Summary

1. An exact method of solving the conductance equations for incompletely dissociated binary electrolytes is presented.

2. A method is described for determining the limiting equivalent conductance and the dissociation constant.

3. Five examples of application of the method are given, in which the constants of solvent and of electrolyte vary as widely as possible. Calculated and observed conductance values agree within the limit of experimental error up to ion concentrations of several thousandths normal.

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The Reaction between Osmium Tetroxide and Hydrobromic Acid. I. Equilibrium Study

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Introduction

A study of the catalytic influence of ruthenium compounds on the decomposition of perchloric acid by hydrobromic acid recently made[1] has led to a similar investigation of the catalytic effect of osmium compounds on this reaction. This work is now under way. Since under certain conditions there is an appreciable action between the hydrobromic acid and octavalent osmium, it became necessary to study the latter effect separately.

The products of the reaction were found to be bromine (largely in the form of tribromide ion) and some form of osmium in a lower valence state. Data obtained in an examination of the reaction rate indicated that a state of equilibrium was reached. In the present paper are presented the results of a study of this equilibrium, together with possible interpretations of the results and an attempt to derive an equilibrium constant at 100°.

Apparatus and Materials

The apparatus used was that employed in the potentiometric determination of bromine, octavalent and quadrivalent osmium.[2] The materials and their preparation have been described in the articles mentioned. In the present work, however, the bromine solution was 1.00 *N* in hydrobromic acid since it was found that the stability of the solution was much greater than in one-tenth normal acid as previously used, the concentration of the bromine solution in the stronger acid remaining unchanged for a period of

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[1] Crowell, Yost and Carter, THIS JOURNAL, **51**, 786 (1929).

[2] (a) Crowell and Kirschman, *ibid.*, **51**, 175 (1929); (b) **51**, 1695 (1929); (c) Crowell, *ibid.*, **54**, 1324 (1932).

several weeks. The quadrivalent osmium solution was made 2.40 *N* in hydrobromic acid since this concentration was most convenient in the preparation of the reaction tubes.

Experimental Procedure

In obtaining the experimental data the equilibrium was approached from both directions using different concentrations of the reacting constituents. From the direct side the initial reactants were octavalent osmium and hydrobromic acid in solutions of the two alone and in solutions of the two containing initially added amounts of bromine. From the reverse side the initial reactants were quadrivalent osmium and bromine in solutions of hydrobromic acid alone and in the acid solutions containing initially added amounts of potassium bromide.

The method of filling the reaction tubes and analyzing their contents was essentially the same as that described in our previous article.[2c] The various constituents were pipetted into Pyrex test-tubes, using such volumes as to secure the desired initial concentrations and a total volume of 10.0 cc. The tubes were sealed and heated in a water-bath at 100° for three or four days. At the end of that time the tubes were chilled in an ice-bath, broken in about 200 cc. of ice water and titrated with hydrazine sulfate solution. During the process of dilution and titration, the bromine was reduced to bromide and any Os_7 or Os_6 present was reduced to Os_4. Since it was impracticable to distinguish between the bromine and the reduced osmium in the hydrazine titration, it has been termed "total bromine titration." From the initial concentrations of osmium and bromine (in the cases where initial amounts were present) and from the results of the "total bromine titration" the concentrations of Os_8 and of reduced osmium can be calculated. In order to calculate the equilibrium concentration of bromine, it is necessary to know the valence state of the reduced osmium. The method of determining this is explained in the next section.

In Table I are recorded the data on the equilibrium experiments and the results of determinations of the "total bromine" in the reaction tubes. In columns 2, 3, 4 and 5 are shown the original concentrations of acid, bromine, octavalent and quadrivalent osmium in mols per liter at 25°. In column 6 appears the concentration of "total bromine" in mols per liter at 25° as determined by potentiometric titration with hydrazine sulfate. For each run these results represent the average value obtained in the titration of three or four tubes. The data in columns 3, 4, 5 and 6 enable us to calculate the equilibrium concentrations of bromine, octavalent and reduced osmium which are shown in columns 7, 8 and 9. The method of calculating these values will be explained in the next section in connection with the presentation of the proposed reactions.

