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

The Heat Capacities of Vanadium, Vanadium Trioxide, Vanadium Tetroxide and Vanadium Pentoxide at Low Temperatures[1]

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In continuation of its general program of study of the thermodynamic properties of the various materials which are important in metallurgical processes, the Pacific Experiment Station of the U. S. Bureau of Mines has determined the heat capacities of especially pure samples of vanadium, vanadium trioxide, vanadium tetroxide and vanadium pentoxide. This study is interesting theoretically as well as from the standpoint of the vanadium oxide catalysis involving both oxidation and reduction.

The methods, apparatus and accuracy have been described previously.[3]

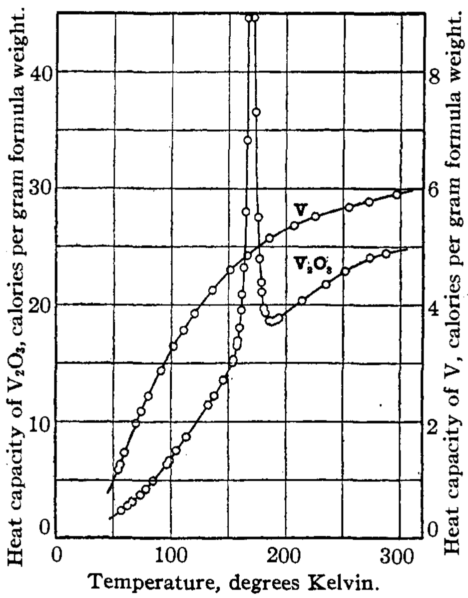

Fig. 1.—The heat capacity of vanadium and vanadium trioxide, in calories per gram formula weight.

Materials

The samples were prepared for this Laboratory through the courtesy of the Vanadium Corporation of America. We are especially indebted to Mr. Jerome Strauss, Chief Research Engineer of this company, for his interest and coöperation in furnishing the samples .According to their analyses all the materials had a purity of 99.5% or better. The vanadium metal consisted of pellets of −8 to +35 mesh.

The oxides were in the form of powder, which was compressed into pellets at a pressure of about 2 tons per sq. in., so that an adequate quantity of the material could be placed in the calorimeter. Density measurements were made on all the samples. The density as well as the quantity of material used in the determinations is shown in Table I.

TABLE I

MATERIALS USED

Material	Density	Density temperature, °C.	Sample, g.
V	6.009	22.5	339.7
V_2O_3	4.843	22.0	136.6
V_2O_4	4.260	21.4	149.8
V_2O_5	3.352	22.6	165.3

The Specific Heats

No previous low temperature measurements have been made on vanadium or its oxides. The results obtained in this Laboratory on the heat capacities of vanadium and vanadium trioxide, expressed in gram calories (15°) per gram formula weight, are shown graphically in Fig. 1, and the values for vanadium tetroxide and vanadium pentoxide are shown in Fig. 2. The experimental

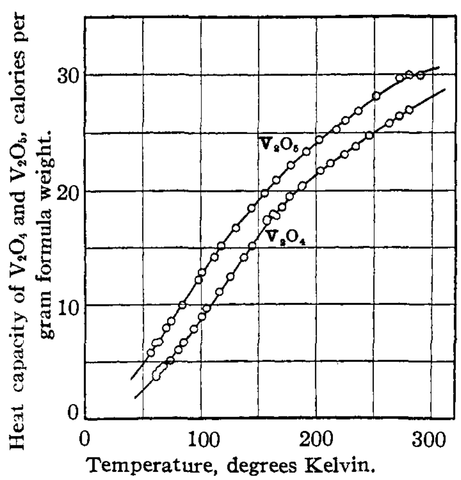

Fig. 2.—The heat capacity of vanadium tetroxide and vanadium pentoxide, in calories per gram formula weight.

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(3) Anderson, THIS JOURNAL, 52, 2296, 2712 (1930); 54, 107 (1932); 55, 3621 (1933).

determinations of the heat capacity for vanadium are given in Table II. The values for vanadium trioxide, except those between 150 and 195°, are given in Table III. The values for the heat capacities for vanadium trioxide between 150 and 195°K. with the temperature rise (ΔT) of the determination are given in Table IV. The experimental values for the vanadium tetroxide and the pentoxide are shown in Tables V and VI. The calculations were made on the basis of V = 50.95 and O = 16.00.

