TABLE I

PHYSICAL PROPERTIES OF HYDROGEN BROMIDE ADDUCTS TO FLUORINATED MONO-OLEFINS

Compound	B. p., °C.	Mm.	d^{25}_4	n^{25}_D	$M_R{}^a$	$M_R{}^b$	$AR_F{}^c$	Mol. wt. Calcd.	Found	Fluorine, % Calcd.	Found
$CF_2Br-CHClF$	46.02	619.5	1.8636	1.3685	23.90	23.86	1.04	197.5	194	28.86	28.71
$CF_2Br-CHF_2$	−3.5 to −3.0	625.6						181	184.5	41.98	41.7
$CF_3-CHF-CBrF_2$	29.82 to 30.25	624.2	1.8016	1.3031	24.20	23.40	1.16	231	229	49.35	49.15
$FH\underbracket{CCF_2CF_2C}BrF$	55.94	632.3	1.8504	1.3402	27.55	26.63	1.24			46.91	46.68
$CBrF_2-CHCl_2$	88.48	621.2	1.9043	1.4349	28.80	28.80	1.03	214	210	17.75	17.2
										C, 11.22	11.3

[a] M_R denotes the molecular refraction calculated by the Lorentz–Lorenz formula. [b] M_R denotes the molecular refraction calculated by adding the customary increments for C, H, O, F and double bond (F = 1.03). [c] AR_F is the atomic refraction of fluorine, obtained from $M_R{}^a$ by subtracting the customary increments for C, H, O and the double bond.

the receiver were tested from time to time with a concentrated silver nitrate solution. A very slight trace, if any, of hydrogen bromide was indicated except for perfluorocyclobutene, where it was appreciable. The excess olefin and hydrogen bromide adduct collected in the receiver were separated by fractionation in a laboratory precision column.

Structure of Addition Compound.—From $CF_2=CFCl$, only $CF_2Br—CFClH$ was obtained, as shown by a treatment with zinc, which produced $CF_2=CFH$ and $ZnClBr$; this would not be possible from the alternate isomer, $CF_2H—CFClBr$. From $CF_2=CCl_2$, only $CF_2Br—CHCl_2$ was obtained, demonstrated in the same way. That $CF_3CF=CF_2$ yielded CF_3CHFCF_2Br was assumed by analogy to the addition of hydrogen fluoride to $CF_3CH=CClF$.[7]

The directions of addition are in agreement with similar reported cases[7] and can be explained on the basis of resonance[7] as well as Price's electrostatic approach.[8]

Physical Properties.—Some physical properties of the hydrogen bromide adducts are listed in Table I. (All of these compounds are new.)

Summary

The catalytic, vapor-phase, continuous flow addition of hydrogen bromide to fluoroölefins has been studied and various physical properties of the adducts determined. The mechanism of the addition is discussed.

BOULDER, COLORADO RECEIVED OCTOBER 25, 1948

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[7] A. L. Henne and R. C. Arnold, THIS JOURNAL, **70**, 758 (1948).

[8] C. C. Price, "Mechanism of Reactions of Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946.

[CONTRIBUTION NO. 1245 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Coulometric Titration of Chromate and of Vanadate by Means of Electrolytically Generated Cuprous Copper and an Amperometric End-Point

BY DALE J. MEIER, ROLLIE J. MYERS AND ERNEST H. SWIFT

Introduction.—Szebellédy and Somogyi[1] have pointed out that there are two types of coulometric processes: those in which the desired reaction is caused to take place directly at a suitable electrode and those in which an intermediate half-cell reaction is caused to take place at the electrode and the electrolytic product then causes the desired reaction. Examples of the first type, which can be designated as a primary or direct process, have been described by Lingane[2] in which certain metal ions were reduced at a mercury cathode. The process was controlled by means of cathode voltage control. Lingane has pointed out the advantage of this method for effecting selective reductions, but has also pointed out that it is characteristic of the method that the current decreases exponentially during the course of the electrolysis and approaches zero asymptotically as the reaction approaches completion.

