

ANALYTICAL STUDIES BY POTENTIOMETRIC METHODS

Thesis by

H. Darwin Kirschman

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THE POTENTIOMETRIC DETERMINATION OF INDIUM

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THE POTENTIOMETRIC DETERMINATION OF INDIUM

BY ULRIC B. BRAY¹ AND H. DARWIN KIRSCHMAN

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Introduction

An accurate and fairly rapid method of analysis of indium solutions has become desirable in order to facilitate further investigations on indium in this Laboratory. The two methods described in the literature are the electrodeposition^{2,3,4} of the metal and the weighing of the indium oxide obtained by igniting the precipitated hydroxide.^{5,6}

The electrodeposition of indium from a chloride solution, either in the presence of formic acid and ammonia or in the presence of Rochelle salt, as suggested by earlier authors, was found unsuitable for an accurate quantitative determination with chloride solutions. However, by using a sulfate solution, with a current density of 0.4 ampere per square decimeter and a potential of about 4 volts, very adherent deposits of indium with no platinum black were obtained with a rotating cathode. But the difficulty of precipitating the last few milligrams of indium from the solution, as observed by the present authors in over a dozen electroplating experiments, makes this an uncertain method of analysis. As mentioned by Dennis and Geer, the electrodeposition of indium was found to be an excellent method of purifying it from iron, since one deposition from a sulfuric acid solution of the crude oxide gave a metal which showed no test for iron with potassium thiocyanate.

Determinations as the oxide, In_2O_3 , were made by essentially the method of Thiel and Koelsch as follows. The hydroxide was precipitated from the solution of the chloride by the addition of a slight excess of freshly filtered ammonium hydroxide. The white, flocculent precipitate was washed by decantation until free from chlorides with a 1% solution of ammonium nitrate and filtered into a Gooch crucible. In the first set of determinations the crucibles were heated over a blast-lamp for thirty minutes, cooled and weighed. This was repeated but a constant weight was not obtained. In the second set of determinations the crucibles were placed in an electric furnace and brought to about 850° for thirty minutes. This was repeated until the weight was constant to 0.2 mg. The crucibles

¹ National Research Fellow in Chemistry.

² Kollock and Smith, *THIS JOURNAL*, 32, 1248 (1910).

³ Dennis and Geer, *ibid.*, 26, 437 (1904).

⁴ Mathers, *ibid.*, 29, 485 (1907).

⁵ (a) Thiel and Koelsch, *Z. anorg. Chem.*, 66, 288 (1910); (b) *ibid.*, 40, 280 (1904).

⁶ Dennis and Bridgman, *THIS JOURNAL*, 40, 1531 (1918).

were then heated in the furnace at about 900° for about forty minutes, when a loss of weight of several milligrams occurred.

Both of these methods were thus found by the authors to be not well suited to the purpose at hand. A new method of analysis was therefore worked out. This consists in titrating the indium with potassium ferrocyanide and determining the end-point potentiometrically. Since indium forms with potassium ferrocyanide a precipitate which is insoluble in nitric and sulfuric acids and in hydrochloric acid up to 4 *N*, and since it does not give an insoluble compound with potassium ferricyanide, the system lends itself to this method of electrotitration. The composition of the insoluble compound formed during the titration has been investigated in order to obtain a convenient method of standardizing the ferrocyanide solution.

Apparatus

The apparatus used consists of (1) a motor-driven stirrer; (2) a 1 *N* KCl-calomel reference half-cell; (3) an oxidation-reduction electrode made by fusing 1 cm. of small (0.05 cm. diameter) platinum wire through the end of a small glass tube; (4) a certified buret; and (5) a Leeds and Northrup "Type K" potentiometer with a high sensitivity galvanometer. A beaker containing the unknown solution diluted to about 300 cc. is a convenient size. For the inert metal electrode a short platinum wire rather than a foil electrode is used. For the reference electrode a 1 *N* calomel half-cell is satisfactory and consequently no attempt has been made to use a system of bimetallic electrodes.^{7,8}

The Method of Titration

Preliminary experiments showed that solutions of indium chloride titrated potentiometrically give curves almost identical in form with those obtained by titrating zinc^{9,10,11,12} in acid solution at 70° with potassium ferrocyanide. During the potentiometric titration, equilibrium is reached at the oxidation-reduction electrode in less than thirty seconds, except in the immediate vicinity of the end-point where the voltage is changing rapidly. The ratio of indium solution to ferrocyanide solution obtained by taking the mid-point of the vertical section of the curve as the end-point was found to be quite constant. Stock solutions of carefully purified indium chloride were prepared by dissolving well-washed precipitates of the hydroxide in a slight excess of a constant-boiling solution of hydrochloric acid and diluting to about 0.03 or 0.07 molal.

The effects of acid, neutral salts, concentration of indium salt and temperature on the ratio of the two solutions were studied. In all experiments the ferrocyanide was added to the indium solution from the buret,

⁷ Willard and Fenwick, *THIS JOURNAL*, **44**, 2504 (1922).

⁸ Van Name and Fenwick, *ibid.*, **47**, 9 (1925).

⁹ Bichowsky, *J. Ind. Eng. Chem.*, **9**, 668 (1917).

¹⁰ Müller, *Z. anorg. Chem.*, **128**, 126 (1923).

¹¹ Treadwell and Chevert, *Helv. Chim. Acta*, **5**, 633 (1922); (b) **6**, 550, 559 (1923).

¹² Verzijl and Kolthoff, *Rec. trav. chim.*, **43**, 380 (1924).

no attempt being made to study the effect of adding the indium to the ferrocyanide, since satisfactory results were obtained by the easier method. Voltages were read to one millivolt as soon as equilibrium was substantially established after each addition. At the beginning of the titration and up to within two or three cubic centimeters of the end-point the ferrocyanide was allowed to run from the buret fairly rapidly, because the final curve was found to be independent of the rate of addition. The first part of the curve is of little or no importance and depends to a considerable extent on the previous treatment of the platinum wire electrode. The voltage gradually rises with the addition of the ferrocyanide solution to about 0.62 volt and then remains practically constant until within a few cubic centimeters of the end-point, after which a gradual decrease of potential occurs. Thereafter additions of 0.5 cc. are made, and finally of 0.1 cc. as the end-point is more closely approached. Curve A of Fig. 1 is typical of the behavior at room temperature.

The effect of acid more concentrated than 0.05 *N* in the final solution is both to decrease the drop in potential at the end-point and to make the decrease take place gradually instead of suddenly. The effect of neutral salt is essentially the same as that of acid; thus, several titrations made with solutions to which both hydrochloric acid and potassium acetate had been added gave curves similar to those obtained by using dilute acid with a corresponding amount of potassium chloride. When the decrease in voltage takes place gradually, as in solutions of high ionic strength, it is very difficult to obtain an accurate end-point. The curves obtained in these cases were similar to Curve B in Fig. 1.

Titration were made at room temperature (about $25 \pm 2^\circ$), at 45° and at 85° . The best curves were obtained at room temperature. At 45° the curve is still fairly good but at 85° the drop in voltage is too gradual. The end-points were in general determined independently by the two

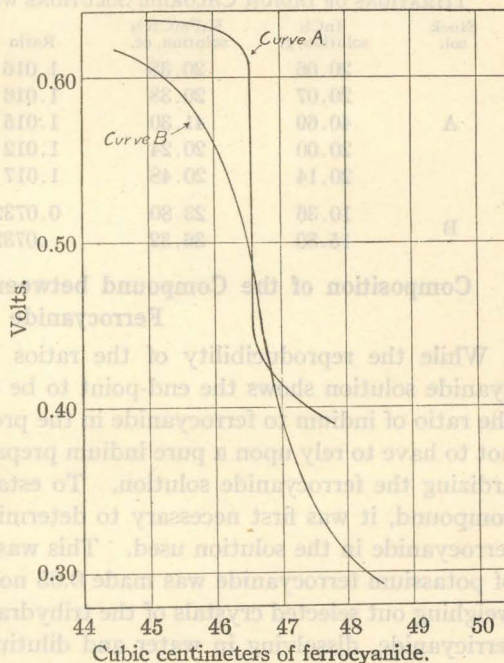


Fig. 1.

authors from the titration data and seldom differed by more than 0.02 cc. The standard ferrocyanide solutions were kept in black lacquered bottles under an atmosphere of nitrogen.

In Table I are given the results of a number of titrations of two stock solutions, A and B, of indium chloride with the ferrocyanide solution. They show the accuracy with which the end-point can be determined under different conditions. The indium chloride solution was always about 0.02 *N* in hydrochloric acid.

TABLE I

TITRATIONS OF INDIUM CHLORIDE SOLUTIONS WITH POTASSIUM FERROCYANIDE

Stock sol.	InCl ₃ solution, g.	K ₄ Fe(CN) ₆ solution, cc.	Ratio	Temp., °C.	Volume of solution
A	20.06	20.38	1.016	Room	350
	20.07	20.38	1.016	Room	350
	40.69	41.30	1.015	Room	350
	20.00	20.24	1.012	Room	700
	20.14	20.48	1.017	45°	350
B	10.36	23.80	0.07321	Room	350
	15.80	36.32	.07326	Room	350

**Composition of the Compound between Indium and Potassium
Ferrocyanide**

While the reproducibility of the ratios of indium solution to ferrocyanide solution shows the end-point to be sharp, it is desirable to know the ratio of indium to ferrocyanide in the precipitated compound, in order not to have to rely upon a pure indium preparation as the means of standardizing the ferrocyanide solution. To establish the composition of this compound, it was first necessary to determine the actual molality of the ferrocyanide in the solution used. This was done as follows. A solution of potassium ferrocyanide was made 0.05 normal as closely as possible by weighing out selected crystals of the trihydrate, adding 0.5 g. of potassium ferricyanide, dissolving in water and diluting to exactly one liter. This 0.05 formal solution was then titrated electrometrically against two very carefully standardized zinc solutions which one of the authors had prepared for electromotive force measurements on zinc sulfate.¹³ Assuming the molality of the potassium ferrocyanide to be 0.05 in correspondence with the weight of crystals taken, the ratio of zinc to ferrocyanide in the titration was found to be 1.505 and 1.508 for the two separate zinc solutions. This is in agreement with Treadwell and Chevert,¹⁴ who have

¹³ U. B. Bray, *THIS JOURNAL*, 49, 2372 (1927). The method of standardizing these zinc solutions was the potentiometric method, using another ferrocyanide solution. The basis of the standardization was Kahlbaum's "zur Analyse" zinc sticks and anhydrous zinc sulfate. All titrations were made under similar conditions of concentration, temperature and acidity.

¹⁴ Ref. 11. Although Verzijl and Kolthoff (ref. 12) report an error of a few tenths of a per cent. from the theoretical potentiometric end-point in ferrocyanide precipita-

shown that the insoluble compound formed between potassium ferrocyanide and zinc is $Zn_3K_2(Fe(CN)_6)_2$. The exact molality of ferrocyanide solutions may therefore be determined by titrating against metallic zinc or standard zinc solutions and then making use of the ratio $3Zn:2Fe(CN)_6$.

The next step in the determination of the composition of the indium ferrocyanide precipitate was to prepare pure indium by electrolysis on a rotating platinum cathode from a carefully purified solution of indium sulfate. The cathode coated with indium metal was washed, dried in an atmosphere of hydrogen at 110° and weighed. The sample taken for a titration was obtained by treating the electrode with 1-2 cc. of 12 *N* hydrochloric acid, washing it, drying and weighing again. This indium chloride solution was diluted to approximately 300 cc. and titrated as usual. The results of these titrations of solutions of weighed quantities of indium metal are given in Table II.

TABLE II
TITRATION OF METALLIC INDIUM AGAINST POTASSIUM FERROCYANIDE OF KNOWN MOLALITY

Milli-atoms of indium	Milli-moles of $K_4Fe(CN)_6$	Ratio In: $Fe(CN)_6$
1.234	0.9874	1.250
1.203	.9634	1.245
3.067	2.437	1.258
0.8328	0.6653	1.252
1.486	1.187	1.251
1.670	1.335	1.254
	Average	1.252

The ratio of indium to ferrocyanide is clearly 1.25 or $5In:4Fe(CN)_6$. Since the only other positive ions in the solution are potassium and hydrogen, the formula for the precipitated compound is presumably $In_5K(Fe(CN)_6)_4$. The determination of this definite ratio of indium to ferrocyanide in combination with the 3 to 2 ratio of zinc to ferrocyanide found by Treadwell and Chevert makes it possible to standardize with metallic zinc the ferrocyanide solutions that are to be used for indium titrations. The availability of pure zinc metal as compared with indium metal makes this method of standardization convenient.

Summary

A method of analyzing indium solutions by titrating with potassium ferrocyanide and determining the end-point potentiometrically has been described. The accuracy of the end-point is estimated at one or two-tenths of a per cent.

The precipitate formed between potassium ferrocyanide and indium solutions has been shown to be definite under the conditions described. In titrations depending upon the electrolyte present, any such small errors would tend to cancel out with the subsequent indium titration.

and to contain indium and ferrocyanide in the ratio 5In:4Fe(CN)₆ (within 0.2%). The formula of the precipitate is therefore presumably In₅K₄(Fe(CN)₆)₄. The determination of the ratio of indium to ferrocyanide in this compound permits using metallic zinc for standardizing the ferrocyanide solution, since the composition of the zinc ferrocyanide precipitate has been determined.

PASADENA, CALIFORNIA

The results of these titrations of solutions of weighed quantities of indium metal are given in Table II.

TABLE II
TITRATION OF METALLIC INDIUM AGAINST POTASSIUM FERROCYANIDE OF KNOWN

Ratio In/Fe(CN) ₆	MOLALITY of indium K ₄ Fe(CN) ₆	Milli moles of indium
1.280	0.0274	1.234
1.245	0.031	1.203
1.288	2.437	3.087
1.283	0.0083	0.8338
1.281	1.187	1.488
1.284	1.332	1.670
1.282	Average	

The ratio of indium to ferrocyanide is clearly 1.26 or 5In:4K₄Fe(CN)₆. Since the only other positive ions in the solution are potassium and hydrogen, the formula for the precipitated compound is presumably In₅K₄Fe(CN)₆. The determination of this definite ratio of indium to ferrocyanide in combination with the 3 to 2 ratio of zinc to ferrocyanide found by Treadwell and Chevert makes it possible to standardize with metallic zinc the ferrocyanide solutions that are to be used for indium titrations. The availability of pure zinc metal as compared with indium metal makes this method of standardization convenient.

