independent of the amount of chromate being determined. As would be expected from the uncertainty in the end-point corrections, the percentage deviations when determining very small quantities become much larger, over 1%, per cent, when determining 17 micrograms, even though the absolute error averages less than 0.2 microgram.

The Determination of Vanadate.—Experiments similar to those for the chromium procedure were made in order to establish the permissible range in the acid and cupric concentration. The results were similar, except that at a cupric ion concentration of 0.02 formal and hydrochloric acid concentration of 1.3 formal copper plated on the generator cathode. Therefore, for the vanadate determinations the values finally selected were 0.04 formal for the cupric copper and 2.6 formal for the hydrochloric acid.

The initial results for vanadate determinations were 0.3–0.5% high. An investigation indicated that oxygen was causing these high results. Ramsey[8] reports that high results are obtained when oxygen was not excluded in his iodometric procedure for vanadate, positive errors resulting from catalysis of the oxidation of iodide by oxygen. Because of this difficulty the vanadate procedure was modified by first boiling the diluted vanadate solution under an atmosphere of carbon dioxide, cooling, adding the desired amount of copper sulfate and hydrochloric acid, then maintaining an atmosphere of carbon dioxide over the solution during the determination. Analyses by this procedure gave much better agreement with the calculated values. The possibility remained that the lower results observed after eliminating oxygen from the solutions by boiling were caused by the presence of a reducing agent in the solutions which reacted with the vanadate when the solution was heated, or by the presence of an oxidizing agent such as chlorine which was driven off by heating. Therefore, in another set of experiments, the vanadate solution was boiled, then resaturated with air after cooling. These determinations gave practically the same values as those with the original unboiled solutions, indicating that the high results were due to the presence of oxygen.

TABLE II

TITRATIONS OF VANADATE SOLUTIONS

The sodium vanadate solutions were added to a sufficient volume of water to bring the total volume to 35 ml., the solution then boiled and cooled under carbon dioxide; 10 ml. of the 0.20 formal cupric sulfate in 12 formal hydrochloric acid was added and the titration made under carbon dioxide. Solutions were oxygen-free and titration made under carbon dioxide. The generation rate was 10 milliamperes. Generation times varied from 7 to 140 seconds.

Expt.	Determinations made	Vanadium, micrograms Taken	Found	Error Average	Maximum
I	4	37.62	37.60	0.08	−0.18
II	4	75.56	76.15	0.59	+0.92
III	3	755.7	755.9	0.9	+1.2
IV	5	755.9	755.7	0.3	−0.6
V	8	774.7	775.7	1.47	+2.2

The data from a series of confirmatory analyses made by the modified vanadium procedure are tabulated in Table II and show that with 750 microgram quantities of vanadium the maximum deviation from the calculated value was about 0.3% and the average deviation about 0.13%. With quantities of vanadium less than 75 micrograms the absolute error was less than 0.6 microgram.

Acknowledgments.—We are obligated to Mr. H. W. Brough and Mr. R. E. Phillips for construction of the titration apparatus and for improvements in its design and operation.

Summary

A secondary coulometric method is described in which electrolytically generated cuprous copper is used for the titration of chromate and vanadate. An amperometric method is used for determining the end-point. The electricity required for the process is measured by a constant-current-time method. Data from titrations of from 17 to 1700 micrograms of chromium (as chromate), and from 37 to 750 micrograms of vanadium (as vanadate) are shown. The chromate titrations resulted in a maximum deviation from calculated values of less than 0.2%, and an average deviation of less than 0.1% for quantities of chromium larger than 170 micrograms; for the vanadate titrations the maximum deviation was less than 0.3% and the average deviation was less than 0.2% for quantities larger than 750 micrograms.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AT THE UNIVERSITY OF WASHINGTON]

The Vapor Pressure of Tantalum Pentabromide

BY EDWARD L. WISEMAN[1] AND N. W. GREGORY

Fundamental thermodynamic data regarding compounds of tantalum and other less familiar elements are seriously lacking. We have measured the vapor pressure of tantalum pentabromide in the temperature interval 200–340° and have determined related physical and thermodynamic properties.