Examples of the second type, which can be designated as a secondary or indirect process, have been described by Szebellédy and Somogyi.[3] In these procedures the intermediate electrode reaction consisted of the anodic oxidation of bromide to bromine; the bromine then oxidized such reducing agents as thiocyanate, hydrazine, and hydroxylamine. These substances are not susceptible to stoichiometric anodic oxidation and, therefore, it is seen that the use of an intermediate electrode reaction serves to extend the number of substances to which coulometric processes can be applied. In addition, since the added intermediate substance, the bromide in the above cases, can be provided in any desired concentration and remains relatively constant during the process, the current can be maintained at any appropriate value throughout the electrolysis. Resultant advantages are the possibility of a more rapid process, the titration at a more practical rate of the very dilute concentrations encountered in semi- or micro procedures, and the substitution

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[1] Szebellédy and Somogyi, *Z. anal. Chem.*, **112**, 313 (1938).

[2] Lingane, THIS JOURNAL, **67**, 1916 (1945).

[3] Szebellédy and Somogyi, *Z. anal. Chem.*, **112**, 385 (1938). **112**, 391 (1938); **112**, 400 (1938).

for the chemical coulometer of the *constant current time* method for determining the quantity of electricity involved in the process.

Recently the use of the bromide–bromine intermediate system has been extended to the coulometric titration of other reducing agents such as thiodiglycol,[4] tripositive arsenic,[5] tripositive antimony,[6] and iodide.[7] In these titrations the method of Szebellédy and Somogyi was modified by the substitution for a chemical coulometer of a constant current time method for the measurement of the electricity, and by the use of an amperometric method for determining the end-point.

There would be obvious advantages in the application of this secondary coulometric process to the determination of oxidizing agents. In order to do so it is necessary that an intermediate half-cell reaction possessing certain essential qualifications be provided. The oxidant of this half-cell reaction must be capable of rapid cathodic reduction with 100% current efficiency. The reductant in turn must be capable of rapid and stoichiometric reduction of the oxidizing agent to be determined. Finally, if the amperometric end-point method mentioned above is to be used, this intermediate half-cell reaction should be capable of causing a current through the indicator electrodes and this current should be linearly dependent upon the concentration of the excess reductant.

Of the various half-cell reactions which were investigated only the cuprous–cupric couple has been found to meet the above qualifications, and then only when used in hydrochloric acid of sufficient concentration to stabilize the chloride complex and thus prevent precipitation of cuprous chloride or of metallic copper.

The application of this intermediate system to the titration of chromate and vanadate is described below.

Experimental

Chemicals.—Standard potassium dichromate solutions were prepared from Bureau of Standards material. The copper sulfate was purified by two recrystallizations from water, the first and last crop of crystals in each recrystallization being discarded; 3 ml. of 3% hydrogen peroxide was added before the first recrystallization and the solution boiled. The resulting crystals were dried and the calculated quantity to give a solution 0.2 formal in copper sulfate was dissolved in reagent grade 12 formal hydrochloric acid. The solution was found to give a titer corresponding to approximately 2×10^{-6} equivalent of reducing material per 10 ml. This effect was shown to arise from the hydrochloric acid and was eliminated by the addition of the requisite amount of a saturated solution of chlorine in hydrochloric acid. Unless prepared in the manner indicated the solution of the copper sulfate in 12 formal hydrochloric acid developed reducing properties upon standing. The sodium vanadate solution was prepared and standardized according to the method of Ramsey.[8] The thiosulfate was standardized against Bureau of Standards potassium dichromate, weight burets being used. This standardization gave values with an average deviation of less than 0.02%.

Occasionally, the laboratory distilled water contained small quantities of an oxidizing agent, thought to be chlorine, which could be removed by boiling the water while passing a current of air through it. At all times boiled distilled water was used in this work.

Apparatus.—The apparatus used was similar to that described by Myers and Swift,[5] except that an electronic circuit was incorporated in order to improve the constant current characteristics and certain modifications made in order to increase the flexibility and convenience of operation. The circuit diagrams are shown in Fig. 1. The stirrer was activated by a four-pole, shaded pole, induction motor which was found to have a speed of 1650 r. p. m. which did not vary measurably between no load and stirrer load and which was constant for a half-hour period within the limits of experimental error (±10 r p. m.).