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A method of analyzing indium solutions by titrating with potassium ferrocyanide and determining the end-point potentiometrically has been described. The accuracy of the end-point is estimated at one or two tenths of a per cent. The precipitate formed between potassium ferrocyanide and indium solutions has been shown to be definite under the conditions described here, titrations depending upon the electrolyte present, any such small errors would tend to cancel out with the subsequent indium titration.

THE POTENTIOMETRIC DETERMINATION OF GALLIUM

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA
AT LOS ANGELES]

THE POTENTIOMETRIC DETERMINATION OF GALLIUM

BY H. DARWIN KIRSCHMAN AND J. B. RAMSEY

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Introduction

The methods of determining gallium so far described in the literature are based on its precipitation as the hydroxide and the subsequent ignition to the oxide. Slightly different procedures for doing this have been described by Porter and Browning¹ and by Dennis and Bridgman.²

To facilitate further study of the chemistry of gallium, an accurate volumetric method is desired.

Since gallium is known to form a slightly soluble ferrocyanide and a soluble ferricyanide, the system might be expected to lend itself to the method of electrometric titration which has been worked out for the related elements, zinc, cadmium, and more recently indium.^{3,4}

The results of the investigation described in this paper show that the method is applicable to gallium. The composition of the insoluble ferrocyanide formed has been determined and the conditions for obtaining accurate results have been studied.

Description of the Apparatus

The apparatus used consisted of (1) a motor-driven stirrer; (2) a 1 *N* potassium chloride-calomel reference half-cell; (3) an oxidation-reduction electrode made by fusing 1 cm. of platinum wire, 0.05 cm. in diameter, into the end of a small glass tube; (4) a certified buret; and (5) a Leeds and Northrup student potentiometer with a Leeds and Northrup galvanometer of 2.84 megohms sensitivity. A 1-liter beaker was found to be a convenient titration vessel.

Preparation of the Materials

Metallic gallium obtained originally from the Bartlesville Zinc Company of Bartlesville, Oklahoma, was the substance used in the preparation of all solutions of gallium salts. The metal was dissolved in 12 *N* hydrochloric acid and to increase the rate of solution, which is slow, a piece of platinum foil was kept in contact with the metal. The resulting solution was diluted with about 250 cc. of water and the gallium precipitated as the hydroxide with a slight excess of ammonia. After heating the solution to boiling for a few minutes to coagulate the precipitate, the hydroxide was filtered off and washed free from all but a trace of chlorides. Later work showed that the gallium was not completely precipitated. Our results indicated that the hydroxide is much more

¹ Porter and Browning, *THIS JOURNAL*, 43, 111 (1921); *ibid.*, 41, 1491 (1919).

² Dennis and Bridgman, *ibid.*, 40, 1531 (1918).

³ Bray and Kirschman, *ibid.*, 49, 2739 (1927).

⁴ Müller and Gäbler, *Z. anal. Chem.*, 62, 29 (1923).

soluble in dilute ammonia than would be inferred from the literature. The precipitate of hydroxide was then dissolved in a measured amount of c. p. 12 N hydrochloric acid and diluted to approximately 0.08 molar in gallium chloride.

The potassium ferrocyanide and potassium ferricyanide used were of the standard c. p. quality. The solutions of potassium ferrocyanide, containing 1 g. of ferricyanide per liter, were made up in brown, glass stoppered bottles and kept in the dark when not in use. The solutions were standardized against metallic zinc by the potentiometric method.⁵

The following series of values, 0.05589; 0.05581; 0.05583, obtained for the molality of one of the ferrocyanide solutions shows the reproducibility of the method.

Results of the Titration Experiments

Preliminary experiments showed that solutions of gallium chloride, titrated potentiometrically with potassium ferrocyanide, give curves similar in form to those obtained in the titration of zinc or indium.³ The results of titrations under varying conditions are shown in Table I.

TABLE I
RESULTS OF TITRATIONS OF GALLIUM CHLORIDE SOLUTIONS WITH POTASSIUM FERROCYANIDE

Expt.	Stock soln.	Wt. of GaCl ₃ soln., g.	Vol. of K ₄ Fe(CN) ₆ , cc.	Ratio	Temp.	Total vol., cc.	Acidity, N
1		10.29	14.10	1.370	Room	450	0.025
2 ^a		10.33	Room	450	.125
3		10.32	14.16	1.372	75°	400	.03
4	A	10.34	14.20	1.373	Room	400	.03
6		10.37	14.22	1.371	Room	325	.03
7 ^b		10.44	Room	425	..
8		10.34	14.21	1.374	Room	425	.01
1		10.12	11.32	1.118	40°	350	.005
2		21.26	22.68	1.119	40°	800	.005
3		20.21	22.61	1.119	Room	800	.005
4	B	20.23	22.77	1.125	60°	800	.005
5		20.21	22.68	1.122	40°	400	.01
6		10.13	11.34	1.120	60°	800	.003
7 ^c		20.24	75°	800	.005

^a Five cc. of 12 N HCl was added.

^b Ammonia added till neutral.

^c Decomposition observed.

These three runs gave curves from which the end-points could not be satisfactorily determined.

During the titration, equilibrium is substantially attained in from 3 to 5 minutes except in the immediate vicinity of the end-point, where the voltage is changing most rapidly. The volume of ferrocyanide solution used was obtained by determining the inflection point of the curve which resulted on plotting voltage against cc. of ferrocyanide solution added.

⁵ Bichowsky, *J. Ind. and Eng. Chem.*, 9, 668 (1917); Müller, *Z. anorg. Chem.*, 128, 126 (1923); Treadwell and Chevert, *Helv. Chim. Acta*, 6, 550 (1923); Verzijl and Kolt-hoff, *Rec. trav. chim.*, 43, 389 (1924).

The end-points were determined independently by the two authors from the titration data and differed on the average by 0.018 cc. in the 11 observations given in Table I.

In all experiments the ferrocyanide was added to the gallium chloride solution. Voltages were read to one millivolt as soon as equilibrium was substantially attained after each addition. At the beginning of the titration and up to within two or three cubic centimeters of the end-point, the ferrocyanide was allowed to run from the buret fairly rapidly. The voltage gradually rises with the addition of the ferrocyanide solution to about 0.60 volt and then remains practically constant until within a few cubic centimeters of the end-point after which a gradual decrease of potential occurs. Thereafter additions of 0.5 cc. were made and finally of 0.10 cc. as the end-point was more closely approached.

The shape of the titration curves obtained is indicative of the suitability of experimental conditions. An increase in concentration of hydrochloric acid was found to decrease the drop in potential at the end-point making this drop more gradual and therefore the inflection point less accurately determinable. The solutions of gallium chloride having the lowest acid concentration gave the most satisfactory curves. The effect of neutral salts was essentially the same as that of acid.

The curves resulting from the experiments at room temperature, 40 and 60° were similar and the corresponding ratios are the same as shown in Col. 5 of Table I. At 75° appreciable decomposition occurred, as evidenced by the blue color which developed during the titration, and the curves obtained were less satisfactory. Since equilibrium was not attained as rapidly at room temperature as at the higher temperatures, 40° was selected for subsequent titrations. It was found desirable to maintain the temperature within two degrees of that adopted because of the large temperature coefficient of the cell.

Three determinations employing an approximately 0.05 molal potassium ferrocyanide were made. Weighed amounts of the ferricyanide were added to the titration vessel. A sixteen-fold variation in the amount of ferricyanide present at the end-point produced no marked change in the type of curve obtained. We conclude that the amount of added ferricyanide can vary within rather wide limits, and since the presence of ferricyanide has been shown to prevent the decomposition of the ferrocyanide⁶ it is preferable to add it with the ferrocyanide.

Composition of the Precipitate

The ratio of the gallium to the ferrocyanide in the precipitate obtained was determined by two independent methods, one employing metallic gallium as a reference substance and the other employing the oxide.

⁶ Kolthoff, *Rec. trav. chim.*, **43**, 380 (1924).

The gallium was prepared by electrodeposition⁷ on a rotating platinum cathode from a solution of gallium sulfate to which sufficient ammonia had been added to produce a slight permanent precipitate of the hydroxide. The cathode coated with the gallium metal was washed, dried in an oven at 110° and weighed. The sample taken for a titration was obtained by treating the electrode with 1-2 cc. of 12 *N* hydrochloric acid, washing it, drying and weighing again. The gallium dissolves less readily than does indium and the solution was heated to hasten the reaction. This solution was diluted to 800 cc. and the titration carried out at 40°. The results of these titrations are shown in Table II.

TABLE II
TITRATION OF METALLIC GALLIUM AGAINST POTASSIUM FERROCYANIDE

Gallium metal, mg.	Milliatoms of gallium	K ₄ Fe(CN) ₆ , ml.	Millimoles of K ₄ Fe(CN) ₆	Ratio Ga: Fe(CN) ₆
33.0	0.473	6.28	0.351	1.348
42.9	.615	8.45	.472	1.304
113.3	1.625	21.71	1.212	1.340
57.9	0.830	11.19	0.625	1.329
81.8	1.173	16.04	.896	1.310
68.3	0.980	13.18	.736	1.331
			Average	1.327

The procedure adopted in the precipitation of the gallium as hydroxide and its subsequent ignition to the oxide was essentially that recommended by Porter and Browning.¹ Ammonium acid sulfite was used as the precipitating agent in a neutral or slightly acid solution. A test was made for complete precipitation by evaporating the filtrate to approximately 50 cc., adding 10 cc. more of the ammonium acid sulfite solution and boiling for a few minutes. No precipitate was formed and only a very faint turbidity was observed on the addition of potassium ferrocyanide to the resulting solution.

The weights of oxide obtained from two equal portions (10.10 g.) of the gallium chloride solution were 0.0804 g. and 0.0809 g. The weights remained constant even after four hours' heating at a temperature of approximately 800°. In this respect it differs from indium oxide which has been found to lose weight when heated to this temperature.³ The gallium oxide was not markedly hygroscopic after this treatment.² The average weight of oxide, 0.08065 g., corresponds to 0.8605 milliatom of gallium. The number of millimoles of ferrocyanide corresponding to 10.10 g. of the stock solution as calculated from the average of four titrations was 0.6432. From these data the ratio of gallium to the ferrocyanide in the precipitate is seen to be 1.337.

From these results the ratio of gallium to ferrocyanide is clearly 1.333,

⁷ Fogg and James, *THIS JOURNAL*, **41**, 947 (1919); Richards and Boyer, *ibid.*, **41**, 133 (1919); Dennis and Bridgman, *ibid.*, **40**, 1537 (1918).

which corresponds to the formula $Ga_4(Fe(CN)_6)_3$ for the precipitate. The precipitate is not of a complex nature and therefore differs from the ferrocyanide of zinc and indium. The determination of this ratio makes it possible to use ferrocyanide solutions, standardized against metallic zinc, for the determination of gallium.

Summary

A method of analyzing gallium chloride solutions by titrating with standard potassium ferrocyanide solution in the presence of ferricyanide and determining the end-point potentiometrically has been described. The accuracy is estimated at two or three tenths of one per cent.

The ferrocyanide precipitate formed under the conditions described has been shown by two independent methods to have the formula $Ga_4(Fe(CN)_6)_3$.

Los Angeles, California	Millimoles of Fe(CN) ₆ ⁴⁻	Millimoles of Fe(CN) ₆ ³⁻	Millimoles of Gallium
1.304	0.477	0.28	33.0
1.310	0.418	0.45	42.9
1.320	0.320	0.212	113.2
1.310	0.230	0.110	57.9
1.321	0.173	0.04	81.8
1.327	0.080	0.18	68.2
Average			

The procedure adopted in the precipitation of the gallium as hydroxide and its subsequent ignition to the oxide was essentially that recommended by Porter and Browning. Ammonium acid sulfate was used as the precipitating agent in a neutral or slightly acid solution. A test was made for complete precipitation by evaporating the filtrate to approximately 50 cc., adding 10 cc. more of the ammonium acid sulfate solution and boiling for a few minutes. No precipitate was formed and only a very faint turbidity was observed on the addition of potassium ferrocyanide to the resulting solution.

The weights of oxide obtained from two equal portions (10.10 g.) of the gallium chloride solution were 0.0804 g. and 0.0809 g. The weights remained constant even after four hours' heating at a temperature of approximately 300°. In this respect it differs from indium oxide which has been found to lose weight when heated to this temperature. The gallium oxide was not markedly hygroscopic after this treatment. The average weight of oxide, 0.08065 g., corresponds to 0.3802 millimoles of gallium. The number of millimoles of ferrocyanide corresponding to 10.10 g. of the stock solution as calculated from the average of four titrations was 0.6432. From these data the ratio of gallium to the ferrocyanide in the precipitate is seen to be 1.337.

From these results the ratio of gallium to ferrocyanide is clearly 1.333. Fogg and James, *Trans. Journal*, 41, 947 (1919); Richards and Boye, *ibid.*, 41, 133 (1919); Dennis and Bridgman, *ibid.*, 40, 1337 (1918).

THE POTENTIOMETRIC DETERMINATION OF OCTAVALENT OSMIUM

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THE POTENTIOMETRIC DETERMINATION OF OCTAVALENT OSMIUM

BY WILLIAM R. CROWELL AND H. DARWIN KIRSCHMAN

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Introduction

In order to facilitate the study of a number of problems concerning the chemistry of osmium, it became desirable to develop a method for the determination of octavalent osmium which would be more rapid and not less reliable than those usually employed. The generally accepted gravimetric methods are those involving the reduction of osmium compounds to the metal; and the most commonly mentioned volumetric method is the iodide method of Klobbie with its modifications. The former methods, while reliable if conducted under proper conditions, are tedious, and require rather elaborate precautions; the latter has a very difficult end-point and, even under the best conditions, it is hard to obtain reproducible results. In the light of the past experience of one of us with ruthenium¹ it was thought that a potentiometric method would prove most satisfactory. It has already been shown² that hydrazine compounds reduce octavalent osmium in an alkaline or alcoholic solution to the tetravalent state. It is shown in this paper that this reduction can be carried out in acid solution, and that the progress of the reaction can be followed potentiometrically. Conditions for obtaining reproducible results have been worked out and comparisons made with results obtained by the iodide and gravimetric methods. A study is being made of other reducing agents, such as titanous, chromous and ferrous salts, the results of which will be presented in a later paper.