TABLE II

HEAT CAPACITY PER GRAM ATOMIC WEIGHT OF VANADIUM

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.2	1.182	101.6	3.290	185.2	5.143
56.0	1.273	110.2	3.564	206.7	5.358
59.7	1.466	120.3	3.851	225.2	5.518
69.7	1.973	135.7	4.248	254.8	5.666
74.3	2.181	151.0	4.596	272.1	5.772
80.2	2.441	166.0	4.482	296.5	5.904
91.5	2.871				

TABLE III

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF VANADIUM TRIOXIDE

Run	T, °K.	C_p	Run	T, °K.	C_p
1	56.9	2.355	10	145.7	13.54
2	62.5	2.741	13	213.8	20.34
3	66.9	3.113	14	234.7	21.70
4	73.4	3.729	15	251.3	22.85
5	78.4	4.235	16	273.0	24.05
6	84.6	4.958	17	287.2	24.41
7	96.2	6.333	37	98.9	6.687
8	113.5	8.698	38	104.4	7.456
9	132.4	11.42	39	137.7	12.20

TABLE IV

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF VANADIUM TRIOXIDE

Run	T, °K.	ΔT	C_p
11	165.7	2.080	34.12
12	189.9	6.656	18.61
18	153.2	5.183	15.11
19	156.9	2.370	16.45
20	159.2	2.186	18.02
21	161.0	2.030	19.53
22	163.0	1.775	23.19
23	164.7	1.530	28.00
24	166.6	1.034	44.53
25	167.7	0.729	66.68
26	168.4	.671	72.79
27	169.2	.606	81.03
28	170.9	.829	53.69
29	171.9	.956	44.61
30	173.0	1.109	36.53
31	175.2	1.300	27.51
32	176.7	1.418	23.96
33	178.2	1.492	21.89
34	180.4	1.560	19.68
35	182.0	1.562	19.30
36	185.2	1.581	18.62
40	153.8	3.238	15.29
41	161.6	2.465	20.90
42	168.4	0.837	76.36
43	169.4	.924	67.54
44	178.8	2.122	21.07
45	187.9	2.658	18.56
46	192.3	3.123	18.73
47	157.6	2.741	16.93
48	186.3	3.757	18.60
49	153.1	3.050	15.05
50	193.9	3.496	18.84
51	152.9	3.011	15.02
52	157.4	3.319	16.71

TABLE V

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF VANADIUM TETROXIDE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
61.4	3.630	147.0	15.31	270.9	26.40
68.8	4.564	154.7	16.83	279.4	26.96
73.5	5.078	170.1	18.62	61.4	3.921
80.5	5.993	176.9	19.52	64.9	4.291
84.9	6.670	188.0	20.47	100.3	8.917
93.6	7.871	203.7	21.73	144.7	15.16
98.1	8.521	212.3	22.35	157.1	17.52
104.7	9.649	224.2	23.13	187.6	20.37
115.7	11.12	234.0	23.82	165.2	18.84
125.6	12.43	245.8	24.77	157.3	17.34
137.4	14.11	262.6	25.80	162.2	18.10

TABLE VI

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF VANADIUM PENTOXIDE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
100.9	12.83	191.4	23.39	289.5	29.91
111.9	14.19	202.6	24.43	56.8	5.773
117.7	15.17	217.8	25.28	60.4	6.656
130.4	16.74	223.8	26.08	63.7	6.711
143.9	18.56	235.7	26.84	69.6	7.917
155.3	19.81	251.0	28.16	73.9	8.503
165.2	20.94	271.3	29.66	83.4	9.920
178.0	22.23	279.9	29.96	98.0	12.19

An anomaly was discovered in the case of the vanadium trioxide, the peak being at 168.8°K. Five measurements were made on the energy necessary to heat the vanadium trioxide through this transition.

The mean of these measurements from 161.3 to 180.0°K. was 692.2 cal. with an average deviation of ±2.4 and a maximum deviation of 3.5 cal. from the mean. The entropy of this transition from 161.3 to 180.0°K. amounts to 4.08 units.

An attempt was made to supercool the vanadium trioxide from room temperature to below 90°K. The first run after this attempt was run 37. There was no evidence of supercooling, as the points fell on the same smooth curve. Specific heat measurements were also made both below and above the peak before and after measurements on the heat of transition. These points also fell on the curve independently of the method of cooling.