The titration cell was essentially the same as that used by Myers and Swift except that the generator anode was isolated from the cell by enclosure in a sintered glass filter stick of "medium" porosity. In order to prevent diffusion of the solution being titrated into the filter stick, the solution therein was made 3 formal in sulfuric acid and was maintained at a higher level than that of the solution in the titration cell.

The linear dimensions of the indicator electrodes were approximately 1.5 by 1.5 cm. and 2 by 3 cm. The instrument was provided with a reversing switch so that the polarity of the indicating electrodes could be changed at will. A potential difference of 200 millivolts was impressed across the indicator electrodes, experiments having indicated that this was the minimum value at which minor fluctuations in the applied indicator potential difference had the least effect on the indicator current.

All titrations were made in 40 × 80 mm. weighing bottles, and at a solution volume of 45 ml.

After use, the electrodes were shorted together and stored in a solution prepared from 10 ml. of the 0.2 formal copper sulfate in 12 formal hydrochloric acid and 35 ml. of water.

The generating circuit was calibrated by measuring by means of a student potentiometer the potential drop across a standardized 199.8-ohm coil from a Leeds and Northrup no. 4716 resistance box. Since the absolute accuracy of the current setting was dependent on the accuracy of the standard cell used, this cell was occasionally checked against a Weston Standard Cell which had been calibrated by the United States Bureau of Standards. During the time of this work the value of the standard cell used did not change by more than 0.2 millivolt. During the latter part of this work the 90 volt power supply was obtained from the laboratory storage battery switchboard instead of by use of two 45 volt "B" batteries in order to give better constant current characteristics to the circuit. When using the B batteries, a linear decay of the current was noticed of about 0.1% per four minutes, necessitating frequent changes in the current setting dial. This current decay was reduced to about 0.1% per twenty minutes by the use of the laboratory power supply.

The titrating instrument provided three rates of generation, approximately 1 milliampere, 4 milliamperes, and 10 milliamperes, corresponding to about 10^{-8} equivalent/second, 4×10^{-8} equivalent/second, and 10×10^{-8} equivalent/second. However, it was found that, even for the smallest quantities titrated, better results could be obtained and less time consumed by using the highest generation rate. Consequently, all determinations were carried out at a rate of approximately 10×10^{-8} equivalent/second.

The titration procedure was essentially the same as that described by Myers and Swift.[5] Blanks were made by diluting 5 ml. of the solution 0.2 formal in copper sulfate and 12 formal hydrochloric acid to 45 ml. and generating for five periods of one second each. The reproducibility and linearity of the measurements on blanks are indicated