Apparatus and Materials

The apparatus used consisted of (1) a motor-driven stirrer; (2) a 1 *N* potassium chloride-calomel reference half-cell; (3) an oxidation-reduction electrode, made by fusing a platinum wire 2 cm. long and 0.05 cm. in diameter into the end of a small glass tube; (4) a certified buret; (5) a Leeds and Northrup student potentiometer, using a Leeds and Northrup portable galvanometer of 2.84 megohms sensitivity; (6) a 125-cc. beaker as a titration vessel. Calibrated precision pipets were used throughout.

A stock solution of osmium tetroxide in potassium hydroxide was prepared as follows. Metallic osmium, either as purchased or as recovered from residues by reduction with zinc and subsequent ignition in a current of hydrogen, was fused with potassium hydroxide and potassium nitrate. The melt was treated with water and distilled with nitric acid into a solution of potassium hydroxide, whereby a solution of osmium tetroxide was obtained free from ruthenium tetroxide. After acidification the metal

¹ Crowell and Yost, *THIS JOURNAL*, 50, 374 (1928).

² (a) Ruff and Borneman, *Z. anorg. Chem.*, 65, 436 (1910); (b) *Ber.*, 50, 484 (1917); (c) Paal and Amberger, *ibid.*, 40, 1378 (1907).

was again precipitated with zinc from this solution and fused with potassium hydroxide and potassium permanganate. The fused material was again treated with water and distilled from sulfuric acid with a current of oxygen into a definite volume of potassium hydroxide solution of known strength (about 0.4 *N*), free from traces of organic matter. The solution of osmium tetroxide thus obtained was free from nitric acid, nitric oxide and other volatile impurities. The alkaline solutions of the tetroxide are much more stable than neutral solutions and behave identically on titration.

Hydrazine sulfate solutions were standardized with potassium iodate by the method of Bray and Cuy.³ The thiosulfate solutions used were frequently compared with a potassium permanganate solution which had been standardized by means of sodium oxalate from the Bureau of Standards.

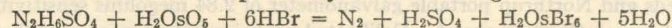
Pure hydrobromic acid was obtained by distillation of the 48% acid. The middle fraction was used. All reagents were of standard c. p. quality.

The Potentiometric Method

In order to determine the best conditions for the potentiometric titration of octavalent osmium with hydrazine sulfate, preliminary experiments were conducted at different temperatures using various concentrations of osmium tetroxide and of acid. The acids used were sulfuric, hydrochloric and hydrobromic. Since the last was found to give the most satisfactory end-point, the results with this acid will be described in detail.

In hydrobromic acid solutions below 2 *N* at room temperatures (20–25°) there is apparently no reaction between hydrazine sulfate and octavalent osmium. As the temperature is raised to 50–60° the occurrence of a reaction is shown by the formation of gas bubbles and by a color change of the solution, which depends upon the acid concentration. At acidities below 1 *N* an amber color of varying intensity or a black precipitate appears, probably due to hydrolyzed compounds of tetravalent osmium. At acidities above 1 *N* the color change is from light yellow to a deep red.

Under the conditions finally adopted a large drop in potential occurs when four equivalents of hydrazine sulfate have been added for every gram atom of octavalent osmium present. Further additions of the reducing agent produce no additional break, even when five or six equivalents are used. It is evident that the osmium is reduced from the octavalent to the tetravalent state, as is the case in an alkaline or alcoholic solution.^{2a} The reaction is probably the following



Analyses conducted at various temperatures between 60 and 80° gave practically the same results. It is desirable, however, to keep the temperature constant to within 2° because of the rather large temperature coefficient of the cell.

Preliminary experiments showed that quantitative results could not be obtained by a titration of octavalent osmium solutions in open vessels, probably because of a loss of the tetroxide from the acidified solution at the temperature used for the titrations. The procedure finally adopted was as follows. By preliminary direct titration the

³ Bray and Cuy, *THIS JOURNAL*, 46, 858 (1924).

amount of hydrazine sulfate necessary was roughly determined, several per cent. less than the theoretical amount being required because of loss by vaporization. Sealed glass tubes were then prepared containing this amount of hydrazine sulfate, sufficient concentrated hydrobromic acid to make the final acidity 1.5 *N*, and the sample of the stock octavalent osmium solution, these being added in the order mentioned. The tubes were then heated in a boiling water-bath from half an hour to several hours. A tube was then cooled, broken and its contents washed into the titration vessel with from 10–20 cc. of a 1.5 *N* hydrobromic acid solution, the potentiometric titration being completed at 70°. A time of heating longer than half an hour was found to be unnecessary. The same results were obtained even if the quantity of hydrazine sulfate added to the tube before heating was as high as 99% of the total required for titration.

During the electrometric titration the equilibrium voltage is attained within two millivolts in less than three minutes, except in the immediate vicinity of the end-point. The volume of hydrazine sulfate used was determined from the point of inflection in the curve obtained by plotting voltage against volume of reagent added. The voltage drop at the end-point is from 30–60 millivolts for a 0.1-cc. change in volume of reagent added, depending upon the acid concentration and the condition of the platinum electrode. It was found necessary to replace the platinum electrode after 10–12 titrations, since the usual methods of reconditioning electrodes did not prove satisfactory. The inflection is sufficiently abrupt, as is shown by the curve in Fig. 1.

Determinations were made with solutions of osmium tetroxide of various concentrations. Corresponding concentrations of the reducing agent were used. The end-points in the most dilute solutions were not so sharp as in those of higher concentrations but the reproducibility was fairly satisfactory. Amounts of tetroxide as small as 10^{-5} mole may be determined by this method.

The Gravimetric and Iodometric Determinations

Comparative analyses by the gravimetric and iodometric methods were carried out at the same time as those by the potentiometric method,

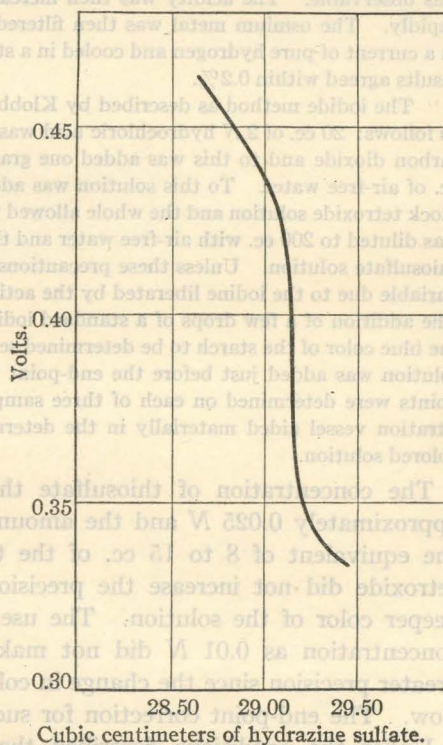


Fig. 1.

since it was found that the alkaline tetroxide solutions slowly decreased in concentration on standing, owing probably to loss of the osmium tetroxide formed by hydrolysis.

The procedure used in the gravimetric determinations was as follows. A measured portion of the stock osmium solution was pipetted into a glass-stoppered flask, several pieces of zinc sticks (Kahlbaum's) added and the solution made slightly acid with hydrochloric acid. The reaction was allowed to continue for several hours, acid being added from time to time. Too great an acid concentration, especially at the start, causes a too violent evolution of hydrogen and a consequent loss of the osmium tetroxide before reduction to a non-volatile compound has taken place. If the acid concentration is too low, there is a precipitation of basic salts of osmium, from which it is very difficult to reduce the osmium completely. To complete the reduction the solution was digested in the presence of an excess of zinc slightly below the boiling-point until no trace of color was observable. The acidity was then increased to dissolve the zinc completely and rapidly. The osmium metal was then filtered into a weighed Gooch crucible, ignited in a current of pure hydrogen and cooled in a stream of pure carbon dioxide. Duplicate results agreed within 0.2%.

The iodide method as described by Klobbie⁴ and Krauss and Wilken⁵ was modified as follows: 20 cc. of 2 *N* hydrochloric acid was heated to boiling, cooled in a current of carbon dioxide and to this was added one gram of potassium iodide dissolved in a few cc. of air-free water. To this solution was added a measured volume (2-10 cc.) of the stock tetroxide solution and the whole allowed to stand for three minutes. The solution was diluted to 200 cc. with air-free water and the liberated iodine titrated with standard thiosulfate solution. Unless these precautions are taken, the results are both high and variable due to the iodine liberated by the action of the oxygen of the air on the iodide. The addition of a few drops of a standard iodine solution enables the disappearance of the blue color of the starch to be determined several times with a given sample. Starch solution was added just before the end-point was reached. Usually from 4 to 6 end-points were determined on each of three samples. A strong light placed beneath the titration vessel aided materially in the determination of the end-point in the deeply colored solution.

The concentration of thiosulfate that seemed most satisfactory was approximately 0.025 *N* and the amounts of osmium solution taken were the equivalent of 8 to 15 cc. of the thiosulfate. The larger sample of tetroxide did not increase the precision of the titration because of the deeper color of the solution. The use of thiosulfate solutions as low in concentration as 0.01 *N* did not make it possible to obtain results of greater precision since the change in color with addition of thiosulfate was slow. The end-point correction for such solutions is comparatively large.

Under the conditions described the average deviation of each end-point determination from the mean was about 0.25%.

Results of the Potentiometric, Gravimetric and Iodometric Determinations

Table I contains the results of the various determinations by the three methods. For the potentiometric process there was always used 2.005 cc.

⁴ Klobbie, *Chem. Centr.*, **11**, 65 (1898).

⁵ Krauss and Wilken, *Z. anorg. Chem.*, **145**, 151 (1925).

of stock osmium solution, which varied from 0.005 to 0.05 mole per liter. The titration was made at 70° in a total volume of 35-45 cc.

TABLE I
DETERMINATIONS OF OCTAVALENT OSMIUM BY POTENTIOMETRIC, GRAVIMETRIC AND IODOMETRIC METHODS

Normality of acid	Hydrazine solution		Calcd. concn. of osmium soln., millimoles/liter		
	Millimoles per liter	Volume used, cc.	Potentiometric	Gravimetric	Iodometric
1.5	2.880	16.86, 16.88, 16.88, 16.93	24.32	...	24.26
1.5	2.880	16.76, 16.65, 16.73, 16.70	24.00	...	24.02
1.5	4.800	19.98, 20.15, 20.05
2.5	4.800	19.97, 19.98	47.94	...	47.82
1.5	2.880	16.48, 16.50	23.69	23.77	...
1.5	3.840	25.49, 25.43
2.5	3.840	25.41, 25.42	48.73	48.83	48.79
1.5	3.840 ^a	12.41, 12.55, 12.57	23.96	...	23.80
1.5	0.960 ^b	9.74, 9.76, 9.83	4.683	...	4.728
..	22.08	22.12

^a The concentration of the hydrazine sulfate used to complete the titration was 0.960 millimole per liter.

^b The concentration of the hydrazine sulfate used to complete the titration was 0.3840 millimole per liter.

From the above table it can be seen that the average difference between the results obtained by the potentiometric titration and those obtained by the gravimetric and iodometric methods is about 0.3%. The agreement of the hydrazine sulfate results among themselves is excellent, the average deviation of each volume required in titration from the mean volume being 0.04 cc.

Summary

A potentiometric method for the determination of octavalent osmium by reduction with hydrazine sulfate solution has been developed and a comparison of the results has been made with those obtained by modifications of the iodometric and gravimetric methods previously described. The accuracy of the method is estimated at 0.2-0.3%.

PASADENA, CALIFORNIA

THE POTENTIOMETRIC DETERMINATION OF BROMINE, OCTAVALENT
AND QUADRIVALENT OSMIUM IN HYDROBROMIC ACID SOLUTION

THE POTENTIOMETRIC DETERMINATION OF BROMINE, OCTAVALENT
AND QUADRIVALENT OSMIUM IN HYDROBROMIC ACID SOLUTIONS

Introduction

Among the problems engaging the attention of this laboratory is that of a study of the rate of reaction between octavalent osmium and hydrobromic acid. Since the products of this reaction are quadrivalent osmium and bromine, it is apparent that its rate might be measured either by a determination at suitable time intervals of the remaining octavalent osmium, or of the bromine or quadrivalent osmium formed. Previous work on ruthenium¹ and octavalent osmium² and preliminary experiments on the potentiometric titration of hydrobromic acid solutions of bromine, octavalent, and quadrivalent osmium indicate that trivalent titanium would be a satisfactory reducing agent for this purpose. In these last experiments the titration curve obtained by plotting voltage readings against cubic centimeters of reagent added showed three inflections. The first inflection corresponded to the reduction of the bromine to bromide ion, the second to the reduction of octavalent osmium to the quadrivalent state, and the third to the reduction of the quadrivalent osmium to the trivalent form.

The present paper deals with an investigation of the suitability of trivalent titanium as a reagent for determining one or more of these constituents with sufficient accuracy to warrant

its use in the rate experiments. It describes the conditions employed and the results obtained in the potentiometric titration of hydrobromic acid solutions of (1) octavalent osmium, (2) bromine, (3) bromine in the presence of octavalent osmium, (4) bromine in the presence of quadrivalent osmium, and (5) bromine, octavalent, and quadrivalent osmium when present together.

Apparatus and Materials

The apparatus used was that employed in the potentiometric determination of octavalent osmium with hydrazine sulfate² except that provision was made for keeping the reducing agent as well as the titration vessel in an atmosphere of nitrogen.

Hydrobromic acid free of bromine was obtained by distilling the 42-48% acid and retaining the middle portion.

The bromine solution was prepared by distilling the c.p. reagent from potassium bromide and sulfuric acid into distilled water.

The stock solutions of osmium tetroxide were prepared as described in the above mentioned article,² and were about 0.5 N in potassium hydroxide.

The thiosulfate solution was frequently checked against a potassium permanganate solution which had been standardized by means of sodium oxalate from the Bureau of Standards.

The titanium solutions were prepared from one normal titanous chloride or sulfate. These were made 0.005-0.01 N in

trivalent titanium and 0.3 N in hydrochloric, hydrobromic, or sulfuric acid. In order to remove traces of hydrogen sulfide, the undiluted acid and reagent were boiled together for one minute before making up to volume. The concentration of these solutions was determined by means of a solution of ferric sulfate which had been standardized against the permanganate solution. Standardizations were made before and after each set of three or four potentiometric titrations and the concentration was usually found constant within 0.1-0.2%. If the change was much greater than this the results obtained were rejected.

