have been summarized by giving the heat content, entropy and free energy increments above 298.16°K. at even temperature intervals.

BERKELEY, CALIF. RECEIVED AUGUST 7, 1944

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Properties of Vanadium Tetrachloride

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Vanadium tetrachloride is an inorganic compound of interesting properties. It is a dark red liquid which hydrolyzes readily, which decomposes slowly at ordinary temperatures to chlorine and the trichloride, and which reacts as a chlorinating agent. It is non-salt-like in character, has a low dielectric constant, is soluble in carbon tetrachloride, has a liquid range from −26 to +152° at atmospheric pressure and has a relatively low boiling point. Its valence is unexpected in view of the existence of the tri- and penta-fluorides, and the non-existence of a tetrafluoride. It is an odd molecule, if the formula VCl_4 is correct; and its intense color may be used as supporting evidence of the free radical assumption.

Vanadium tetrachloride was prepared by Roscoe[1] by the reaction of chlorine on vanadium or vanadium nitride at red heat. From the analysis of his product and the determined vapor density, he assigned the formula VCl_4 to the compound. He found the liquid density to be 1.8584 g./cc. at 0°, 1.8363 at 8°, and 1.8159 at 30°. He was unable to obtain the pentachloride by the reaction of the tetrachloride with chlorine. He found its boiling point to be 154° at 760 mm. pressure. Biltz and Kuenecke[2] found the boiling point to be 148.5° at 755 mm. pressure, and Ruff and Lickfett[3] report 153.7° at 768 mm. pressure. The freezing point was found by Biltz and Kuenecke[2] to be −109°, but Morette[4] obtained the value of $-28 \pm 2°$. Voigt and Biltz[5] found the electrical conductivity to be too small to measure. Loomis and Schlundt[6] determined the dielectric constant at room temperature. Their average value was 3.05.

From a series of thermochemical reactions Ruff and Friedrich[7] concluded the heats of formation of the chlorides of vanadium to be

$$V(s) + Cl_2(g) = VCl_2(s) + 147 \pm 4 \text{ kcal.}$$
$$V(s) + 3/2\ Cl_2(g) = VCl_3(s) + 187 \pm 8 \text{ kcal.}$$
$$V(s) + 2Cl_2(g) = VCl_4(l) + 165 \pm 4 \text{ kcal.}$$

From this the following equation for the decomposition of vanadium chloride results

$$2VCl_4(l) \longrightarrow 2VCl_3(s) + Cl_2(g) + 44 \pm 20 \text{ kcal.}$$

Preparation.—Vanadium tetrachloride was prepared by a modification of the method given by Mentes.[8] Dry chlorine was passed over ferro-vanadium contained in a glass combustion tube in an electric furnace. One-quarter-inch mesh ferro-vanadium containing 90% vanadium was used. The entering chlorine passed through a pair of sulfuric acid bubblers for the purpose of drying. The product from the exit side of the combustion tube was received in a 500-cc. flask. This was the part of an all-glass fractionating column which contained no stopcock and its attendant grease.[9] On the take-off of the fractionating column was sealed a small condenser and a fraction cutter. This fraction cutter had a number of 50-cc. flasks sealed onto it to receive the fractions. Each of these receivers was provided with a side arm containing an internal capillary for breaking off purposes. Rotation of the fraction cutter on a ground joint provided a means of directing the liquid stream into the different receivers. The entire apparatus was sealed together so that the product came in contact only with glass.

The temperature of the reaction tube was adjusted to 200°. This is a lower temperature than has been previously used but was employed to reduce the amount of ferric chloride in the product.

At the end of the reaction, the connection between the reaction tube and receiver was sealed, and the product was distilled. The receivers were sealed off from the fraction cutter after they were filled.

The samples collected boiled at 149.7° at a pressure of 731 mm. These samples were found to remain in a satisfactory condition for several months without appreciable decomposition, if kept in the dark.

Vanadium trichloride was prepared from vanadium tetrachloride by heating it at 140° for one week, while passing dry carbon dioxide over it. The vanadium trichloride was dried by heating it at 160° for three days. It was analyzed for vanadium by titrating with potassium permanganate and found to contain 32.30%. The theoretical is 32.39%. A gravimetric analysis for chlorine gave 67.10%, while the theoretical is 67.61%.

The Equilibrium Constant for the Reaction $2VCl_3(s) + Cl_2(g) \rightleftharpoons 2VCl_4(g)$.—The equilibrium constant for this reaction was determined by subjecting a sample of vanadium trichloride to a known volume of chlorine and determining the increase in pressure when equilibrium was attained.