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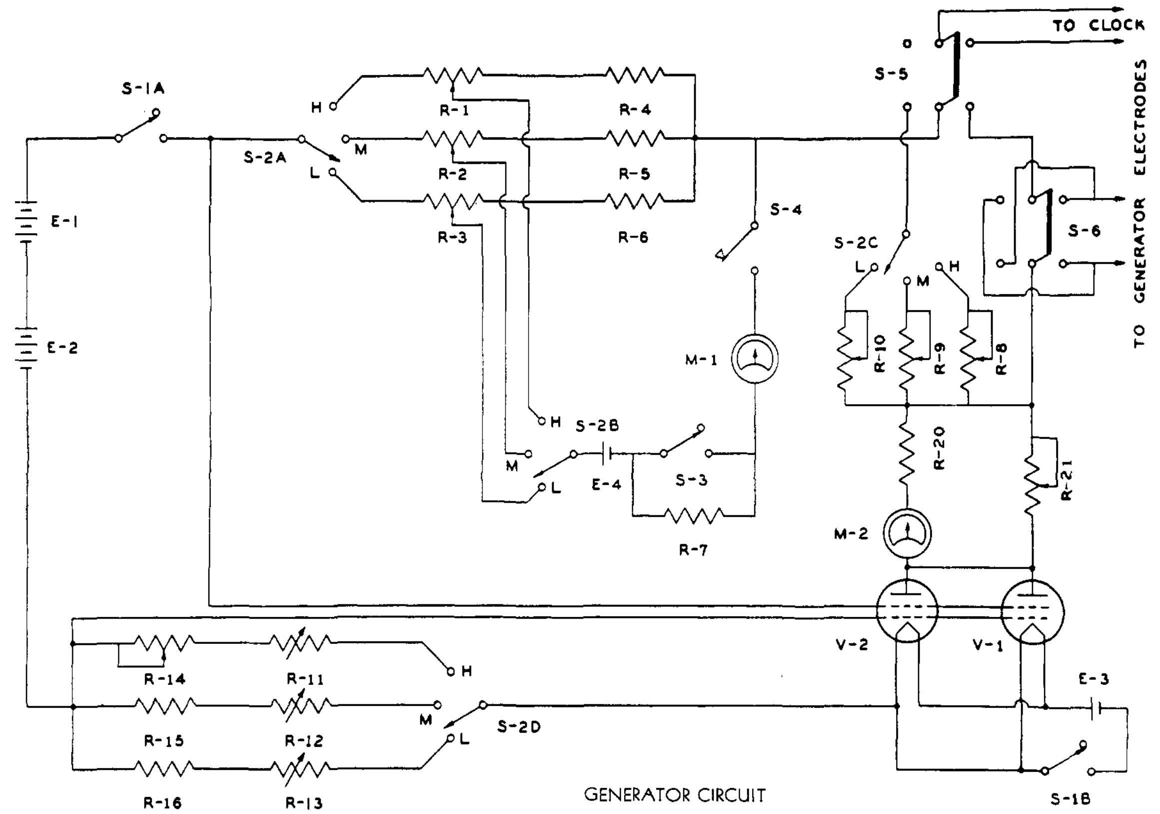
[4] Sease, Niemann and Swift, *Ind. Eng. Chem., Anal. Ed.*, **19**, 197 (1947).

[5] Myers and Swift, THIS JOURNAL, **70**, 1047 (1948).

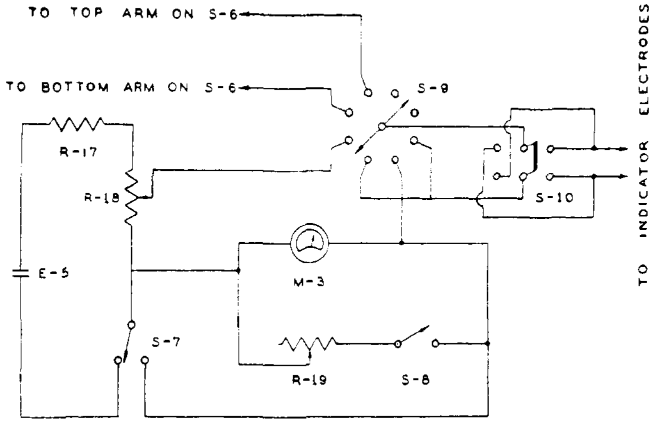
[6] Unpublished experiments by Mr. Raymond A. Brown.

[7] Unpublished experiments by Mr. Warren Wooster.

[8] Ramsey, THIS JOURNAL, **49**, 1138 (1927).