Titration of Octavalent Osmium with Titanous Chloride

Definite volumes of the standardized osmium tetroxide solution were titrated with a titanous solution in the presence of sulfuric, hydrochloric, or hydrobromic acid. The procedure was as follows: the osmium solution was pipetted into the titration beaker containing about 50 cc. of the acid solution at room temperature, the cover of the beaker placed in position, a volume of titanous solution within 1-2 cc. of that required to reduce the osmium to the quadrivalent state added immediately, and nitrogen then admitted slowly (one bubble every 2 seconds). This procedure was found necessary for accurate work on account of the volatility of the tetroxide. After the octavalent osmium had been reduced to quadrivalent, the nitrogen was bubbled through the solution more rapidly (1-2 bubbles per second). An amount of titanous solution

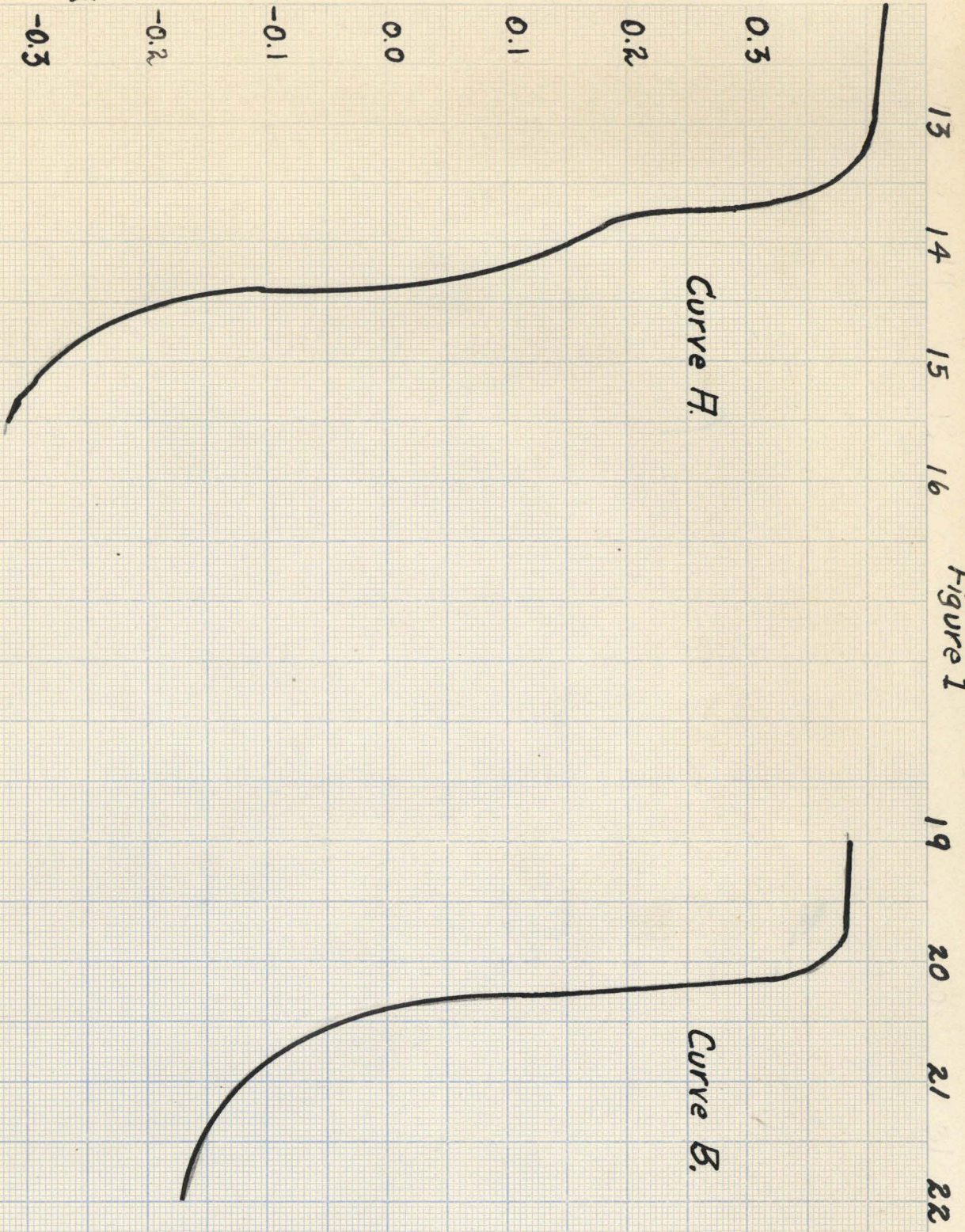
was then added whose volume was within about 1 cc. of that necessary to effect reduction to the trivalent form and the titration continued until well past the inflection point.

The effect of different acids and of variations in the concentration of these acids upon the color of the osmium solutions is an interesting feature of these titrations. The neutral or slightly acid solutions of octavalent osmium are colorless. When the reduction with titanous ion took place in a sulfuric acid solution an amber color developed which persisted even after sufficient reagent had been added to reduce the osmium to the trivalent state. With this acid it was possible to obtain only one recognizable inflection in the titration curve, viz., that corresponding to the reduction from the octavalent to the quadrivalent state. On addition of titanium reagent in the presence of hydrochloric acid the solution at first became light yellow, but when five equivalents of reducing agent per gram atom of osmium had been added, the solution became practically colorless. However, only one marked inflection in the titration curve was obtained, that corresponding to the octa-quadrivalent change. With hydrobromic acid (Curve B, Fig. 1) the solution became a deep orange-red as soon as reduction to the quadrivalent form was complete. Further addition of titanous solution produced a gradual change in color to a light yellow and when five equivalents of trivalent titanium per gram atom of osmium had been added, the solution became almost colorless. Two easily recognizable inflections were obtained; one when reduction to the trivalent form had taken place. Since the most satisfactory drops in potential

were obtained in solutions containing the hydrobromic acid, a more detailed study of the influence of the temperature and concentration changes was made with solutions containing this acid.

The concentration of hydrobromic acid which gave the largest drop in potential at the octa-quadrivalent end-point was found to be about 0.2-0.3 N. At acid concentrations below 0.1 N the solution became amber colored due probably to hydrolysis. At concentrations of acid higher than 0.3 N the drop in potential at this end-point was noticeably smaller and less abrupt. At room temperature a double inflection in the titration curve was obtained, (Curve A, Fig. 1) while at 60° a single large drop in potential was obtained (Curve B, Fig. 1). Except in the immediate vicinity of the inflection point the voltage was considered constant when the rate of change was less than 3 millivolts per minute. In the reduction from the quadrivalent to the trivalent state the best inflections were obtained at a temperature of about 80° and at an acid concentration of about 1 N (Curve B, Fig. 1). A decided drift upward in the voltage readings was noticed at acidities below 1 N. The best results were obtained when the tetroxide solutions were first heated with strong hydrobromic acid in sealed tubes at the temperature of the steam bath. On diluting these heated solutions to an acidity of about 1 N and titrating the quadrivalent osmium at 80°, sharper and greater drops of potential were obtained than when the titrations were carried out at the same temperature and acid concentration but without previous continued heating at

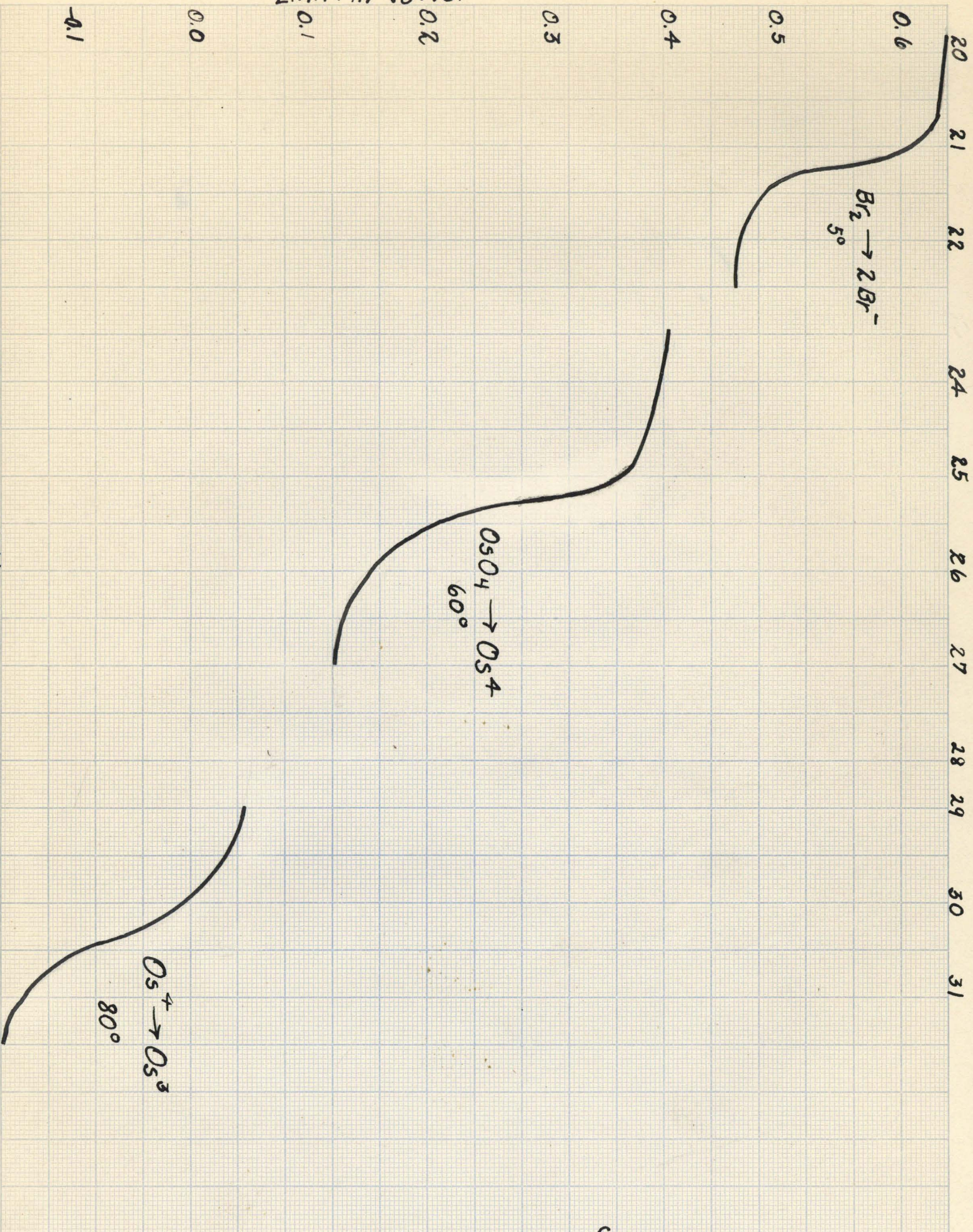
E.M.F. in volts



Milliliters of T₁⁺⁺⁺ added

Figure 1

E.M.F. in Volts.



Millimeters Ti^{+++} added

Figure 2.

Moreover, there was very little drift in the voltage readings. Results obtained in this manner will be described in more detail in the last section.

Table I contains the results of four typical titrations of a stock solution of octavalent osmium with titanous chloride. The end-points were determined from the inflection points of a curve obtained by plotting voltage against cubic centimeters of reagent added. The inflections could be determined to within 0.02-0.05 cc. The results are compared with those obtained by the modified iodometric method.²

TABLE I

Potentiometric Titration of Octavalent Osmium
Solutions with Titanous Chloride

Initial volume = 52-55 cc.

Norm- ality HBr	OsO ₄ soln. cc.	Cc. TiCl ₃ used		OsO ₄ found millimols / liter		Iodide Method
		Os ⁸ - Os ⁴ Inflection	Os ⁴ - Os ³ Inflection	Os ⁸ - Os ⁴ Inflection	Os ⁴ - Os ³ Inflection	
0.2	4.96	18.30	23.70	6.33	6.56	6.35
0.2	4.96	18.28	---	6.30	--	6.35
0.3	2.005	9.80	12.25	6.26	6.26	6.35
0.4	2.005	10.20	12.90	6.26	6.33	6.35

In the second experiment, no satisfactory inflection corresponding to the reduction from quadrivalent to trivalent osmium was obtained. While the third and fourth experiments indicate that the quadri-trivalent break gives as good results as the octa-quadrivalent break, probably the data of the first experiment are more

typical, since the general tendency is for the second inflection to give decidedly high results. The results determined from the first inflection point are usually lower than those obtained by the modified iodide method due probably to loss of the volatile tetroxide during the titration and to the fact that the volatility of tetroxide even from an alkaline solution causes such a rapid decrease in concentration that it is important to make the potentiometric and iodometric determinations simultaneously. In the later experiments, improved technique made this difference much smaller as shown by the results given in Table 3.

The Potentiometric Titration of Bromine with Titanous Sulfate

To determine the feasibility of estimating bromine in the presence of hydrobromic acid, octavalent, and quadrivalent osmium, four series of experiments were conducted. Since Hendrixson³ has shown that it is possible to determine bromine potentiometrically in its sulfuric acid solutions by means of trivalent titanium, the first series was merely to confirm his results and consisted in the potentiometric titration of sulfuric acid solutions of bromine with the titanous sulfate. The second series was conducted in the presence of hydrobromic acid, the third series in the presence of this acid and 2 cc. of osmium tetroxide solution, and the fourth series in the presence of this acid and 2 cc. of quadrivalent osmium solution.

In the first three series, the samples of stock bromine solution were pipetted into 50-80 cc. of ice-cold distilled water containing the other constituents. A volume of titanous solution within 1 cc. of that required in a preliminary titration was added immediately and the titration rapidly completed below 5° while nitrogen was bubbled through the solution at the rate of one bubble every 2-3 seconds. Unless the bromine solution was run into a fairly large volume of cold solution the loss was incredibly high. It was found that if the contents of a 50-cc. pipette was allowed to drain into the empty titration vessel at room temperature and the titration conducted in this solution, the loss was over 10%.

The fourth series of experiments was carried out as follows: a 2-cc. sample of the stock tetroxide solution and 5 cc. of 8 N hydrobromic acid were heated for several hours at 98° in a closed tube. The tube was cooled in an ice bath, opened under about 40 cc. of ice water, washed into the titration vessel with an additional 40 cc. of ice water, and the liberated bromine titrated with the titanous solution. To this quadrivalent osmium solution, which now contained no free bromine, was added a known volume of the stock bromine solution and the titration carried out as before. In these solutions there was always present a small amount of octavalent osmium.* During a titration of the bromine the voltage readings became constant to within a millivolt in less than two minutes.

