−1.4% at 373°K., +2.2% at 578°K., and +4.9% at 732°K., the temperatures being those reported by Sato.

Table II gives heat content values read from smooth curves at 100° intervals, together with the corresponding entropy increments above 298.16°K. The latter were computed from and exactly match the former.

TABLE II

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K. (SMOOTH VALUES)

	VC		VN	
T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$H_T - H_{298.16}$, cal./mole	$S_T - S_{288.16}$, cal./deg./mole
400	890	2.55	1,010	2.91
500	1,850	4.70	2,080	5.30
600	2,870	6.55	3,200	7.34
700	3,950	8.22	4,370	9.14
800	5,090	9.74	5,590	10.76
900	6,280	11.14	6,850	12.25
1000	7,510	12.43	8,130	13.60
1100	8,770	13.64	9,430	14.84
1200	10,060	14.76	10,750	15.99
1300	11,380	15.81	12,090	17.06
1400	12,720	16.80	13,450	18.07
1500	14,080	17.74	14,820	19.01
1600	15,450	18.63	16,200	19.90

High temperature heat content equations were derived by the method of Shomate[5]; using all the data of Table I and the molal heat capacities[2] at 298.16°K., $C_{p,\ 298.16} = 7.970$ for vanadium carbide and $C_{p,298.16} = 9.080$ for vanadium nitride. The resulting equations, which follow, fit the measured data to within an average deviation of 0.3% in each instance.

$$\text{VC: } H_T - H_{298.16} = 9.18T + 1.65 \times 10^{-3}T^2 + 1.95 \times 10^5T^{-1} - 3538$$

$$\text{VN: } H_T - H_{298.16} = 10.94T + 1.05 \times 10^{-3}T^2 + 2.21 \times 10^5T^{-1} - 4096$$

The corresponding molar heat capacity equations are:

$$\text{VC: } C_p = 9.18 + 3.30 \times 10^{-3}T - 1.95 \times 10^5T^{-2}$$

$$\text{VN: } C_p = 10.94 + 2.10 \times 10^{-3}T - 2.21 \times 10^5T^{-2}$$

Summary

High temperature heat contents above 298.16°K. of vanadium carbide and vanadium nitride were measured from about 400° to 1611°K. A table of heat content and entropy increments above 298.16°K. is reported, and heat content and heat capacity equations are derived.

(5) Shomate, THIS JOURNAL, **66**, 928 (1944).

BERKELEY, CALIFORNIA RECEIVED SEPTEMBER 16, 1948

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

Low-Temperature Heat Capacity and High-Temperature Heat Content of Ammonium Vanadate

BY S. S. TODD[1] AND J. P. COUGHLIN[1]

Ammonium vanadate is the commercially most readily obtainable, substantially pure, vanadium-containing substance and frequently is the source material in the preparation of other vanadium compounds. Consequently, considerable interest attaches to its properties. This paper reports the results of low temperature heat capacity measurements in the temperature range 51.4 to 298.16°K. and of high temperature heat content measurements in the temperature range 298.16 to 550°K. No previous similar data are available for this substance.

Material.—Ammonium vanadate of 96.7% purity was dissolved in hot concentrated hydrochloric acid until saturation, diluted by two volumes of distilled water, and filtered. The filtrate was heated to boiling, oxidized with ammonium persulfate in the presence of a small amount of nitric acid, and again filtered. The oxidized solution was neutralized with ammonium hydroxide in the presence of an excess of ammonium chloride. The precipitated ammonium vanadate was filtered off, washed several times with 1:40 ammonium hydroxide and once with distilled water, and finally dried for twenty-four hours at 75 to 80°. The product was analyzed by dissolving in 10% sulfuric acid, reducing the vanadium with sulfur dioxide, expelling excess sulfur dioxide by bubbling with a stream of carbon dioxide, and titrating with 0.1 N potassium permanganate. The analysis gave 43.55% vanadium content, which is the theoretical value for ammonium vanadate.