GENERATOR CIRCUIT



INDICATOR CIRCUIT

Fig. 1.—The electrical circuits. Parts list: S-1, S-5, S-6, S-10, DPDT radio toggle switches; S-3, S-7, S-8, SPST radio toggle switches; S-4, micro switch; S-2, three-position, four-pole wafer switch; S-9, four-position, two-pole wafer switch; M-1, Leeds and Northrop no. 2320 galvanometer; M-2, Weston no. 301 0–1 milliammeter; M-3, Weston no. 301 0–50 microammeter; E-1, E-2, Burgess no. 21308 45-v. battery; E-3, E-5, Burgess no. 4FH 1.5-v. battery; E-4, Weston standard cell; V-1, V-2, radio tubes 1C5 GT/G; wire wound potentiometers: R-1, 2 ohms; R-2, 5 ohms; R-3, 10 ohms; R-11, 100 ohms; R-12, 400 ohms; R-13, 4,000 ohms; R-18, 100 ohms; wire wound resistors: Shallcross precision ± 1%, R-4, 100 ohms; R-5, 250 ohms; R-6, 1,000 ohms; fixed 10 watts, R-20, 600 ohms; R-15, 1,750 ohms; R-16, 7,500 ohms; semi-variable 10 watts, R-8, 350 ohms; R-9, 750 ohms; R-10, 9,000 ohms; R-14, 1,000 ohms; R-19, 2,000 ohms; R-21, 100 ohms; carbon resistors: R-7, 60,000 ohms 0.5 watt; R-17, 450 ohms 2 watts.

by Fig. 2 in which data from three measurements have been plotted. Except for the *initial indicator current* reading, the values so obtained were linear. Experiments were carried out to determine if the presence of either chromic ion or vanadyl ion had any effect on the sensitivity of the indicator electrodes. Chromic ion was observed to have no appreciable effect and end-point corrections could be made by directly reading from the graph of indicator currents *vs.* time for the blanks the time correction for the current at the end-point. However, the presence of the vanadyl ion tended to increase the sensitivity of the indicator electrodes; therefore, another procedure had to be adopted to obtain the end-point corrections for the vanadate titration. By extrapolation of the graph of the indicator current *vs.* time of the blanks back to zero generation time, the *initial indicator current* could be determined. (This could not be directly determined with sufficient accuracy since the indicator current reached an equilibrium value very slowly at currents less than 5 microamperes.) After the vanadate had been reduced in a titration and the indicator current had started to rise, the sensitivity of the indicator system was determined by taking four indicator current readings at intervals of one second generation time. By plotting these values and extrapolating the graph back to the current at zero generation time (the *initial indicator current* obtained from the blanks) the equivalent generation time for the vanadate could be determined. This procedure is illustrated in Fig. 3.

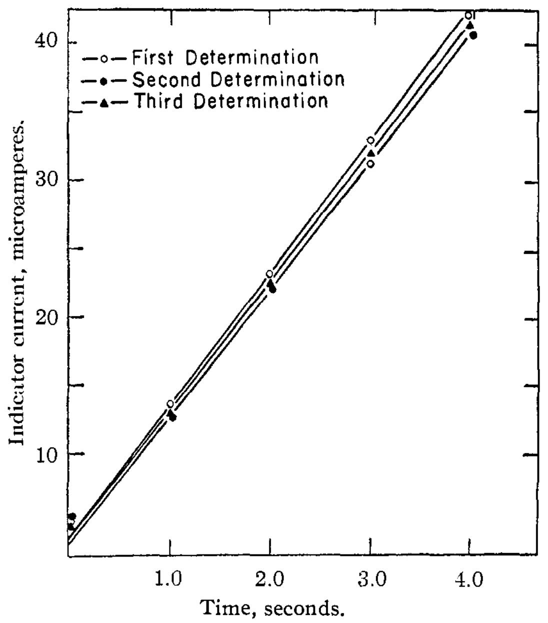


Fig. 2.—Reproducibility of measurements on blanks (indicator current *vs.* generation time).

Determination of Chromate.—Preliminary experiments indicated that the concentration of the cupric copper and of the hydrochloric acid in the cell would have to be closely controlled.

With the cupric ion concentration at 0.02 formal the hydrochloric acid concentration had to be above 0.6 formal or copper would be deposited on the generator cathode; if the cupric concentration were raised to 0.16 formal no deposit resulted with 0.6 formal acid, but was obtained with 0.3 formal acid.