Experimental Part

Preparation and Analysis.—$TaBr_5$ was prepared by bromination of a mixture of Ta_2O_5 (Eimer and Amend, C. P.) and charcoal at 700–860°.[2] Upon resublimation of the product under high vacuum ($p < 10^{-5}$ mm.) at 190–200° beautiful yellow-orange crystals bearing a resemblance to potassium dichromate were obtained. This material was later sublimed into the vapor pressure apparatus.

Analyses were performed on samples which had been used for the vapor pressure measurements. Tantalum was determined by precipitation of tantalum hydroxide with ammonium hydroxide, the precipitate ignited, and weighed as Ta_2O_5. The bromide was determined as the silver salt in the usual manner. Tantalum pentabromide is exceptionally hygroscopic and has a high heat of solution. Samples were dissolved in a partially evacuated

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[1] Present address: Research Department, Union Oil Company, Wilmington, California.

[2] W. K. Von Haagen, THIS JOURNAL, 32, 728 (1910).

container to prevent loss of hydrogen bromide with water being admitted carefully through a stopcock.

The vapor pressure data were obtained from three different samples of the pentabromide. The analyses tabulated below were performed on sample no. 1.

	A	B	C	Theoretical
Ta, %	32.92	31.73	31.42	31.16
Br, %	67.08	67.80	67.78	68.84

In A, only the tantalum–bromine ratio was determined. With other samples, the percentage tantalum was determined without determination of bromine (results: 31.97, 31.33). Although careful dry box technique was employed during transfer operations (removal of sample from apparatus, etc.) a slight contamination by traces of moisture is regarded as practically unavoidable. Since the probability of contact with moisture did not become appreciable until removal of the compound from the apparatus, the purity at the time the vapor pressure measurements were made is believed to have been considerably greater than that indicated by the analytical results.

Apparatus and Procedure.—Measurements were made using a thin glass membrane manometer. The method was a modification of that described by Daniels[3] and others. Motion of the membrane resulting from the pressure of the vapor was detected by an electrical contact established between a wire anchored in the wall of the vessel and a wire anchored in a small glass rod fused to the diaphragm. The contacts were adjusted so that a slight positive pressure (calibrated over the pressure and temperature range involved) on the manometer side of the diaphragm was required to complete the circuit. The sensitivity of the gage used in this work was estimated as ±0.5 mm.

Tantalum pentabromide was sublimed into the apparatus under high vacuum using an auxiliary furnace. The whole apparatus had been previously baked out under vacuum at 450° overnight. After sublimation, the sample tube and tube connecting the vacuum line were sealed off under high vacuum. The furnace used in the measurements consisted of an aluminum block with nichrome resistance wire wound on the exterior. The entire unit was insulated with asbestos and asbestos used to close the open end around the gage. An auxiliary heating unit was placed on the inside of the furnace at the open end. By adjusting the current in this resistance independently of the main furnace, the temperature was controlled so that identical readings were obtained from a thermocouple in contact with the top of the glass vessel and a thermocouple in a well at the bottom of the furnace.

Data were obtained by simply bringing the temperature to a constant value for a minimum of five minutes and measuring the minimum pressure in the external system necessary to complete the circuit. This, together with the calibration, gave the total pressure inside the apparatus.

Results and Discussion

The data recorded in Table I are given in the order in which they were measured. The three samples represent entirely independent measurements with different material employed in each. Values below 10 mm. have not been recorded because of their greater relative uncertainty. The average deviation of the values from that calculated from the analytical expressions in Table II are given for each series. Data in both the liquid and solid range are included, with increasing and decreasing temperature.

A plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature was made to determine the constants given in Table II.