A diagram of the apparatus used is shown in Fig. 1. This consisted essentially of a reaction vessel containing a boat of vanadium trichloride in an electric furnace. This was connected with capillary tubing to a U-tube of sulfuric acid which in turn was connected to an adjustable mercury manometer. The sulfuric acid U-tube was calibrated in cubic centimeters.

As the apparatus was originally sealed together, the reaction vessel was open at the end opposite the capillary tubing. A stream of dry nitrogen was passed through the apparatus. A sample of vanadium trichloride was transferred to a small porcelain boat, the operation being performed in a dry box. It was placed in a glass tube and transported in an atmosphere of dry nitrogen. After introduction of the porcelain boat, the end of the reaction tube was drawn out to form a capillary, using care to pre-

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(1) Roscoe, *Ann. Chem.*, Supplement **7**, 70 (1869).

(2) Biltz and Kuenecke, *Z. anorg. allgem. Chem.*, **147**, 171 (1925).

(3) Ruff and Lickfett, *Ber.*, **44**, 506 (1911).

(4) Morette, *Compt. rend.*, **202**, 1846 (1936).

(5) Voigt and Biltz, *Z. anorg. allgem. Chem.*, **133**, 277 (1924).

(6) Loomis and Schlundt, *J. Phys. Chem.*, **9**, 734 (1915).

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

(8) Mentes, THIS JOURNAL, **35**, 671 (1913).

(9) Simons, *Ind. Eng. Chem., Anal. Ed.*, **10**, 29 (1938).

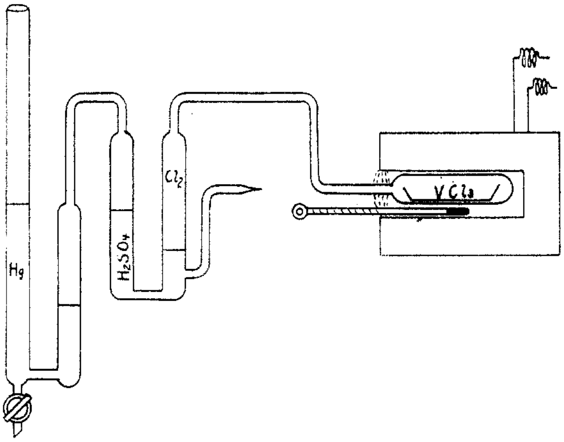

Fig. 1.—Equilibrium apparatus.

vent the entrance of water. Chlorine was then admitted through the sulfuric acid tube and allowed to escape from the end of the capillary on the end of the reaction tube. As the trichloride was prepared by decomposition of the tetrachloride at 140°, as the tetrachloride decomposes to the trichloride slowly at atmospheric pressure and room temperature, and as the intense color of the tetrachloride would have made it visually evident, there is little chance of the trichloride being contaminated with the tetrachloride by this treatment. After at least one hour, this capillary was sealed off and an electric furnace placed around the reaction tube. A thermometer was inserted and the furnace was packed with copper shot and sealed with rock wool.

The volume of the reaction vessel was about 25 cc. and was obtained by determining the volume of chlorine outside of the vessel at different pressures. The furnace was then brought to the desired temperature, and the capillary tubing near the furnace heated electrically about five degrees higher than the furnace temperature. The heating of the capillary tubing, combined with the fact that the chlorine pressure was externally increased with time and so tended to sweep any VCl_4 in the capillary tube back into the furnace, prevented condensation of the VCl_4 in the colder parts of the apparatus. The intense color of liquid VCl_4 enabled a very small amount of condensation to be detected, and when this occurred, the measurements were discarded. The temperature was maintained within ±0.1°, and the pressure was measured within 0.5 mm. From the increase in pressure and the known volumes, the partial pressures of both VCl_4 and Cl_2 can be obtained. The value of $K = (P_{VCl_4})^2/P_{Cl_2}$ should remain constant if equilibrium is established, and K was calculated from the data as the reaction proceeded. The results taken at 160° are shown in Table 1. Similar measurements at 170° and 180° gave average values of K of 2070 and 3000 respectively. Equilibrium was assumed to be established within the precision of the measurements when the pressure remained constant at constant gas volume. This was then confirmed by proceeding with the measurements for an additional period of time equal to or greater than the time required to reach the apparent equilibrium after the furnace [illegible] stancy of the values of K obtained during this additional period confirmed the establishment of at least an apparent equilibrium. Critically the equilibrium should be approached from both directions, but the approach of this equilibrium from the reverse direction presents certain experimental difficulties. On calculating the heat of the reaction from the temperature coefficient of the equilibrium constant in the usual manner, it was found to be 13,800 calories by either the extreme values of K or the average of the middle value with each of the end values. Thus

