

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA
AT LOS ANGELES]

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

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Introduction

In a study of the reaction between octavalent osmium and hydrobromic acid at 100° now in progress, it has been found that the products are quadrivalent osmium and bromine and that a state of equilibrium is reached. However, in concentrated hydrobromic acid solutions (about 8 *N*) the reaction goes to practical completion in the direction of formation of quadrivalent osmium and bromine, while in dilute acid solutions (about 0.1 *N*) the reaction goes to completion in the reverse direction. This behavior suggests (1) that octavalent osmium may be determined by heating it in a closed tube with concentrated hydrobromic acid and titrating the liberated bromine; (2) that quadrivalent osmium may be determined by heating it in a closed tube with a dilute hydrobromic acid solution containing excess bromine, titrating the bromine remaining and calculating the amount of osmium present from the amount of bromine used up. Because of the deeply colored solution formed in (1) and because of the presence of octavalent osmium in (2), potentiometric methods are found to be most satisfactory.

We have already shown that octavalent osmium may be determined with an accuracy of about 0.2% by direct potentiometric titration with hydrazine sulfate.¹ We have also shown that bromine may be determined in hydrobromic acid solutions of octavalent and quadrivalent osmium with an accuracy of about 0.5% by potentiometric titration with titanous sulfate.² The present paper presents results and describes how hydrazine sulfate may be used in an improved method of determining bromine in hydrobromic acid solutions of the two forms of osmium and shows how this method may be applied to indirect determinations of octavalent and quadrivalent osmium.

The value of hydrazine sulfate as a reducing agent in analytical work is well known. Bray and Cuy³ have developed methods of standardization based on its oxidation by iodic acid, iodine, bromine and hypochlorous acid. Wellman has employed a potentiometric method for the determination of bromine in his study of the equilibrium between bivalent and

¹ Crowell and Kirschman, *THIS JOURNAL*, 51, 175 (1929).

² Crowell and Kirschman, *ibid.*, 51, 1695 (1929).

³ Bray and Cuy, *ibid.*, 46, 4 (1924).

quadrivalent palladium and chlorine in hydrochloric acid solution.⁴ As a standard reagent, hydrazine sulfate is to be preferred over titanous salts because of its great stability in air and the ease with which it may be obtained in a pure form.

Apparatus and Materials.—The apparatus used was that employed in the potentiometric determination of octavalent osmium⁵ and in the determination of bromine in the presence of octavalent and quadrivalent osmium.²

The hydrobromic acid free from bromine was obtained by distilling the 42–48% acid and retaining the middle portion.

The bromine solution was prepared from the c. p. reagent and was made 0.1 *N* in hydrobromic acid.

The osmium tetroxide solution was prepared by heating osmium metal in a tube in a current of oxygen at about 300° and absorbing the resulting osmium tetroxide in 0.4 *N* potassium hydroxide. The stock solutions, approximately 0.04 and 0.08 molal in OsO₄, were prepared by diluting this solution.

The hydrazine sulfate solution was prepared from the c. p. reagent and was standardized with recrystallized potassium iodate by the method of Bray and Cuy. The sodium thiosulfate was also standardized with potassium iodate.

The quadrivalent osmium solutions, approximately 0.04 and 0.08 molal in quadrivalent osmium, were prepared by heating known volumes of the stock osmium tetroxide solution in sealed tubes with enough concentrated hydrobromic acid to make the acid concentration about 8 normal, evaporating in a vacuum desiccator containing solid sodium hydroxide and sulfuric acid and diluting to the desired volume with 0.1 or 3.8 normal hydrobromic acid. Since there was an excess of potassium hydroxide in the stock osmium tetroxide solutions, the resulting product was really a solution of the potassium salt of quadrivalent osmium.

Experimental Results

The experimental results are recorded in Tables I and II.

The data in Table I were obtained from results of potentiometric titrations of bromine in solutions of sulfuric acid, hydrobromic acid and of hydrobromic acid solutions of octavalent and quadrivalent osmium. In series 1, the bromine solution was forced by pressure into a pipet and run directly into an ice-cold solution of sulfuric acid containing slightly less than an equivalent amount of hydrazine sulfate. The titration was completed and the results obtained were compared with those obtained by the iodimetric method. In the table, the term "initial volume" means the volume before the addition of the hydrazine sulfate. In series 2 results of titrations of bromine in 0.2 *N* hydrobromic acid solution were compared with those also obtained potentiometrically when the bromine was added to water alone. In the latter case the acidity of the solution as determined by the amount of hydrobromic acid in the stock bromine solution was about 0.001 *N*. The purpose of these experiments was to determine whether or not there was an appreciable amount of bromine present in the hydrobromic acid used. In series 3 and 4 the procedure

⁴ Wellman, *THIS JOURNAL*, 52, 3 (1930).