Calculation of Entropies

The entropies of vanadium and its oxides were calculated by the usual graphical method. The experimental heat capacity curves coincided at low temperatures with Debye functions having the following parameters (Θ): for vanadium, 374; vanadium trioxide, 275; vanadium tetroxide, 258; and vanadium pentoxide, 206.

It is obvious that no combination of Debye and Einstein functions can completely represent the heat capacity of vanadium trioxide. However, the combination

$$C_{V_2O_3} = D\,\frac{(275)}{T} + 4E\,\frac{(551)}{T}$$

was found to fit the experimental data up to nearly 150°K., where the transition is beginning to have considerable influence on the heat capacity. The following combinations were found to fit the experimental data on vanadium tetroxide and vanadium pentoxide to nearly room temperature.

$$C_{V_2O_4} = D\,\frac{(258)}{T} + 2E\,\frac{(394)}{T} + 3E\,\frac{(709)}{T}$$

$$C_{V_2O_5} = D\,\frac{(206)}{T} + 2E\,\frac{(268)}{T} + 4E\,\frac{(744)}{T}$$

Table VII gives the results of the entropy calculations.

TABLE VII

ENTROPY DATA

	V	V_2O_3	V_2O_4	V_2O_5
Extrap. (0–56.2)°K.	0.48	1.03	1.23	2.47
Graph. (56.2–298.1) °K.	6.53	22.50	23.29	28.81
S°_{298} graphical	7.01 + 0.1	23.5 ± 0.3	24.5 ± 0.3	31.3 ± 0.5
S°_{298} calcd. from functions			24.4	31.2

Related Thermal Data

An attempt was made to fit the equilibrium data of Kobayashi,[4] Müller,[5] and Spencer and Justice,[6] with the entropy data and reasonable specific heats at high temperatures. Using Kobayashi's data for the reaction $V_2O_3 + 3H_2 = 2V + 3H_2O$ a ΔS of +56.0 is obtained, while the value of ΔS from the entropies is +32.34, a discrepancy of nearly 24 entropy units. For the reaction $V_2O_4 + CO = V_2O_3 + CO_2$, Spencer gives −3.76 for ΔS. From entropy data $\Delta S = +2.8$. Since none of the data give results consistent with the entropy data it may be assumed that true equilibria were not measured or that the reactions involved were other than those for which the data were given.

Ruff and Friedrich[7] have measured the heat of formation of vanadium trioxide and vanadium pentoxide, giving the values, −302,000 cal. and −437,000 cal., respectively. No values were reported for the tetroxide. Using Ruff and Friedrich's values in combination with the entropy values given above and 49.03 for the entropy of oxygen, the free energy of vanadium trioxide and vanadium pentoxide may be calculated as −282,900 and −405,600, respectively.

If a free energy expression based on Ruff and Friedrich's thermal data and the measured entropies is set up and recalculated to the temperature range of Kobayashi's experiments and compared with the combination of Kobayashi's two equilibrium constants for the reduction of vanadium dioxide to vanadium and vanadium trioxide to vanadium dioxide, giving the apparent equilibrium constant of vanadium trioxide to vanadium, it is found that the calculated values are approximately of the order of 1/1000 to 1/10,000 of those derived by Kobayashi.

This would seem to indicate that the ratio H_2O/H_2 in the temperature range that Kobayashi worked is too small to be determinable and that Kobayashi's experiments determined the oxidation of vanadium due to minute amounts of impurities or to some color change of the impurities themselves.

Summary

The heat capacities of vanadium, vanadium trioxide, vanadium tetroxide and vanadium pentoxide from about 55 to 300°K. have been determined and their corresponding entropies calculated. The following table contains the summarized results:

SUMMARY OF ENTROPIES, FREE ENERGIES AND HEATS OF FORMATION

	$S_{298.1}$	$\Delta F^\circ_{298.1}$	$\Delta H^\circ_{298.1}$
V	7.01	....	....
V_2O_3	23.5	−282,900	−302,000
V_2O_4	24.5	....	....
V_2O_5	31.3	−405,600	−437,000

BERKELEY, CALIF. RECEIVED JUNE 14, 1935

(4) Kobayashi, *Bull. Chem. Soc. Japan*, **8**, 231 (1933).

(5) Müller, W. Biltz's Festschrift, Hannover, 1927, given also in Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, Vol. IX, 1929, pp. 741 and 744.

(6) Spencer and Justice, THIS JOURNAL, **56**, 2306 (1934).

(7) Ruff and Friedrich, *Z. anorg. Chem.*, **89**, 279 (1914).