*This seems to indicate that the osmium is not completely reduced even on protracted heating in concentrated hydrobromic acid but that an equilibrium is reached in which the concentration of octavalent osmium is very small but measurable.

Results of the four series of titrations together with those obtained by the iodide method of bromine determination are recorded in Table II. The results with sulfuric acid confirm those of Hendrixson. The results also show that bromine can be determined potentiometrically with trivalent titanium in the presence of hydrobromic acid. The average difference between the potentiometric and iodometric methods in Series 1 and 2 where these acids were present is 0.3-0.4%. In Series 3 where osmium tetroxide was present the percentage difference between the titanous sulfate and iodide-thiosulfate methods varies from about 3% for the highest concentrations of OsO_4 and HBr to about 0.5% for the lowest concentrations of these substances. In the latter case the concentration of the octavalent osmium is approximately 0.1 millimol per litre while the concentration of the HBr is 0.1 N. The experiments of series four indicate that bromine can be determined without appreciable error in the presence of quadrivalent osmium as high in concentration as 0.5 millimol per litre when the hydrobromic acid is as high in concentration as 0.3 N.

TABLE II

Potentiometric Titration of Bromine Solutions with Titanous Sulfate

Volume of bromine solution taken = 25.00 cc.

Volume of osmium solution taken = 2.005 cc.

Volume of solution before titration = 87-112 cc.

Concentration of thiosulfate = 0.03124 N.

Series	Acid Concentration	OsO ₄ conc. Millimols / litre	Os ⁴⁺ conc. / litre	Ti(SO ₄) ₂ Normality	cc. used	Bromine found	
						Potentiometric Iodide-thiosulfate	Milliequivalents/litre
1	1.4 N H ₂ SO ₄			0.00845	14.55	4.918	4.910
	"			0.00845	14.55	4.918	4.910
	0.7 N H ₂ SO ₄			0.00845	14.53	4.911	4.910
	Neutral			0.00845	15.05	4.935	4.910
2	0.5 N HBr			0.01053	24.55	10.34	10.40
	"			0.01053	24.60	10.36	10.40
3	0.5 N HBr	0.1		0.01053	25.20	10.61	10.40
	"	0.1		0.01053	25.07	10.56	10.40
	"	0.5		0.01053	25.45	10.72	10.40
	0.2 N HBr	0.1		0.01029	23.54	9.69	9.62
	1.0 N H ₂ SO ₄						
	0.1 N HBr	0.1		0.01053	25.55	10.76	10.71
	0.1 N HBr	0.1		0.01053	25.55	10.76	10.71
	0.7 N H ₂ SO ₄	0.5		0.01048	25.74	10.80	10.71
4	0.27 N HBr		0.5	0.00896	29.10	10.43	10.42
	"		0.5	0.00896	28.95	10.38	10.39

Potentiometric Titration of Bromine, Octavalent and
Quadrivalent Osmium in Hydrobromic Acid Solutions
containing all Three Constituents

The next step in the investigation was the determination of bromine, octavalent and quadrivalent osmium in hydrobromic acid solutions containing the three constituents in such proportions as to require on titration suitably large volumes of the reducing agent. These solutions were prepared as follows: Samples of 1.996 cc. of stock tetroxide solution which contained approximately 23 millimols per litre and 5 cc. of 2.4 N hydrobromic acid were sealed into glass tubes of about 20 cc. capacity and heated at 98° for about three hours. The tubes were then cooled in an ice bath; broken under about 40 cc. of the ice-cold water, rinsed into the titration vessel with an additional 40 cc. of the cold water; and the titration carried out immediately. As soon as the bromine-bromide ion inflection had been determined an amount of titanous solution within 1-2 cc. of that necessary to reach the octa-quadrivalent end-point was added immediately. The temperature was then raised to 60° and the titration continued until the $\text{Os}^8 \rightarrow \text{Os}^4$ break had been passed. Next, 2.5-8.0 cc. of 8 N hydrobromic acid was added, the temperature was raised to 80°, and the quadrivalent-trivalent inflection point was determined. During the titration the nitrogen was bubbled through the solution in the same manner as in the titration of osmium tetroxide. A typical titration curve showing the three inflections is shown in Fig. 2.

The concentration of the stock osmium tetroxide was determined by the modified iodometric method, care being taken to conduct the potentiometric and iodometric determinations simultaneously.

The results obtained by the two methods are shown in Table III. For convenience, the final results have been expressed in terms of milli-equivalents of bromine. On this basis, if amounts of tetroxide are expressed as equivalent bromine, the titration of the 1.996 cc. of tetroxide solution before heating should be equal to the liberated bromine plus the undecomposed tetroxide after heating.

An inspection of Table III shows that for the last four tubes, the average deviation of the results of the bromine titrations from the mean is about 0.6%. The general tendency of this bromine value is to increase somewhat. However, the total bromine values (i.e., the free bromine plus the undecomposed tetroxide) are of more significance and are in satisfactory agreement with that obtained by the iodometric method, the average difference between the latter and the individual potentiometric values being about 0.5%.

TABLE III

Potentiometric Determination of Bromine, Octavalent and Quadrivalent Osmium
in Hydrobromic Acid Solutions

Volume of OsO_4 solution used = 1.996 cc.
Initial volume = 90-100 cc.
Initial concentration of HBr in bromine titration = 0.17 N.
Initial concentration of HBr in OsO_8 titration = 0.15 N.
Initial concentration of HBr in OsO_6 titration = 0.4-0.8 N.

Titanous Solution Normality	Titanous Solution Used		Bromine Found		Total Bromine Calculated	
	$\text{Br}_2\text{-Br}^-$ cc	$\text{Os}^8\text{-Os}^4$ cc	$\text{Br}_2\text{-Br}^-$ Milliequivalents	$\text{Os}^8\text{-Os}^4$ me	$\text{Os}^4\text{-Os}^3$ me	Iodide Method me
0.00909	10.00	...	0.0909	0.1837
0.00907	9.95	20.24	0.0903	0.1856	0.1872	0.1837
0.00906	10.15	20.40	0.0919	0.1849	0.1882	0.1837
0.00906	...	20.12	...	0.1822	...	0.1837
0.00905	10.20	20.40	0.0923	0.1845	...	0.1837

It seems evident that it is possible by this method to conduct analyses of solutions in reaction tubes containing the four constituents and obtain results of determinations of bromine and of bromine plus octavalent osmium reliable to within 0.6%. In the rate experiments for which this method is primarily intended, this reliability is quite sufficient. The accuracy can be somewhat increased if desired, by determining the concentration of the tetroxide solution added to the tubes before heating by potentiometric titration with hydrazine sulfate,² titrating only the liberated bromine with the titanous solution, and obtaining the undecomposed tetroxide by difference.

In the experiments where it was possible to obtain fairly good inflections in the curve corresponding to the reduction of the quadrivalent osmium to the trivalent, it will be seen that the values obtained are 2.0-2.5% higher than those obtained by the iodometric method.

Summary

A method is described for the potentiometric determination of bromine and octavalent osmium in hydrobromic acid solutions containing bromine, octavalent and quadrivalent osmium by titration with solutions of titanous salts. The voltage-cubic centimeter curves obtained show three inflections - the first corresponding to the reduction of the bromine to bromine ion; the second to the reduction of the osmium from octavalent to quadrivalent; and the third to the reduction of the quadrivalent osmium to trivalent.

Results reliable to 0.6% were obtained using the first two inflections. The third inflection was not found to be satisfactory for quantitative work.

The potentiometric titration of acid solutions of osmium tetroxide is described and some interesting color changes noted.

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THE IONIZATION CONSTANT OF p-CYANOBENZOIC ACID
BY A POTENTIOMETRIC COMPARISON METHOD

A COMPARISON METHOD FOR DETERMINING IONIZATION CONSTANTS
WITH A QUINHYDRONE REFERENCE ELECTRODE

I. p-CYANOBENZOIC ACID

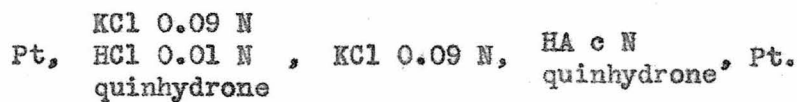
Introduction

Within recent years the potentiometric method of determining ionization constants of weak acids has begun to displace the conductivity method. One disadvantage of the latter is that it is necessary to make conductance measurements not only of solutions of the acid but also of those of a salt of the acid in order to compute Δ_{∞} ; another disadvantage arises from the fact that in order to obtain moderately accurate results very pure water must be used for the preparation of the dilute solutions.

The usual potentiometric method in which the acid is titrated with a standard base to give a titration curve is not entirely satisfactory since (1) the accuracy of the constant is seriously affected by the difficulty of determining the inflection point in the voltage-ml. plot when the acid is weak, and (2) the liquid junction potentials vary while the titration is being carried on due to the continued addition of water and of the positive ion. The method described in this paper has an advantage over the titration method in that the liquid junction potentials are for the most part eliminated.

Method

The method consists in determining the potential of the reference electrode represented at the left end of the cell below, first against a saturated solution of quinhydrone containing HCl at various concentrations, and then against similar solutions containing the acid under investigation at a series of concentrations. The whole cell may be represented thus:



HA represents hydrochloric acid in one series of measurements and the acid under investigation in the other series.

From the data obtained when hydrochloric acid is used a curve is drawn by plotting the measured voltages against the logarithms of the mean ion activities, C^{α} , of the hydrochloric acid. When any other acid is used as HA in the above cell, it is possible to obtain the logarithm of the mean ion activity of this acid at any concentration from the corresponding voltage.

It is difficult to evaluate the liquid junction potentials when the junction is being continuously renewed, but it seems certain that the difference between the liquid junction potential when HCl is used and when an organic acid of the same mean ion activity replaces it will introduce an error in the constants well within the limit of experimental error of the measurements.

Method of Calculation of Results

The ionization constant is calculated from the experimental data by means of the expression

$$\frac{a_{\pm}^2}{\left(c - \frac{a_{\pm}}{\alpha}\right)} = K$$

where a_{\pm} is the mean activity of the ions,

c is the molal concentration of the acid, and

α is the mean activity coefficient.

This assumes

1. That the activity of the undissociated acid is equal to its concentration.
2. That the mean ion activity in the organic acid solution is the same as the mean ion activity in the HCl solution giving the same potential against the reference cell.
3. That the quinhydrone will affect the mean ion activity to the same extent in solutions of the same mean ion activity.

The work of Randall and others² shows that at the concentrations of acid (0.02-0.003 M) used in these measurements the first assumption is fully justified. Since the determination of the individual ion activities is a difficult operation it is desirable to make the second assumption, which seems justifiable at the low concentrations of ions prevailing.

The solubility of the quinhydrone is small, 0.018 moles per liter at 25°, and presumably about the same in the various solutions so that the last assumption is a reasonable one.

Apparatus and Materials

The cell used was similar to the type proposed by Kohn⁴ and is shown in Figure 1. The inner cell containing the reference solution consisted of a glass tube 1.5 cm. in diameter and 15 cm. in length fitted with a ground-on glass cap and a removable electrode carrying a piece of bright platinum foil. The outer cell consisted of a 400 cc. beaker fitted with a rubber top through which passed the mechanical stirrer, the nitrogen bubbling tube, the inner cell, and a glass tube carrying a piece of bright platinum foil which served as the second electrode.

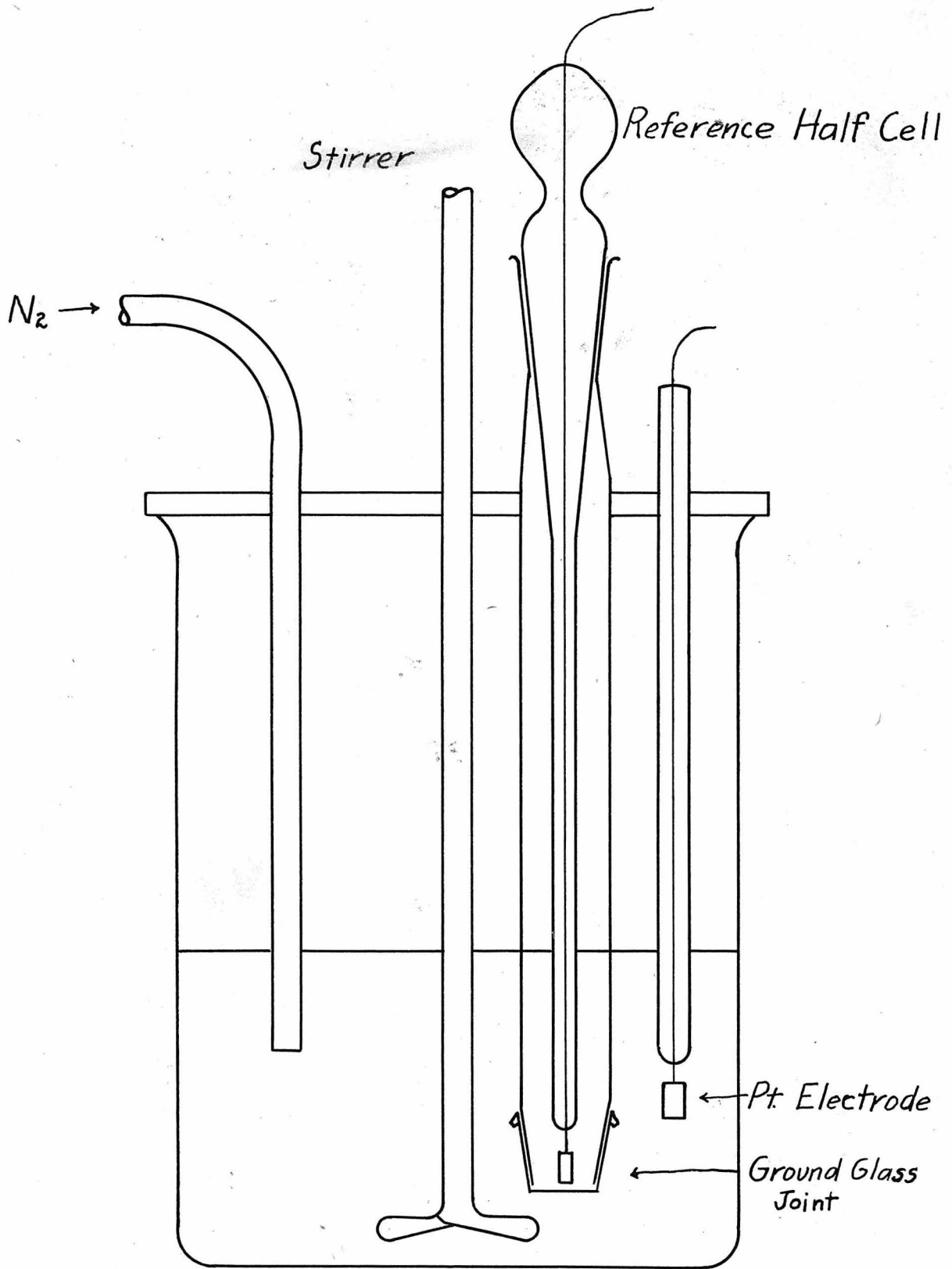
The E.M.F. measurements were made with a Leeds and Northrup Type K potentiometer. The cell was immersed in an oil thermostat maintained at $25^{\circ} \pm 0.02^{\circ}$.

