}{T}\right) + 3E\left(\frac{295}{T}\right) + 4E\left(\frac{585}{T}\right)$$
$$(52-225°K.)$$

$$Na_2Ti_3O_7: \quad D\left(\frac{136.5}{T}\right) + 4E\left(\frac{266}{T}\right) + 6E\left(\frac{606}{T}\right)$$
$$(52-275°K.)$$

The symbols D and E denote, respectively, Debye and Einstein functions. These functions were used for extrapolating the heat-capacity curves to 0° K. (broken lines in Fig. 1).
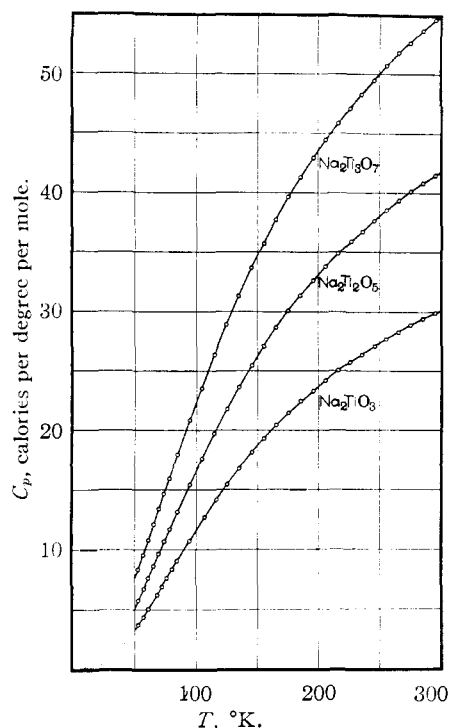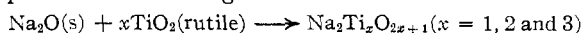

Fig. 1.—Heat capacities.

Table II summarizes the entropy calculations for the three titanates.

TABLE II

ENTROPIES AT 298.16°K. (E.U./MOLE)

	Na_2TiO_3	$Na_2Ti_2O_5$	$Na_2Ti_3O_7$
0-52.00°K. (extrapolated)	1.42	2.52	3.98
52.00-298.16°K. (measured)	27.64	39.02	51.93
$S^0_{298.16}$	29.1±0.1	41.5±0.2	55.9±0.3

The above results afford a means of estimating the entropy of Na_2O. It has previously been shown that as a first approximation the entropy of a silicate or a titanate at 298.16° K. may be taken as the sum of the entropies of the constituent oxides.[3,9,10] Assuming, therefore, that the entropies of the following reactions

$$Na_2O(s) + xTiO_2(rutile) \longrightarrow Na_2Ti_xO_{2x+1} \ (x = 1, 2 \text{ and } 3)$$

(8) Mueller and Rossini, Am. J. Phys., 12, 1 (1944).

(9) Parks and Kelley, J. Phys. Chem., 30, 1175 (1926).

(10) Kelley, THIS JOURNAL, 65, 339 (1943).

are zero, and using the value $S^0_{298.16} = 12.4$ E.U./ mole for TiO_2 (rutile),[11] the following values for the entropy of $Na_2O(s)$ are calculated: $S^0_{298.16} =$ (1) 16.7, (2) 16.7 and (3) 18.7 E.U./mole, with a mean of 17.4 E.U./mole. This value may be compared with the mean value of 17.2 E.U./mole similarly obtained by Kelley from data on three sodium silicates.[12]

(11) McDonald and Seltz, *ibid.*, **61**, 2405 (1939).
(12) Kelley, *ibid.*, **61**, 471 (1939).

Summary

The heat capacities of Na_2TiO_3, $Na_2Ti_2O_5$ and $Na_2Ti_3O_7$ were measured in the temperature range 52 to 298°K.

The following molal entropies at 298.16°K. were computed: Na_2TiO_3, 29.1 ± 0.1; $Na_2Ti_2O_5$, 41.5 ± 0.2 and $Na_2Ti_3O_7$, 55.9 ± 0.3 E.U.

From these entropy values and a value for rutile reported in the literature, the entropy of $Na_2O(s)$ at 298.16°K. is estimated to be 17.4 ± 0.8 E.U./mole.

The Effects of Radioactivity on Fatty Acids[1,1a]

By Charles W. Sheppard[2] and Virginia L. Burton

The genesis of petroleum remains an unanswered scientific question. Pyrolysis and high pressure have been proposed as factors contributing to the reduction to petroleum fractions of the complex organic substances found in source sediments. However, there is good reason to believe that petroleum is usually formed at much lower average temperatures than are necessary for pyrolytic conversion of organic compounds. The effect of high pressures on such transformations has never been definitely established.

The suggestion that radiations from the radioactive constituents of sedimentary rocks might be a factor in the conversion of gaseous paraffins to petroleum was first made by Lind and Bardwell[3] about twenty years ago. More recently, Bell, Goodman and Whitehead[4] and Tiratsoo[5] stated that a more likely process for the genesis of petroleum by radioactivity is the decomposition and conversion of the solid and semi-solid organic compounds in marine sediments by alpha radiation. According to Trask and Wu[6] and Wells and Erickson[7] from 2 to 34 parts of fatty acids per 100,000 parts of sediment have been found in various marine muds. Clarke and Mazur[8] have recently shown that the ether-extractable lipids of diatoms contain 60 to 80% of free fatty acids.

To test the radioactivity hypothesis, certain organic compounds likely to be found in source sediments have been bombarded by alpha particles from radon[9] and its active deposit. Since the molecular weights of the above fatty acids are not entirely certain, four acids of varying molecular weights were bombarded in the present experiments. These acids were acetic, caprylic, lauric and palmitic. Acetic acid was bombarded in the vapor state at 130°, and the others as solids. In all four cases the gas phase was analyzed after bombardment and, in addition, the solid residues of lauric and palmitic acids were examined.

Results

Decomposition of the solid acids during bombardment yielded a complex gas–liquid–solid system. As shown in Fig. 1, the production of gas from solid acids in the initial stages was proportional to the fraction of radon decayed. As the pressure of the gas increased, however, the relationship became non-linear because of partial absorption of radiation in the gas produced.

In each experiment the gas consisted mainly of carbon dioxide and hydrogen, with small amounts of carbon monoxide, water, methane, and higher hydrocarbons as shown in Table I. The per-

(2) Present address: Vanderbilt University, Medical School, Nashville, Tennessee.
(3) Lind and Bardwell, This Journal, **48**, 1556 (1926).
(4) Bell, Goodman and Whitehead, *Bull. Am. Assoc. Petroleum Geol.*, **24**, 1529 (1940).
(5) Tiratsoo, *Petroleum*, **4**, 58 (1941).
(6) Trask and Wu, *Bull. Am. Assoc. Petroleum Geol.*, 14, 1451 (1930).
(7) Wells and Erickson, *U. S. Geol. Survey Professional Papers*, **186-D**, 69 (1940).
(8) Clarke and Mazur, *J. Biol. Chem.*, **141**, 283 (1941).

Table I

Gaseous Products from Bombardment of Fatty Acids with Alpha Particles

Constituents	Volume %			
	Acetic	Caprylic	Lauric	Palmitic
H_2	18	33	42	48
CO_2	37	51	41	34
CO	22	10	11	6
H_2O^a	..	3	4	10
$CH_4{}^a$	20	0.7	0.6	0.4
$C_2H_6{}^a$	3.7	1.0	.5	.6
$C_3H_8{}^a$	..	0.4	.1	.1
$C_4H_{10}{}^a$	..	0.7	.2	.8

a Mass spectrometric analyses.