⁵ Crowell and Kirschman, *ibid.*, 51, 175 (1929).

TABLE I

POTENTIOMETRIC TITRATION OF BROMINE SOLUTIONS WITH HYDRAZINE SULFATE
 Volume of bromine solution taken, 1.996 cc. Volume of osmium solution taken,
 1.00 cc. Initial volume, 240 cc. Concentration of hydrazine sulfate, 0.01017 *N*.

Series	Acid and concn.	Osmium in titration beaker, millimole/liter		$N_2H_4SO_4$ used, cc.	Bromine found, millieq./liter		Iodimetric stock soln. alone
		Os_4	Os_8		Stock soln. added to H_2SO_4 , HBr and Os solns.	Stock soln. + water alone	
1	0.30 <i>N</i> H_2SO_4	0.00	0.00	31.82	162.2		162.3
	.30 <i>N</i> H_2SO_4	.00	.00	31.83	162.3		162.3
	.30 <i>N</i> H_2SO_4	.00	.00	31.78	162.0		162.3
2	.20 <i>N</i> HBr	.00	.00	32.77	167.1	166.9	
	.20 <i>N</i> HBr	.00	.00	32.73	166.9	166.9	
3	.10 <i>N</i> HBr	.00	.15	32.32	164.8	164.0	
	.10 <i>N</i> HBr	.00	.15	32.37	165.1	164.0	
	.075 <i>N</i> HBr	.00	.15	32.10	163.6	164.0	
	.083 <i>N</i> HBr	.00	.15	32.02	163.2	163.3	
4	.10 <i>N</i> HBr	.15	.00	32.52	165.8	166.0	
	.10 <i>N</i> HBr	.15	.00	32.63	166.4	166.3	
	.050 <i>N</i> HBr	.15	.00	32.43	165.3	166.0	
	.020 <i>N</i> HBr	.15	.00	31.20	159.0	160.2	

TABLE II

THE POTENTIOMETRIC DETERMINATION OF OCTAVALENT AND QUADRIVALENT OSMIUM
 Volume of osmium stock solutions used, 1.001 cc. Initial volume in titration
 beaker, 240 cc. Volume of constituents in reaction tubes, 10.0 cc.

Series	Constituents in reaction tubes	0.01017 <i>N</i> $N_2H_4SO_4$ required, cc.		Calculated concn. of osmium, millieq./liter	
		Titration of bromine liberated	Equivalent to bromine absorbed	From bromine titration	From titration of Os_4 soln. used
1	OsO_4 + 8 <i>N</i> HBr	30.80		313.6	313.9
		30.78		313.4	313.9
		30.83		313.9	313.9
2	Os_4 + 0.1 <i>N</i> HBr + bromine		31.00	315.6	315.1 ^a
			30.87	314.3	315.1 ^a
			30.92	314.8	315.1 ^a

^a Result of titration of OsO_4 solution used to prepare the Os_4 solution.

was practically the same as that used in the analysis of the equilibrium mixtures consisting of bromine, hydrobromic acid and the two forms of osmium in relatively high concentrations. The bromine was added to a test-tube containing 8 cc. of an ice-cold solution 3.0 *N* in hydrobromic acid and approximately 0.004 molal in the osmium compound. In series 3 the osmium was in the form of OsO_4 . The tube was sealed and then opened in ice water or dilute sodium hydroxide solution contained in a heavy-walled Pyrex beaker of 600 cc. capacity. The tip of the tube was broken against the side of the beaker beneath the surface of the solution, a small tube inserted into the opening and the contents forced out by gentle blowing. The solution was stirred just long enough to become thoroughly mixed, the hydrazine sulfate added and the titration com-

pleted. It was found that at this temperature there is an appreciable reaction between the hydrazine sulfate and the OsO_4 , if the acidity is too high in any portion of the solution. By adding a small amount of dilute sodium hydroxide solution to the water in the titration beaker and stirring in the contents of the tube before the addition of hydrazine sulfate, the effect of the action of the acid on the OsO_4 is practically offset by the mechanical loss of bromine. In series 4, osmium was present in the quadrivalent form. The tubes were broken in a solution containing slightly less than an equivalent amount of hydrazine sulfate and, in the last two experiments, a small amount of base. After stirring, the titration was completed as in the other determinations. In these experiments the danger is in having the acidity so low that there is an appreciable reaction between the bromine and the quadrivalent osmium. The results obtained in both series 3 and 4 were compared with those obtained from potentiometric titrations of solutions formed by the addition of the bromine stock solution to water alone.