Eastman's quinhydrone was recrystallized twice from water at 70° and was dried over sulfuric acid in a vacuum desiccator.

Constant boiling hydrochloric acid was prepared by the distillation in an all-Pyrex apparatus of concentrated c.p. HCl previously diluted to a specific gravity of 1.11. At the observed pressure of 744.6 mm.⁵ one mol of hydrogen chloride is contained in 179.864 grams of solution. A tenth normal solution was prepared by diluting a weighed amount of this standard acid with a weighed amount of water. Lower concentrations were made by volume dilutions from this solution.

The potassium chloride was recrystallized four times from hot water and fused to dryness.

Figure 1



Benzoic acid of standard quality was purified by three crystallizations from hot water and a subsequent sublimation.

The p-cyanobenzoic acid was the same as that used in the research of Valby and Lucas.⁶ A stock solution was prepared by dissolving a weighed quantity of the solid organic acid in water to a definite volume. This stock solution was diluted by volume to obtain the lower concentrations.

The water used in the preparation of all solutions was obtained by distillation of distilled water from sodium carbonate and potassium permanganate in an all-Pyrex apparatus in an atmosphere of nitrogen. Care was taken to prevent absorption of carbon dioxide and oxygen from the atmosphere.

Experimental Method

The glass cap of the reference half-cell was filled with 0.09 N KCl solution and fastened to the cell with a rubber band. This provided a bridge of 0.09 N KCl through the ground glass joint which experience had shown to be desirable since it increased the constancy of the voltage readings. The excess liquid was removed by three washings with the reference solution and the half-cell filled to a depth of 3-4 cm. with the reference solution. The liquid levels were kept about the same in the outer and inner half-cells to minimize the drift in potential due to diffusion through the ground glass joint during the measurements. To the 400 cc. beaker, which served as the outer half-cell, was added about 200 cc. of the hydrochloric or organic acid solution. The outer parts of the reference half-cell were washed with a small amount of the same solution, the two half-cells were assembled in the oil thermostat and connected to the potentiometer. Stirring was carried on at a slow rate by the motor driven stirrer while purified nitrogen was passed through the outer half-cell at the rate of about 20 bubbles a minute. Voltage readings were made at five minute intervals until equilibrium to within 0.1 millivolt was attained, which in general was from 10 to 15 minutes. This equilibrium value was usually about one millivolt lower than the initial reading. The bright platinum foil electrodes were found to give reproducible results throughout the entire series of measurements.

The reference half-cell was filled anew before each determination, since otherwise the observed voltage on a succeeding run would be materially lower.

All solutions used were saturated with quinhydrone at 45° by vigorous shaking for 15 minutes in the presence of a small excess of the solute. The solutions were then brought to 25° by immersion in the thermostat and were shaken at intervals to aid crystallization of the excess quinhydrone.

Reference Plot

Using the apparatus and methods described, measurements were made of the voltages produced by solutions of known concentrations of hydrochloric acid saturated with quinhydrone against the reference solution 0.09 N in potassium chloride and 0.01 N in hydrochloric acid, saturated with quinhydrone. The results are given in Table I.

TABLE I

Concentration HCl mols per liter	Log α	Log αC	Observed E.M.F. volts
0.01023	-0.0432	3.9669	+0.0020
"	"	"	+0.0026
"	"	"	+0.0021
"	"	"	+0.0025
0.00511	-0.0325	3.6759	-0.0142
0.001023	-0.0151	4.9950	-0.0544
"	"	"	-0.0543
" =	"	"	-0.0533
"	"	"	-0.0568
0.000511	-0.0110	4.6974	-0.0725
0.000204	-0.0075	4.3021	-0.0963
"	"	"	-0.0950
0.0001023	-0.0050	4.0051	-0.1126
"	"	"	-0.1157
"	"	"	-0.1161
"	"	"	-0.1174
0.00001023	-0.0009	5.0090	-0.1745

The activity coefficients at the higher concentrations are those of Randall and Young?

At concentrations below 0.001 N the activity coefficients were calculated by means of the Debye-Hückle equation.⁸

The observed voltages were plotted against the corresponding values of $\log \alpha C$ and a straight line was drawn through the points. The curve may be reproduced from the values given in Table II.

TABLE II

$\log \alpha C$	$\bar{2}.000$	$\bar{3}.000$	$\bar{4}.000$	$\bar{5}.000$
Voltage	+0.0045	-0.0515	-0.1138	-0.1728

The small amount of carbon dioxide which may have contaminated the solution in spite of our precautions would not modify the curve appreciably in the region employed.

Application of the Method

In Table III are tabulated the data obtained with benzoic and para-cyanobenzoic acids using the apparatus and experimental technique as previously described.

TABLE III

Acid concentration mols per liter <u>Benzoic Acid</u>	Observed E.M.F.	$\log a_{\pm}$	$K_A \times 10^5$
0.02129	-0.0511	$\bar{3}.057$	6.47
0.01065	-0.0598	$\bar{4}.910$	6.73
"	-0.0595	$\bar{4}.915$	6.90
0.004258	-0.0719	$\bar{4}.706$	6.90
"	-0.0720	$\bar{4}.705$	6.87
0.002129	-0.0819	$\bar{4}.538$	6.72
0.02032	-0.0517	$\bar{3}.047$	6.49
"	-0.0511	$\bar{3}.057$	6.64
0.01016	-0.0606	$\bar{4}.888$	6.38
"	-0.0603	$\bar{4}.902$	6.82
0.004064	-0.0725	$\bar{4}.695$	6.90
0.001016	-0.0926	$\bar{4}.351$	6.38
			Average, $6.68 \pm 0.25 \times 10^{-5}$
<u>para-Cyanobenzoic Acid</u>			
0.007294	-0.0465	$\bar{3}.135$	3.17
"	-0.0465	$\bar{3}.135$	3.17
0.003647	-0.0570	$\bar{4}.960$	3.08
"	-0.0570	$\bar{4}.960$	3.08
0.001459	-0.0707	$\bar{4}.727$	3.01
"	-0.0704	$\bar{4}.732$	3.12
0.0007294	-0.0823	$\bar{4}.531$	3.02
"	-0.0823	$\bar{4}.531$	3.02
0.0003647	-0.0946	$\bar{4}.325$	2.99
			Average, $3.10 \pm 0.10 \times 10^{-4}$

The values of the logarithm of the mean ion activity in the organic acid solutions were obtained from the plot of the data of Table I. The values of the constant were calculated from the expression

$$K = \frac{a_{\pm}^2}{\left(C - \frac{a_{\pm}}{\alpha}\right)}$$

These values were then plotted against the logarithm of the concentration to obtain the constants at round concentrations which are compared in the case of benzoic acid in Table IV with those of some previous investigators obtained from conductance measurements.

TABLE IV

Conc.	Ostwald ⁹	Euler ⁹	Schaller ⁹	White and Jones ⁹	Kortright ⁹	This paper
0.02	5.98	6.68	6.80	6.70	6.19	6.63
0.01	5.98	6.67	6.77	6.77	6.30	6.84
0.004	6.04	6.70	6.84	6.87	6.31	6.86
0.002	6.05	6.69	6.77	6.83	6.34	6.76
0.001	5.89	6.69	6.61	6.51	6.41	6.50

It is seen that the values obtained by any one investigator agree very well, but the divergence of the results of different investigators is quite considerable. These constants were calculated using ion concentrations rather than mean ion activities, but this difference is much less than the variation in results.

The maximum deviation from the mean in the values for the ionization constant of the para-cyanobenzoic acid is three percent. The mean value agrees with the value of 3.09×10^{-4} which Valby and Lucas⁶ obtained by the conductance method.

Summary

Ionization constants of organic acids may be determined by means of a quinhydrone cell in which the reference half-cell is standard hydrochloric acid solution saturated with quinhydrone and containing potassium chloride.

The method is tested in the case of benzoic acid by comparison of the values herein obtained with those reported by previous investigators and found to be in satisfactory agreement.

The ionization constant of para-cyanobenzoic acid is found to be $3.10 \pm 0.10 \times 10^{-4}$. This result likewise agrees well with the value recently obtained by the conductance method.

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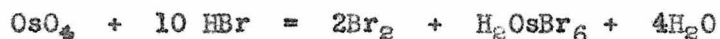
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THE RATE OF REACTION BETWEEN OSMIUM TETROXIDE
AND HYDROBROMIC ACID

THE RATE OF REACTION BETWEEN OSMIUM TETROXIDE
AND HYDROBROMIC ACID

Introduction

A study of the catalytic influence of ruthenium compound on the decomposition of perchloric acid by hydrobromic acid has recently been made in this laboratory.¹ A similar investigation of the catalytic effect of octavalent osmium on this reaction is now in progress. Since under certain conditions there is an appreciable action between the hydrobromic acid and this form of osmium in accordance with the following reaction



it became necessary to study the latter effect separately. This paper describes the methods employed, the empirical rate curves, and discusses the probable interpretation of the results.

Apparatus and Materials

The apparatus used in the potentiometric titration consisted of a motor-driven stirrer, a Leeds and Northrup student type potentiometer with a Leeds and Northrup galvanometer of 2.84 megohms sensitivity, a certified burette, a titration vessel of 125 cc. capacity. The titanous solution employed in the titration vessel was kept under an atmosphere of purified carbon dioxide during and between titrations.

The osmium tetroxide was prepared by passing oxygen over the metal in a tube heated to about 300°. The resulting osmium tetroxide was absorbed in 0.5 molal potassium hydroxide solution kept in an ice bath. Stock solutions approximately 0.04 and 0.02 molal were prepared by dilution of this concentrated reagent.

Chemically pure hydrobromic acid free from bromine was made by distillation in an all-pyrex apparatus of the 42-48% reagent. This was diluted to 8.0 molal for use in the rate experiments.

The titanous chloride was prepared each day by boiling together for one minute sufficient 8.0 molal HBr and 1.0 molal $TiCl_3$ to give on dilution a solution approximately 0.008 normal in reducing power. This solution was standardized several times during the course of the day by means of ferric alum which had been titrated against standard potassium permanganate. Sodium oxalate from the Bureau of Standards was used to standardize the permanganate. The concentration of the titanous solution usually changed less than 0.1% during the day.

Water used throughout the investigation was prepared by distilling the laboratory distilled water from potassium permanganate and potassium hydroxide in an all-pyrex still.

Method

The reaction rate measurements were carried out essentially as follows. Into test tubes of about 12-15 cc. capacity were run in succession distilled water, one cc. of osmium tetroxide solution, and hydrobromic acid, the water and acid being measured from a burette in such amounts as to give the acidity desired in the run. The use of pressure rather than suction in filling the pipette with the osmium tetroxide solution caused so little change in the concentration that the solution remained essentially constant over a period of several weeks. The tubes were quickly sealed off and placed in the water bath at the desired temperature.

At suitable time intervals a tube was removed from the bath, cooled, broken under about 45 cc. of ice water in a mortar, the contents washed into the titration vessel with an additional 45 cc. of the ice water, and the bromine present quickly determined by potentiometric titration with the titanous solution as described in a previous paper.²

In some of the earlier runs the bromine titrations were carried out in a volume of 250 cc. The variation in bromine content of duplicate tubes was such that this refinement was unjustified and the more rapid procedure was therefore adopted.

At intervals during the investigation the total osmium content of a tube was determined by titration at 60° with titanous solution² and found to agree with the standardization of the stock solution by the iodide and hydrazine methods.

Reaction Rate Results

The results of the reaction rate measurements at different temperatures, various concentrations of hydrobromic acid and of osmium tetroxide are given in Table I. For convenience in later calculations, the results of the titrations are expressed in terms of percent conversion of the osmium tetroxide into the reaction products.

The curves of Figures 1 - 4 result from plotting the percent conversion of osmium tetroxide against the time in hours.

To assist in the interpretation of the rate measurements plots were made of the slopes of the first portions of the curves shown in Figures 1 - 4 against the corresponding temperatures and hydrobromic acid concentrations. These are shown in Figures 5 and 6 and were constructed from the data of Table II.