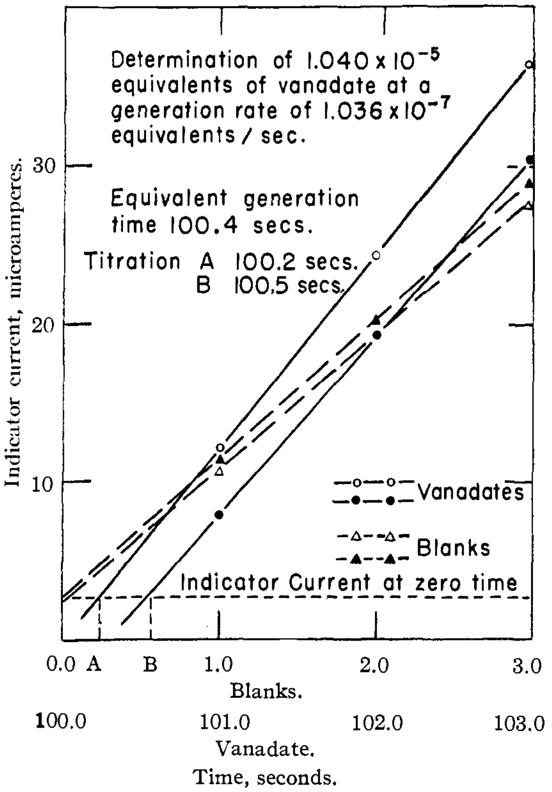


Fig. 3.—Procedure for determining equivalent generation time for vanadates.

If the hydrochloric acid concentration was 2.4 formal or greater, oxidation of chloride by chromate or vanadate took place at an appreciable rate and low results were obtained.

The oxidation of chloride ion to chlorine was indicated by a rise in indicator current during the course of a titration. The cause of the indicator current increase can be shown to be chlorine and not cuprous ion by reversing the polarity of the indicator electrodes. Since the indicator current is limited by the diffusion of either chlorine to the indicator cathode or cuprous ion to the anode, and since the diffusion current is proportional to the area of the electrode, then an increase in the indicator current should be noticed when the larger electrode is made the cathode if the indicator current is caused by the chlorine–chloride couple. This was the effect observed. If the indicator current had been caused by the cuprous–cupric couple a decrease would have been observed upon making the cathode the larger electrode. Figure 4 shows typical titration curves for chromate determinations at two hydrochloric acid concentrations, one at 1.3 formal and one at 5.3 formal.

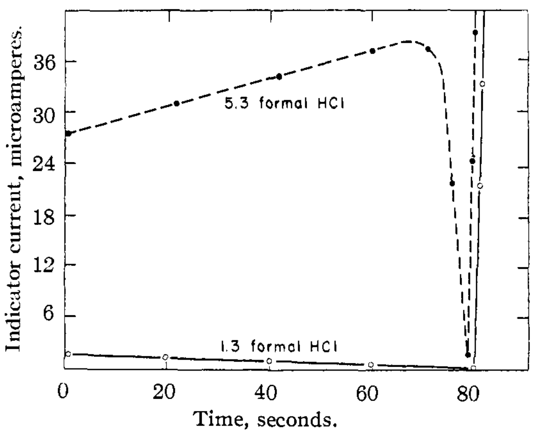


Fig. 4.—Effect of HCl concentration on indicator current during titration.

On the basis of the above experiments the cupric ion concentration was set at 0.02 formal and the hydrochloric acid concentration at 1.3 formal for the chromate determinations.

The data obtained from a series of confirmatory analyses made with various quantities of chromate are tabulated in Table I. With quantities greater than 150 micrograms, the percentage error is of the order of 0.1% and is

TABLE I

TITRATION OF CHROMATE SOLUTIONS

The potassium dichromate solutions were added to 5 ml. of 0.2 formal cupric sulfate in 12 formal hydrochloric acid and sufficient water to bring the final volume to 45 ml. The generation rate was 10 milliamperes. The generation times varied from 10 to 1000 seconds

	Determinations	Chromium, micrograms		Error	
Expt.	made	Taken	Found	Average	Maximum
I	4	17.81	17.99	0.18	+0.29
II	4	35.79	35.89	0.13	+0.19
III	4	178.4	178.4	0.1	−0.2
IV	4	358.3	358.5	0.3	+0.5
V	4	716.7	716.9	0.5	+0.7
VI	2	1784.0	1786.0	2.0	+2.0

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.

RECEIVED JANUARY 15, 1949

[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).