The data in Table II are results of determinations of octavalent and quadrivalent osmium. Series 1 are indirect determinations of octavalent osmium. A measured volume of the stock OsO_4 solution was sealed into a Pyrex tube containing an ice-cold solution of concentrated hydrobromic acid, the tube heated for one hour in the water-bath, cooled again, the contents broken into hydrazine sulfate solution and the titration of the bromine completed as in the previous experiments. The results obtained are compared with those found by direct potentiometric titration of the OsO_4 solution used. Series 2 are indirect determinations of quadrivalent osmium. A measured volume of stock bromine solution was sealed into a tube containing a known volume of stock Os_4 solution diluted with 0.1 *N* hydrobromic acid and chilled to near the freezing point. This tube was heated and the bromine left was titrated in the same manner as in the other experiments. The amount of bromine used up was determined, the concentration of the osmium calculated and the results compared with those obtained by direct potentiometric titration of the OsO_4 solution used to prepare the Os_4 .

In the titration of the solutions in which only bromine and acid were present the fall in voltage at the end-point with the addition of one drop of reagent was 0.3–0.4 volt and was very rapid. In the presence of osmium the corresponding voltage drop was 0.2–0.3 volt and the rate of fall was much slower.

The results in Table I indicate that for a concentration of osmium as high as 0.15 millimole per liter there is no serious error in the titration of bromine by hydrazine sulfate in the presence of OsO_4 if the concentration of hydrobromic acid is no greater than about 0.08 *N*. In the case of quadrivalent osmium, the acidity should not be much lower than this.

In the determinations of octavalent and quadrivalent osmium the agreement between the results obtained by this method and those obtained by other methods is somewhat better than 0.2%.

Summary

Potentiometric methods are described (1) for the determination of bromine in hydrobromic acid solutions of octavalent and quadrivalent osmium, (2) for the determination of octavalent osmium by titration of the bromine liberated when it is reduced by concentrated hydrobromic acid and (3) for the determination of quadrivalent osmium by determining the bromine required to oxidize it to the octavalent form when the reaction takes place in dilute hydrobromic acid. The reagent used is hydrazine sulfate. The accuracy of the method is about 0.2%.

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THERMAL CONDUCTIVITY OF THE NORMAL PRIMARY SATURATED ALCOHOLS

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Accurate quantitative information as to the variation of thermal conductivity of successive members of homologous series with molecular weight and with temperature is essential for the formulation of a defensible molecular theory of liquids. At the present time systematic data available on the subject under comparable conditions are scattered and incomplete.¹

To supply this deficiency the thermal conductivity of seven normal primary saturated alcohols at 30, 75 and 100° and at atmospheric pressure have been determined by the writer by means of a special form of radial heat flow calorimeter comprising a thin cylindrical sheath of liquid.

The alcohols were obtained from the Eastman Kodak Chemical Company, Rochester, N. Y., and were of a very high order of purity as is shown by their range of boiling temperatures given in the summary of the results (Table I). Shipped in sealed bottles with ground-glass stoppers the samples were and remained perfectly colorless.

The apparatus used consisted chiefly of Bridgman's cylindrical calorimeter and is fully described elsewhere.²

¹ "International Critical Tables," 1929, Vol. V, p. 227, Table VI and p. 228, Tables X-XI; Landolt-Börnstein, "Physikalisch-Chemische Tabellen," 1931, Table 271, p. 1278; II Erg. Bd.; also ed. of 1927, I Erg. Bd.; Table 271, p. 715; Glazebrook's "Dictionary of Applied Physics," Article on "Thermal Conductivity," Vol. I, p. 429.

² P. W. Bridgman, "The Thermal Conductivity of Liquids under Pressure," *Proc. Am. Acad. Arts Sciences*, 59, 7 (1923); J. F. Downie-Smith, "Thermal Conductivity of Liquids," *Ind. Eng. Chem.*, 22, 1246 (1930).