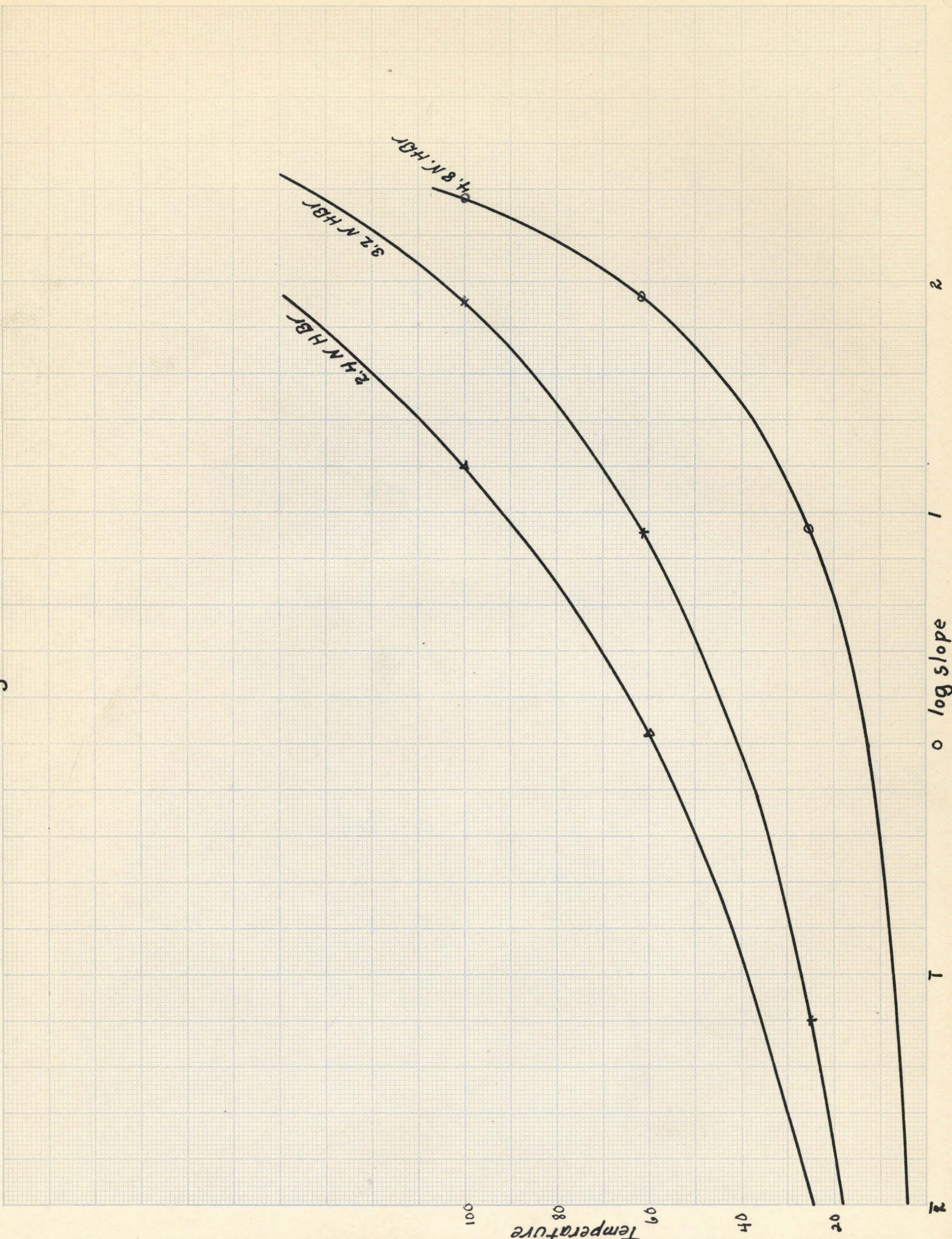


Figure 5

Figure 6

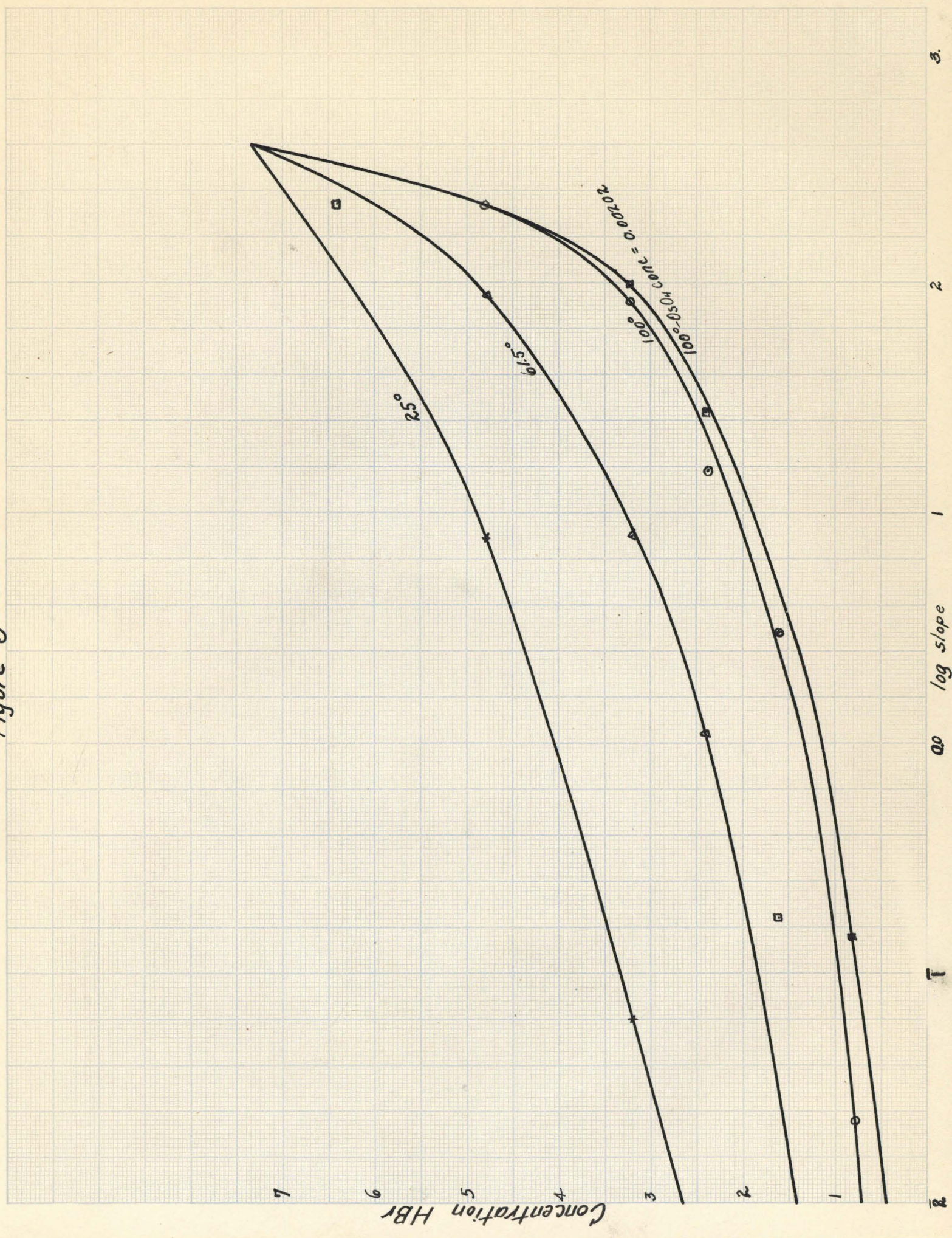


Figure 4 Temp. 100° Conc. O₂O₄ 0.00202 Mols/Liter

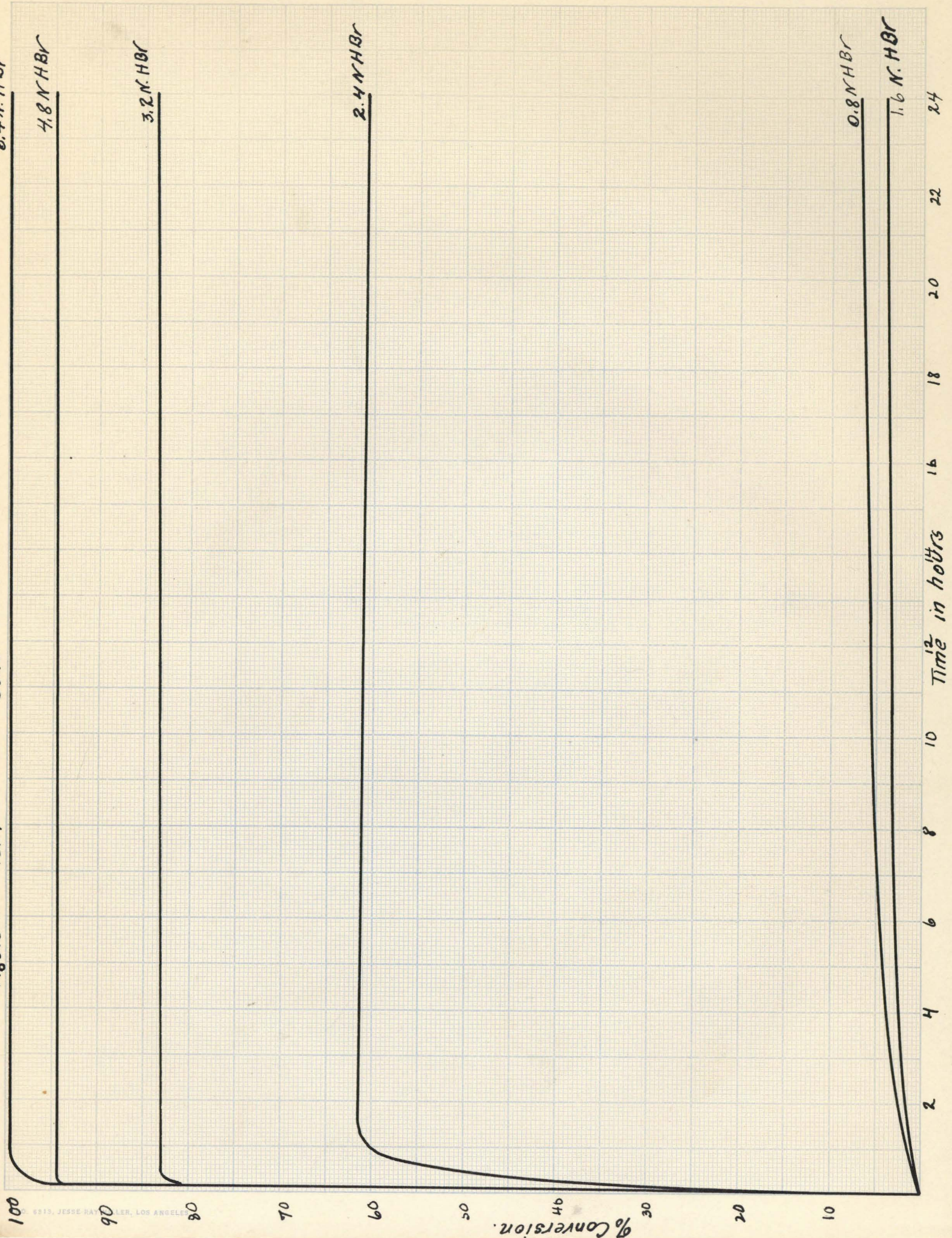


Figure 3. Temp. 100° Conc. O_2O_4 0.00404 Mols/Liter

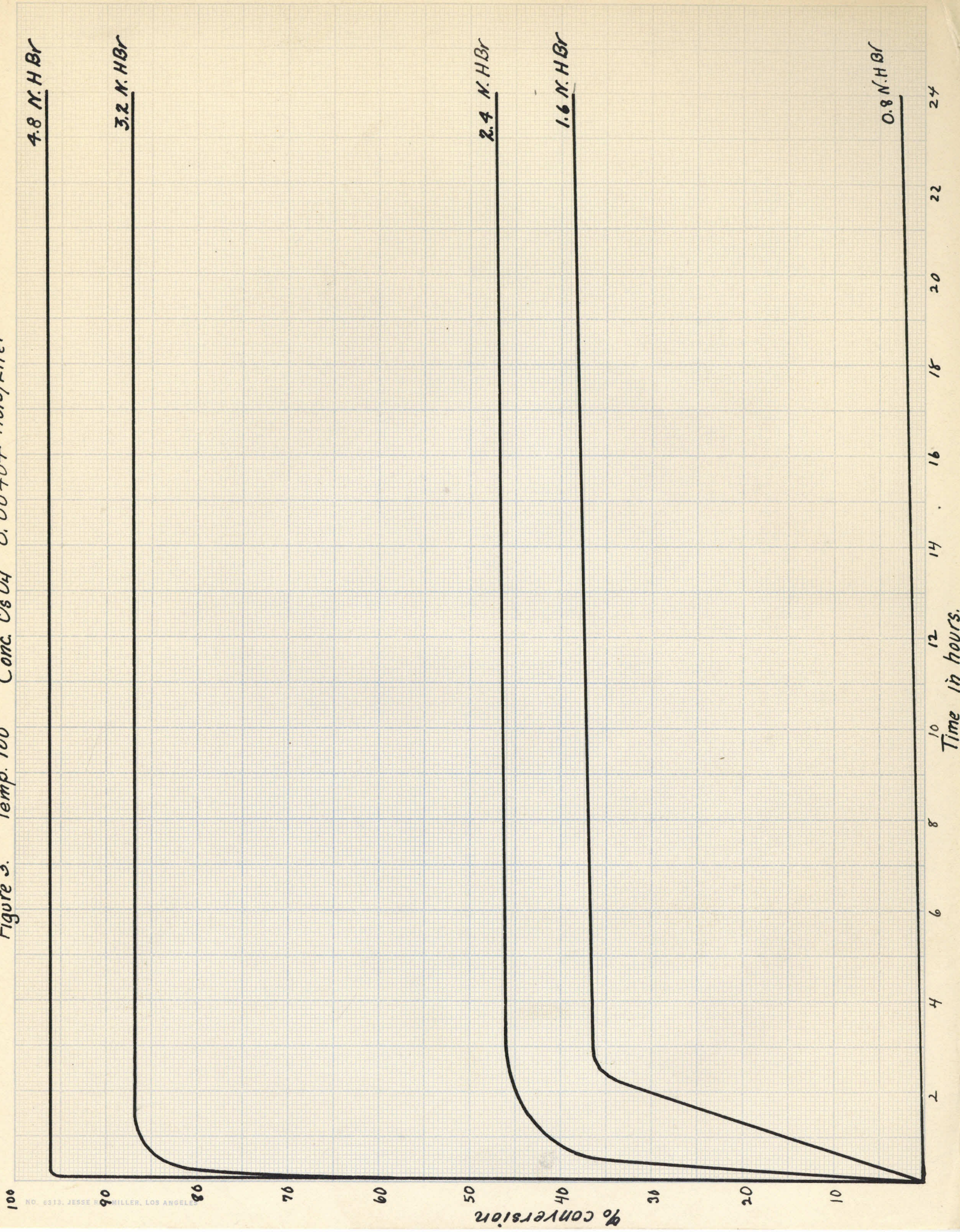


TABLE I

Results of the Rate Measurements

Temp. °C	OsO ₄ conc. mols/liter	HBr conc. mols/liter	Percent conversion of OsO ₄ after Time in hours												
			1/12	1/6	1/4	1/2	1	2	4	8	24	72			
25	0.00404	3.2				0	1.5	2.7	7.3	24.6					
25	0.00404	4.8				27.8	67.5	75.0	78.6	95.5	97.6				
61.5	0.00404	2.4			5.2	7.3	11.3	20.6	43.8	55.3	56.0				
61.5	0.00404	3.2		4.0	15.7	33.3	62.0	87.5	87.9	89.2	89.6				
61.5	0.00404	4.8	75.0	95.0	96.5	99.4	99.4	99.4	99.4	97.8					
100	0.00404	0.8						1.4	0.9	2.7	4.0				
100	0.00404	1.6				15.3	30.0	36.6	36.8	38.9	41.7				
100	0.00404	2.4	6.8		38.7	50.4	44.0	46.2	46.2	46.2					
100	0.00404	3.2	34.6	68.5	81.0	82.5	80.6	87.0	87.0	87.0	85.5				
100	0.00404	4.8	95.0	96.0	96.0	95.5	95.5	95.5	95.5	96.7	97.2				
100	0.00202	0.8				0.7	1.6	3.6	5.3	6.9	2.7				
100	0.00202	1.6				0.9	1.7	2.5	3.1	4.0	3.1				
100	0.00202	2.4			54.5	51.4	60.6	59.0	56.3	60.8	45.8				
100	0.00202	3.2	34.2		35.0	64.0	63.0	59.0	56.3	50.8	51.3				
100	0.00202	4.8	41.8	76.0	88.6	88.6	85.5	85.6	84.0	87.4	89.0				
100	0.00202	4.8	94.9	95.0	92.9	94.5	94.5	94.5	94.4	92.5	96.0				
100	0.00202	6.4	94.3	94.3	94.3	99.9	98.0	98.0	94.5	100.	97.				