Measurements and Results

Both the low temperature heat capacity and high temperature heat content measurements were made by means of previously described[2] apparatus and methods. The defined calorie (1 cal. = 4.1833 int. joules) is used throughout. All weighings were corrected to vacuum and the molecular weight of ammonium vanadate is taken as 116.99 in accordance with the 1947 International Atomic Weights. The ice point is taken as 273.16°K.

A 41.810 g. sample was employed in the low temperature heat capacity measurements. The measured results are given in Table I and are plotted against temperature in Fig. 1. The heat capacity curve is normal, there being no indication whatever of the transition encountered in similar measurements of the ammonium halides[3,4,5] and

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[1] Chemist, Pacific Experiment Station, Bureau of Mines.

(2) Kelley, Naylor and Shomate, U. S. Bureau of Mines, Tech. Paper 686, 1946, 34 pp.

(3) Simon, *Ann. Physik* (4), **68**, 241 (1922).

(4) Simon Simson, and Ruhemann, *Z. physik. Chem.*, **129**, 344 (1927).

(5) Extermann and Weigle, *Helv. Phys. Acta*, **15**, 455 (1942).

Table I

Low-Temperature Heat Capacity of NH_4VO_3

T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole
53.5	6.041	115.1	15.32	216.6	25.50
57.6	6.703	124.9	16.58	226.7	26.19
62.0	7.397	136.2	17.96	236.6	26.87
66.3	8.059	146.3	19.07	246.2	27.59
70.8	8.776	156.0	20.09	256.3	28.29
75.7	9.583	166.2	21.13	266.5	28.91
80.1	10.29	176.3	22.12	276.5	29.62
84.2	10.90	186.3	22.98	286.8	30.19
95.1	12.55	196.2	23.86	296.8	30.87
104.8	13.91	206.7	24.68	298.16	(30.91)

ammonium sulfate.[6] In this respect the substance behaves similarly to both hydrated and anhydrous ammonium–aluminum sulfate.[6] (The heat capacity value at 298.16°K., included in Table I, was read from a smooth curve.)

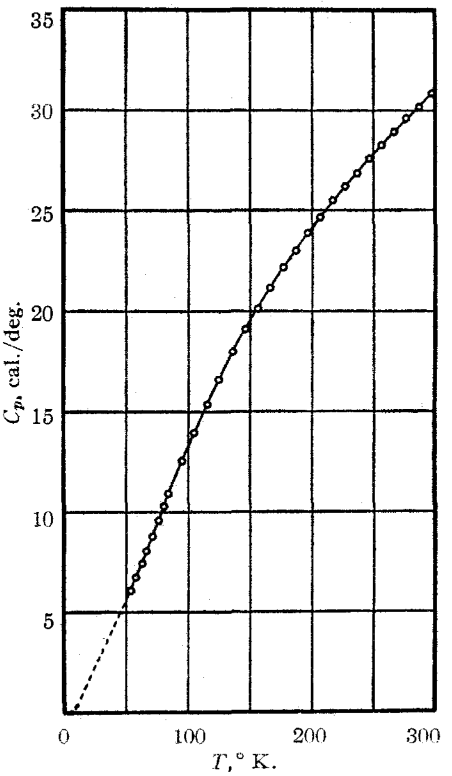

Fig. 1.—Molal heat capacity at low temperatures of ammonium vanadate.