$2VCl_3(s) + Cl_2(g) = 2VCl_4(g) \qquad \Delta H = 13.8$ kcal

$$2VCl_3(s) + Cl_2(g) = 2VCl_4(g) \qquad \Delta H = 13.8 \text{ kcal}$$

at 170°. This value is considerably less than the value obtained from thermochemical data by Ruff and Friedrich.[7]

TABLE I

EQUILIBRIUM MEASUREMENTS

$2VCl_3(s) + Cl_2(g) = 2VCl_4(g)$

Time	Temp. furnace, °C.	Total pressure,[a] mm.	Pressure VCl_4, mm.	Pressure Cl_2, mm.	$K = \frac{(P_{VCl_4})^2}{P_{Cl_2}}$, mm.
8:50	26	768.9			
10:25	160	905.2	140.5	764.7	258.1
11:28	160	918.6	518.6	400.0	675.0
12:30	160	940.2	559.7	380.5	823.3
1:30	160	957.1	585.7	371.4	919.5
2:25	160	971.3	614.6	356.7	1049
3:30	160	982.7	638.9	343.8	1187
4:25	160	996.8	654.6	342.2	1252
5:20	160	1006.6	671.6	335.0	1347
6:25	160	1018.6	697.6	321.0	1516
7:25	160	1025.7	695.1	330.6	1461
8:30		1039.9	707.3	332.6	1504
2:30		1140.1	757.6	382.5	1501
3:30	160	1147.4	756.0	391.4	1461
4:25	160	1157.0	762.7	394.3	1476
				Final Av.	1480

[a] After each determination the total pressure was increased by decreasing the external volume.

Melting Point of Vanadium Tetrachloride.—The melting point was obtained by determining the warming curve of a freshly distilled and degassed sample sealed in a glass container. The vessel containing the sample was surrounded with a copper jacket and placed in a cool Dewar vessel. The sample was distilled into the freezing point vessel, frozen, and evacuated, then warmed to 0° and reëvacuated to remove traces of free chlorine, and frozen again. The warming curve was followed by a copper–constantan thermocouple connected to the laboratory potentiometer. The thermocouple was calibrated at the melting points of both mercury and ice. The melting point thus found was −25.7°.

Vapor Pressure.—The vapor pressure of vanadium tetrachloride was determined in an apparatus similar to that reported by Menzies.[10] The vanadium tetrachloride was distilled into the apparatus and boiled for a few minutes to remove any free chlorine. Dry nitrogen was used as the inert gas, exterior to the protecting, balancing manometer. Pressure determinations were made with the temperature both ascending and descending. Temperatures were read on a calibrated thermometer, and stem corrections were applied. Readings were made to 0.1°. Pressure readings were estimated to 0.1 mm. and corrected to the density of mercury at 0°. Consistency of the measurements indicates that the pressure is probably correct within ±0.5 mm. and the temperature ±0.5°. The measurements made with rising and falling temperatures agree within these limits as do the values calculated by the equation below. Between the temperature of 39.5° and 80.2, the vapor pressure was found to follow the equation

(10) Menzies, THIS JOURNAL, **32**, 1413 (1910).

$$\log_{10} P_{\text{mm.}} = -\frac{1998}{T} + 7.581$$

By extrapolation of this equation the normal boiling point is calculated to be 152 ± 2°. The Trouton constant or the entropy of vaporization at the normal boiling point is 21.3, as the heat of vaporization, calculated from the above equation, is 9100 calories per formula weight.

Polymerization of Vanadium Tetrachloride.—From the formula of this compound and its apparent existence in the

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[10] Menzies, THIS JOURNAL, **32**, 1413 (1910).

vapor as an odd molecule, it could be expected to exist under certain conditions in polymeric form, analogous to the polymerization of hydrogen atoms, nitric oxide, triphenylmethyl, etc. The determination of the vapor density by Roscoe[1] indicates that it is monomeric in the vapor state at about 200°. The question arises as to the possible polymerization to form V_2Cl_8 at low temperatures and in a liquid state. To test this, we have determined the freezing point depression of a solution of VCl_4 in carbon tetrachloride. We appreciate the inherent difficulties of the interpretation of this kind of measurement and the uncertainty of identifying molecular species in the liquid state. The reported measurements indicate a polymerization of the form $2VCl_4 = V_2Cl_8$ for which an equilibrium constant is calculated in carbon tetrachloride solution at its freezing point.