TABLE I

VAPOR PRESSURE OF TANTALUM PENTABROMIDE

Sample 1				Sample 2				Sample 3	
T, °C.	$P_{\text{mm.}}$	T, °C.	$P_{\text{mm.}}$	T, °C.	$P_{\text{mm.}}$	T, °C.	$P_{\text{mm.}}$	T, °C.	$P_{\text{mm.}}$
217	11	261	105	244	43	329	546	213	10
226	16	256	78	274	163	295	277	223	15
235	27	270	135	270	145	256	80	257	83
		290	215	285	213	224	17	266	122
213	9	297	256	302	321	215	11	226	18
218	11	310	343	304	330	231	24	246	47
232	24	324	466	324	500	234	26	238	35
240	35			342	708				
Av. dev. from $P_{\text{calcd.}}$ 4.8%				Av. dev. from $P_{\text{calcd.}}$ 3.3%				Av. dev. from $P_{\text{calcd.}}$ 4.2%	

TABLE II

PHYSICAL AND THERMODYNAMIC PROPERTIES OF TANTALUM PENTABROMIDE

Vapor pressure (liquid 267–345°C.)	$\log p_{\text{mm.}} = -3265/T + 8.171$
Normal boiling point, °C.	345
Heat of vaporization	14.9 kcal./mole
Entropy of vaporization (Trouton constant)	24.1 e. u.
Vapor pressure (solid 200–267°C.)	$\log p_{\text{mm.}} = -5650/T + 12.571$
Triple point, °C.	267
Heat of sublimation	25.8 kcal./mole
Heat of fusion	10.9 kcal./mole

Average absolute deviation of log p (calcd.) from log p (exptl.): 0.018 (average deviation same for both equations, all samples included). This corresponds to an average deviation of the vapor pressures of 4.2% at all temperatures.

Estimated uncertainty in molar heats: ±0.8 kcal. (based on possible variations of lines drawn through the experimental points).

Since the triple point found from these data was not in close agreement with the melting point reported previously (240°),[2] a redetermination of the melting point was made with sample 1. The glass diaphragm was broken and the system maintained under one atmosphere of helium. Although a precise value of the melting point could not be obtained in the vapor pressure apparatus, the sample was observed to melt at 265° with an uncertainty of not more than ±5°. This value is in good agreement with the vapor pressure data. The normal boiling point observed here is also above the previously reported value (320°).

In order to investigate the possibility that the measured pressure in the system might include some bromine arising from thermal decomposition of the pentabromide, a sample was heated in an evacuated container to which a capillary tube connecting a mercury manometer was attached. No perceptible darkening of the surface of the mercury was observed upon heating the sample well over 300°. Additional evidence for the stability of tantalum pentabromide vapor at these

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(3) Daniels, THIS JOURNAL, 50, 1115 (1928).

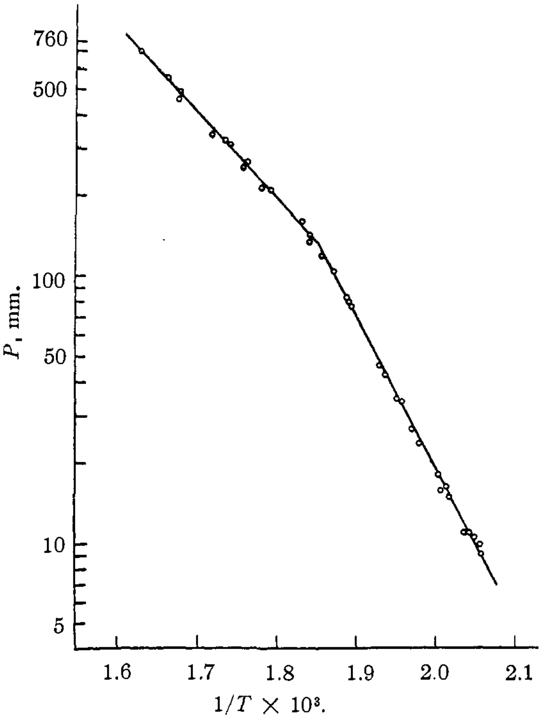

Fig. 1.—Vapor pressure of tantalum pentabromide.

temperatures is afforded by the study of the hydrogen reduction of tantalum pentabromide to tantalum tribromide at 700°.[4] Reduction at this temperature proceeds relatively slowly. In our many sublimations of tantalum pentabromide under various conditions formation of tantalum tribromide was never observed. Considering these observations and the conditions under which the pentabromide is prepared from the oxide, it seems unlikely that tantalum pentabromide dissociates appreciably below its boiling point.