The entropy of ammonium vanadate, obtained from these heat capacity measurements, is $S^\circ_{298.16}$ = 33.6 ± 0.3 cal./deg./mole. Of this amount, 30.00 is the measured portion between 51.00 and 298.16°K., and 3.61 is the extrapolated portion between 0 and 51.00°K. The former was obtained by numerical integration of a plot of the measured heat capacity against log T. The latter was obtained from the following empirical sum of Debye and Einstein functions, which represent the measured heat capacity over the entire experimental range to within 1%

$$D\left(\frac{125}{T}\right) + 3E\left(\frac{331}{T}\right) + 3E\left(\frac{919}{T}\right).$$

Combination of this entropy value and the entropies of the elements[7] leads to $\Delta S^\circ_{298.16} = -132.3$ as the entropy of formation of ammonium vanadate. Bichowsky and Rossini[8] give $\Delta H_{293.16}$ = −283,500 cal. per mole as the heat of formation. (The correction of the latter value to 298.16°K. is negligible.) The free energy of formation from the elements is, therefore, $\Delta F^\circ_{298.16} = -244{,}050$ cal. per mole.

Table II

High Temperature Heat Contents of NH_4VO_3

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
351.7	1785	525.7	8,460	569.3	(10,730)
401.5	3625	554.7	(9,795)	576.8	(10,920)
452.8	5575	564.1	(10,320)	597.4	(12,290)
502.7	7510				

A 4.3485-g. sample of ammonium vanadate was used in the high temperature heat content measurements. During measurement the substance

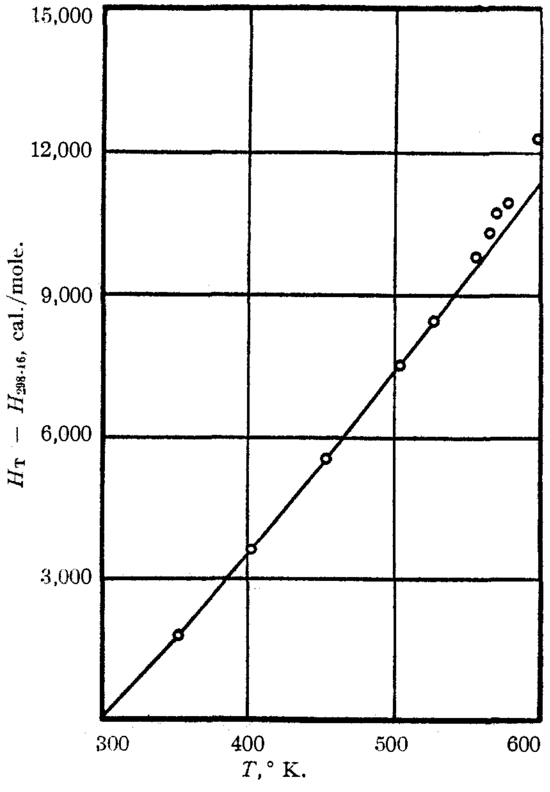

Fig. 2.—High temperature heat content of ammonium vanadate.

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[6] Shomate, This Journal, 67, 1096 (1945).

[7] Kelley, U. S. Bureau of Mines, Bull. 434, 1941, 115 pp.

[8] Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

was contained in a platinum–rhodium capsule which was sealed gas tight by gold soldering. The heat content of the capsule was determined by separate measurements. The experimental results are listed in Table II and are plotted in Fig. 2.

The substance behaved satisfactorily up to about 550°K. Above that temperature the results are somewhat discordant and become progressively too high. This is attributed to beginning of thermal decomposition of the substance, which is confirmed by the fact that the gas pressure within the platinum–rhodium capsule became large enough to cause rupture at 610°K. All values in parentheses in Table II show decomposition effects. Between 298.16 and 550°K., the results are represented to within an average deviation of 0.8% by the equation

$$H_T - H_{298.16} = 45.42T + 12.90 \times 10^5 T^{-1} - 17,869$$

The corresponding molal heat-capacity equation is

$$C_p = 45.42 - 12.90 \times 10^5 T^{-2}$$

These equations, however, should not not be employed for extrapolation to higher temperatures.

Table III gives smooth values of the high-temperature heat content and corresponding entropy increments above 298.16°K.