The freezing point apparatus, shown in Fig. 2, consisted of an all-glass vessel with a sealed-in mechanical stirrer and contained a thermocouple well so arranged as to provide a sufficient length of the thermocouple wire within the liquid phase to ensure protection against error due to the thermal conduction of the wire. The stirrer consisted of a hollow glass plunger operating in a dash-pot containing an exit hole near its lower end. The plunger connected to a sealed-in iron core which could be raised by an external magnet. A mechanical commutator provided an intermittent direct current for the magnet. The plunger was alternately lifted by the magnet and allowed to fall by its own weight in the periods in which the magnet was not activated. The thermocouple was calibrated at the melting points of carbon tetrachloride and ice, and the standard thermocouple curve was fitted to these points.

The carbon tetrachloride was saturated with chlorine and subjected to the direct rays of the sun for three months. The chlorine was then boiled out and the material distilled in a fractionating column which contained no stopcocks.[9] During the distillation and transfer of the carbon tetrachloride, extreme care was used to prevent the admission of water. The vanadium tetrachloride was transferred to small weighing vials by distillation. These vials contained capillary tips. The solution was made by breaking the capillary tips of the vials under carbon tetrachloride, the operation being done in a dry-box. The dilution of the solution in the freezing point apparatus was obtained by admitting a weighed portion of carbon tetrachloride.

TABLE II

FREEZING POINT LOWERINGS OF SOLUTIONS OF VANADIUM TETRACHLORIDE IN CARBON TETRACHLORIDE

Solution	Wt. VCl_4 per 1000 g. Cl_4	ΔT, C.	Apparent mol. wt.	Concn. V_2Cl_8, mole per 1000 g. CCl_4	Concn. VCl_4, mole per 1000 g. CCl_4	$K = (VCl_4)^2/(V_2Cl_8)$
Pure CCl_4	0	...				
1	66.834	5.97	335.5	0.1474	0.0519	18.29×10^{-3}
2	58.292	5.249	332.7	.1272	.0480	18.11×10^{-3}
3	46.43	4.254	327.0	.0988	.0432	18.89×10^{-3}
4	38.58	3.564	324.2	.0811	.0379	17.71×10^{-3}
1 A	75.192	6.657	338.2	.1672	.0551	18.15×10^{-3}
2 A	60.26	5.415	333.3	.1318	.0490	18.22×10^{-3}
3 A	49.86	4 530	329.6	.1073	.0440	18.04×10^{-3}
					Average	18.2×10^{-3}

After the solution had been placed in the apparatus, it was alternately frozen, evacuated, and remelted several times to remove dissolved gases. A copper jacket was placed around the lower portion of the apparatus, and cooling curves were made while it was placed in a large Dewar vessel containing Dry Ice. Time-temperature curves were obtained while the stirrer was in operation—the period of measurements being thirty seconds. Some supercooling occurred and so the freezing point was evaluated by extrapolating the two branches of the cooling curve to a common point. Checked determinations were made, and a series of determinations were made with different original solutions. The results from these experiments are shown in Table II, in which it is assumed that the equilibrium exists between the VCl_4 and V_2Cl_8, and the equlibrium constant for this reaction is calculated.

For the freezing point constant, the value of the heat of fusion of carbon tetrachloride of 640 calories per mole was used. This is the value recommended by the Bureau of Mines[11] after a survey of the available published data.

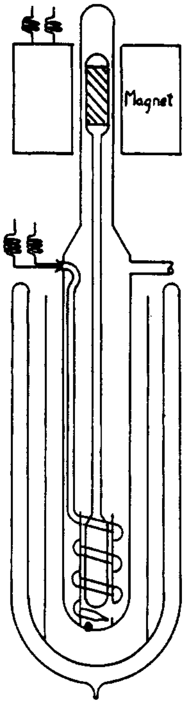

Fig. 2.—Freezing point apparatus.

Summary

A technique for the preparation of pure vanadium tetrachloride has been described, and the physical properties of the substance studied. K_p in mm. for the reaction $2VCl_3\ (s) + Cl_2\ (g) = 2VCl_4\ (g)$ was found to be 1480 at 160°, 2070 at 170°, 3000 at 180°, with a calculated ΔH of 13.8 kcal.

The freezing point was determined to be $-25.7°$.

The vapor pressure followed the equation $\log_{10} P_{\text{mm.}} = -1998/T + 7.581$ between 29.5 and 80.2°. This extrapolates to give a normal boiling point of 152 ± 2° and a Trouton rule constant of 21.3.

Freezing point measurements of VCl_4 dissolved in CCl_4 have been made. From these the equilibrium constant at approximately $-25°$ is 18.2×10^{-3} for the assumed equilibrium $V_2Cl_8 = 2VCl_4$, and the concentrations expressed in moles per 1000 g. of CCl_4.

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RECEIVED JULY 27, 1944

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[11] Bureau of Mines, United States, Department of the Interior, Bull. 393, page 37 (1936).