Figure 1 Temperature 25° Conc. OsO₄ 0.00404 Mols/Liter

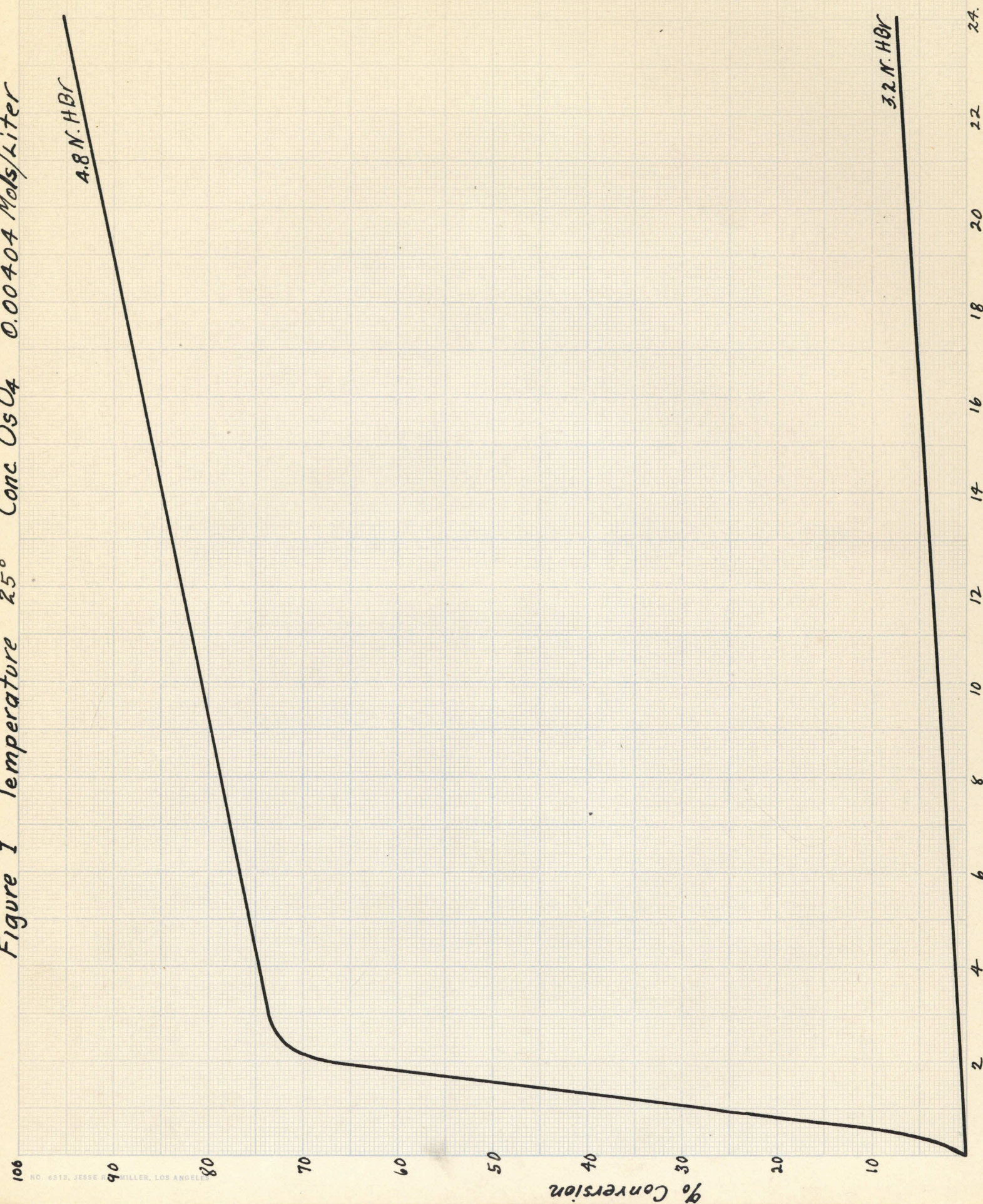


Figure 2 Temp. 61.5° Conc. 0.00404 Mols/Liter

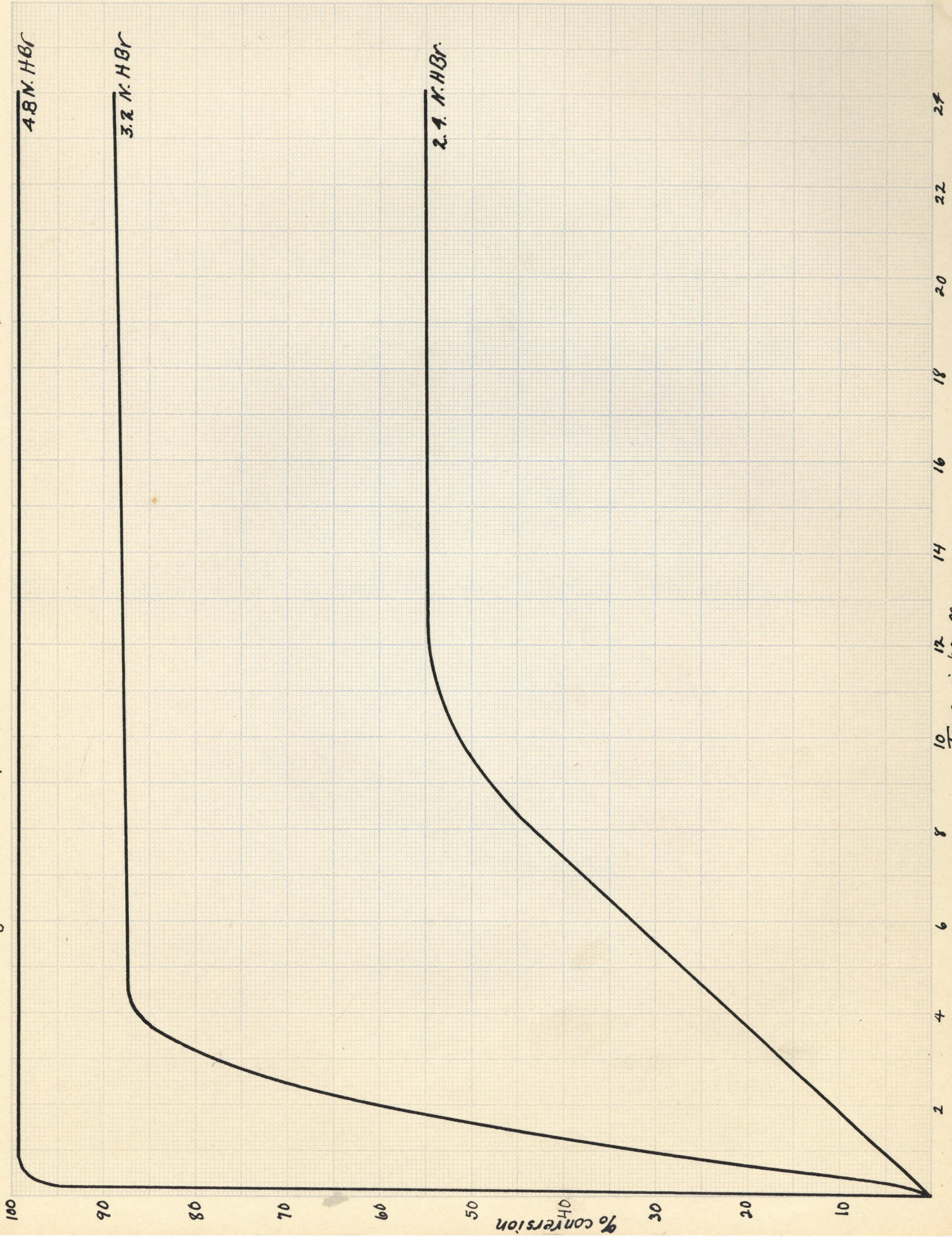


TABLE II

Slope of Reaction Rate Curves

Concentration $\text{OsO}_4 = 0.00404$ mols/liter

Temp.	Molality HBr	$\tan \frac{\theta}{2 \text{ hr.}}$		log tan
25°	3.2	0.063	3°35'	8.796
25	4.8	7.70	82°36'	0.886
61.5	2.4	1.087	45°15'	0.036
61.5	3.2	7.88	82°46'	0.896
61.5	4.8	89.3	89°22'	1.951
100°	0.8	0.023	1°19'	8.360
100	1.6	3.05	71°51'	0.484
100	2.4	15.6	86°20'	1.193
100	3.2	82.2	89°19'	1.915
100	4.8	226 (?)	89°45'	2.354

Concentration $\text{OsO}_4 = 0.00202$ mols/liter

100°	0.3	0.14 (?)	7°58'	9.146
100	1.6	0.18	10°12'	9.255
100	2.4	27.4	87°55'	1.438
100	3.2	100	89°26'	2.000
100	4.8	226	89°45'	2.354
100	6.4	226 (?)	89°45'	2.354

Calculation of the specific reaction rate constants in accordance with a first order and zero order reaction shows that during the initial stages the disappearance of osmium tetroxide proceeds at a rate which is approximately proportional to its concentration. The dependence of the rate of reaction upon the concentration of hydrobromic acid is seen to vary with both the temperature and with the concentration of acid.

For the present the results must be taken as empirical values to use in correction of the catalyzed decomposition of hydrobromic acid by perchloric acid for the rate of the uncatalyzed reaction.

It was observed (see curves of Figures 1-4) that the fraction of OsO_4 converted reached a maximum value after the reaction had proceeded for a period of time which was less for the higher concentrations of hydrobromic acid and which was independent of the temperature and of the concentration of osmium tetroxide. This indicated that perhaps an equilibrium state had been reached and an experiment was performed to determine whether the reverse reaction would take place. A tube was prepared containing H_2OsBr_6 and bromine sufficient stoichiometrically to oxidize it to osmium tetroxide in the presence of 1.6 N hydrobromic acid. After a half hour in the steam bath, it was observed that the characteristic red color of the H_2OsBr_6 had disappeared. On titration of the contents of the tube with titanous chloride solution it was found that the bromine had completely been used up and that an equivalent quantity of the

osmium tetroxide had been formed. The odor of osmium tetroxide was also readily detected on opening the tube.

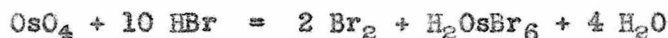
Experiments are now in progress to determine the rate of formation of osmium tetroxide from bromine and H_2OsBr_6 in the presence of varying concentrations of hydrobromic acid and to approach the equilibrium from that side in order to better determine the equilibrium constant for the reaction.

The Equilibrium Constant

From the expression

$$K = \frac{\text{Br}_2^2 \text{H}_2\text{OsBr}_6}{\text{OsO}_4 \text{HBr}^{10}}$$

corresponding to the reaction



were calculated the equilibrium constants given in columns 3 and 7 of Table III. Concentrations used in the calculations were mols per liter. The percentage conversion values employed were taken from the horizontal portions of the curves of Figures 1 - 4. More weight was given in drawing the curves to the larger values for the percentage conversion since all errors in the measurements would tend to give low values of bromine found by titration. Since these measurements were not carried out primarily to determine the equilibrium of the reaction, the calculated constants must be regarded as preliminary and possibly subject to minor change when the experiments on the reverse reaction now in progress have been completed.

Columns 4 and 8 of Table III give values of the equilibrium constant calculated as before except that the ninth power of the concentration of the hydrobromic acid was used.

TABLE III

Equilibrium Constants

Concentration $\text{OsO}_4 = 0.00404 \text{ m/l}$				Concentration $\text{OsO}_4 = 0.00202 \text{ m/l}$			
Temp. °C	Molality HBr	$K_{10} \times 10^{10}$	$K_9 \times 10^{10}$	Temp.	Molality HBr	$K_{10} \times 10^{10}$	$K_9 \times 10^{10}$
25	3.2	0.12	0.387				
25	4.8	3.80	18.2				
61.5	2.4	41.0	98.6				
61.5	3.2	40.5	129				
61.5	4.8	20.0	96.4				
100	0.8	68.0	7.3	100	0.8	20.0	2.2
100	1.6	765	1220	100	1.6	0.10	0.15
100	2.4	22.0	53	100	2.4	15.0	36.0
100	3.2	31.0	98	100	3.2	13.0	42.5
100	4.8	10.0	48	100	4.8	1.0	2.7
				100	6.4	1.4	9.2

At lower concentrations of hydrobromic acid and at the lowest temperature, the rate of reaction is so small that equilibrium was apparently not reached even after 72 hours and the constants are distinctly lower than those at intermediate acid concentrations. At the highest acid concentrations the percentage conversion is so great that an error of 0.1 percent would change the value of the constant appreciably. More consistent values for the constant would be obtained by using the concentration of HBr to the 9.5 power. This dependence is possible due to the partial ionization of the H_2OsBr_6 and hence the equilibrium is dependent upon the hydrogen and bromide ions to a different degree. A more detailed analysis of the results can be better carried out after the equilibrium has been approached from both sides.

Summary

The reaction between OsO_4 and hydrobromic acid to form bromine and H_2OsBr_6 has been found to be reversible.

Rate measurements during the early part of the reaction have been made at different temperatures and concentrations of HBr and of OsO_4 . The results are shown in a set of empirical curves.

Provisional values for the equilibrium constant are calculated and agree reasonably well.

Further work on the equilibrium is planned.

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