TABLE III

HEAT CONTENT AND ENTROPY INCREMENTS FOR AMMONIUM VANADATE ABOVE 298.16°K.

T, °K.	$H^\circ_T - H^\circ_{298.16}$, cal./mole	$S^\circ_T - S^\circ_{298.16}$, cal./deg./mole
350	1730	5.35
400	3580	10.29
450	5480	14.76
500	7420	18.85
550	9390	22.61

Summary

The low temperature heat capacity of ammonium vanadate was measured throughout the temperature range 51.4 to 298.16°K. The entropy is $S^\circ_{298.16} = 33.6 \pm 0.3$ cal./deg./mole.

The high temperature heat content of ammonium vanadate was measured throughout the temperature range 298.16 to 550°K. Thermal decomposition precluded obtaining satisfactory results at higher temperatures. Heat content and entropy increments above 298.16°K. are tabulated.

BERKELEY, CALIFORNIA RECEIVED AUGUST 2, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Thermodynamic Data on the Cadmium Chloride Complexes Determined from the Solubility of Cadmium Ferricyanide

BY EDWARD L. KING[1]

In this paper data on the solubility of cadmium ferricyanide in solutions containing chloride ion will be presented. It is possible to interpret these data in terms of the formation of the cadmium chloride complexes: $CdCl^+$, $CdCl_2$ and $CdCl_3^-$. These complexes have been studied previously by I. Leden[2] and others.[3] The solubility measurements have been carried out at several temperatures making it possible to calculate heats of formation and entropies of the several complex species as well as the several equilibrium constants.

Experimental Work

Preparation of Solutions Used in These Experiments.—All solutions were prepared using doubly distilled water, the second distillation being from an alkaline permanganate solution. Analytical reagent grade chemicals were used in all cases without further purification. In the preparation of the sodium perchlorate solution, equivalent amounts of perchloric acid and sodium carbonate were mixed.

Preparation of the Cadmium Ferricyanide.—The solid used in the solubility measurements was prepared by precipitating cadmium ferricyanide at room temperature from a freshly prepared dilute solution of potassium ferricyanide by the addition of cadmium nitrate solution. The solid separates as a very finely divided yellow material. Analyses of the material used in the solubility measurements as well as several other samples of solid precipitated in the presence of a low (less than 0.1 *M*) excess of potassium ferricyanide or in the presence of an excess of cadmium nitrate were performed. The solid was decomposed by heating with concentrated sulfuric acid. The iron and cadmium were then separated by isopropyl ether extraction of iron as described by Swift.[4] The iron was analyzed iodometrically[5] and cadmium was determined gravimetically by conversion to the sulfate. The ratio of cadmium to iron in the five different samples analyzed ranged from 1.47 to 1.52 with an average of 1.49. Thus the finely divided yellow solid is $Cd_3\{Fe(CN)_6\}_2 \cdot xH_2O$. The degree of hydration of the solid was not determined as in no case was the solid dried and weighed; only the ratio of cadmium to iron was determined.

Solubility Measurements.—Before using the $Cd_3\{Fe(CN)_6\}_2 \cdot xH_2O$ in a solubility determination, it was washed several times with a dilute solution of sodium perchlorate. Then each portion was washed with a solution of the composition to be used in the solubility experiment. The solubility equilibrium is established very rapidly; in no experiment was a slowness detected even though in the experiments at 47.5° samples were removed after two minutes stirring. In several experiments equilibrium was approached from the supersaturated side as well as from the other side. Because of the high rate of solution, it was possible to carry out the measurements in open vessels; no errors due to evaporation would be expected. The

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[1] Present address: Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

[2] Leden, *Z. physik. Chem.*, **188A**, 160 (1941).

[3] Reference 2 contains a comprehensive review.

[4] E. H. Swift, "A System of Chemical Analysis," Prentice Hall, New York, N. Y., 1946, pp. 291-298.

[5] E. H. Swift, *op. cit.*, pp. 298-300.