Approximate vapor density calculations based on measurements where complete vaporization of the material occurred indicate that tantalum pentabromide is not appreciably associated in the vapor phase. This is to be expected from the electron diffraction results reported by Skinner and Sutton.[5]

Summary

The vapor pressure of tantalum pentabromide has been studied between 200 and 345°. The results may be expressed by the equations: solid (200–267°): $\log p_{\text{mm.}} = -5650/T + 12.571$; liquid (267–345°): $\log p_{\text{mm.}} = -3265/T + 8.171$.

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(4) Young and Hastings, This Journal, **64**, 1710 (1942).

(5) Skinner and Sutton, *Trans. Faraday Soc.*, **36**, 668 (1940).

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[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL CO-OPERATION, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Exchange between Cobaltous Ion and Cobaltic Hydroxide in the Presence and Absence of Hydrogen Peroxide

BY D. B. BROUGHTON, R. L. WENTWORTH AND M. E. FARNSWORTH

It has been shown previously, by radioactive tracers, that no exchange takes place between manganous ion and colloidal manganese dioxide in aqueous solution.[1] However, when hydrogen peroxide is added, the catalytic decomposition of the peroxide is accompanied by rapid and complete exchange.[2] This has been attributed to cyclic oxidation and reduction of manganese by the peroxide.

The work described herein was done to determine whether hydrogen peroxide would induce a similar exchange between cobaltous ion and colloidal cobaltic hydroxide.

Experimental

Tests for exchange were made both between radioactive cobaltous ion and non-radioactive cobaltic hydroxide and between non-radioactive cobaltous ion and radioactive cobaltic hydroxide. This was done because of the possibility that the addition of hydrogen peroxide might change the distribution of cobalt between the cobaltous and cobaltic forms, and thus give a false indication of exchange on a single combination.

A sample of radioactive 5-year Co^{60}, prepared by bombardment in a cyclotron, was furnished by the M. I. T. Radioactivity Center. This was converted to a 0.138 *M* solution of cobaltous sulfate. The activity, as measured on a Geiger counter was about 45 counts per minute per mg. of cobalt. The scheme followed in determining exchange in the presence of peroxide is illustrated in Fig. 1.

Solutions 1, 2, 3 and 4 were made up, as shown, from cobalt sulfate, sodium hydroxide, and redistilled hydrogen peroxide, and the peroxide was allowed to decompose completely. This gave solutions containing part of the cobalt content as soluble divalent cobalt and the remainder as colloidal cobaltic hydroxide. The quantities of base were adjusted to give approximately equal distribution of cobalt between the two valence stages. (The relatively large quantity of base required was due to the presence of free sulfuric acid in the cobalt sulfate solutions.) The solutions were then filtered and the precipitates washed. P_1, F_2, F_3*, P_4 were analyzed for total cobalt by the method of Young and Hall,[3] to determine distribution between valences. The remaining filtrates and precipitates were then cross-mixed as shown in Fig. 1, so that one solution contained radioactive cobalt only in the soluble divalent form and the other only in the colloidal trivalent form; ten cc. of redistilled 38% peroxide was then added to each mixture and allowed to stand for twenty-four hours. During this period, the bulk of the peroxide decomposed, and the cobaltic hydroxide remained well dispersed. Traces of peroxide still remaining were then destroyed by treating with platinum foil. The solutions were filtered,

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(1) Polissar, This Journal, **58**, 1372 (1936).

(2) Broughton, Wentworth and Laing, *ibid.*, **69**, 741 (1947).

(3) Young and Hall, *Ind. Eng. Chem., Anal. Ed.*, **18**, 246 (1946).