TABLE I

RESULTS OF TITRATION OF BROMINE IN THE REACTION TUBES

Run	Initial concentration m./l. at 25° HBr	Br_3^- × 10^3	Os_8 × 10^3	Os_4 × 10^3	Total Br_2[a] titration m./l. × 10^3	Equilibrium conc. m./l. × 10^3 at 25° Br_3^-	Os_8	Os_7	$\frac{Os_7 \times Br_3^{-1/3}}{Os_8} = K_I$
1	0.800	8.22	0.00	4.00	0.78	0.37	3.72	0.28	0.046
2	1.20	8.24	0.00	4.00	1.80	0.62	3.22	0.78	0.191
3	1.60	0.00	4.04	0.00	3.00	0.76	2.53	1.51	0.520
4	1.60	8.22	0.00	4.00	3.20	0.96	2.51	1.49	0.581
5	1.60	0.00	8.22	0.00	6.75	1.69	4.84	3.38	0.907
6	1.60	0.00	7.70	0.00	6.75	1.69	4.32	3.38	1.02
7	1.60	15.44	0.00	7.74	6.34	1.55	4.55	3.19	0.873
8	2.00	0.00	4.11	0.00	4.35	1.09	1.93	2.18	1.18
9	2.00	0.00	3.80	0.00	4.03	1.01	1.78	2.02	1.14
10	2.00	8.23	0.00	4.00	4.17	1.21	2.03	1.97	1.07
11	2.00	0.00	8.22	0.00	7.70	1.93	4.37	3.85	1.23
12	2.00	0.00	7.70	0.00	7.35	1.84	4.02	3.68	1.24
13	2.00	15.44	0.00	7.74	7.38	1.81	4.03	3.71	1.24
14	2.40	0.00	3.86	0.00	5.27	1.32	1.22	2.64	2.48
15	2.40	0.00	3.68	0.00	5.02	1.26	1.17	2.51	2.40
16	2.40	0.00	3.75	0.00	4.92	1.23	1.29	2.46	2.12
17	2.40	10.24	0.00	3.95	7.46	3.62	1.39	2.56	3.50
18	2.40	0.00	7.67	0.00	8.59	2.15	3.37	4.30	1.87
19	2.40	0.00	7.57	0.00	8.37	2.09	3.38	4.19	1.79
20	2.40	8.06	3.69	0.00	12.16	9.08	1.64	2.05	3.77
21	2.40	10.26	3.86	0.00	14.70	11.37	1.64	2.22	4.56
22	2.40	7.33	7.60	0.00	16.33	9.58	3.10	4.50	4.50
23	2.40	20.44	0.00	3.95	17.06	13.67	1.69	2.26	4.95
24	2.40	14.65	7.60	0.00	23.31	16.81	3.27	4.33	5.43
25	2.40	39.69	3.75	0.00	42.95	40.50	2.12	1.63	4.89
26	2.40	51.42	0.00	3.95	46.88	44.36	2.27	1.68	4.92
27	2.40	51.47	3.86	0.00	54.83	52.31	2.18	1.68	5.57
28	3.20	0.00	3.79	0.00	7.03	1.76	0.270	3.52	17.3
29	3.20	0.00	7.60	0.00	14.00	3.50	0.598	7.00	21.9
30	3.20	0.00	7.70	0.00	14.42	3.61	0.488	7.21	28.1
31	3.20	15.43	0.00	7.73	14.36	3.56	0.534	7.20	25.5
32	3.20	7.62	3.79	0.00	14.52	9.34	0.341	3.45	30.9
33	3.20	15.36	7.58	0.00	28.70	18.69	0.910	6.67	31.7
34	3.20	38.52	7.57	0.00	51.00	41.64	1.33	6.24	30.2

[a] From hydrazine sulfate titration of contents of reaction tube.

Derivation of the Equilibrium Constant

In runs 20 to 27 inclusive, in which the acid concentration was constant at 2.40 *N* and in which the total concentration of tribromide was high enough to be of the same order of magnitude as its equilibrium value, the functional relation of the tribromide concentration in the equilibrium expression was calculated on the assumption that the two forms of osmium appeared as the first power of their concentrations

$$\frac{Os_{reduced}}{Os_8} \times (Br_3^-)^m = K_I$$

The data indicated clearly that m was approximately 0.50. Similar treatment of runs 32 to 34 inclusive, in which the acid concentration was 3.20 N, gave a like value for m.

In order to determine the effect of the activity of the hydrobromic acid upon the equilibrium an attempt was made to estimate the values of the activities of the hydrobromic acid at the different concentrations used and to determine the approximate value of n in the expression

$$\frac{\mathrm{Os_{reduced}}}{\mathrm{Os_8}} \times \frac{(\mathrm{Br_3^-})^{1/2}}{(\mathrm{HBr})^n} = K$$

The values of the mean ion activity coefficients of hydrobromic acid at 25° were estimated from the data of Bates and Kirschman[3] and of Livingston.[4] There was a considerable gap between the minimum values calculated from the vapor pressure measurements of the former and those obtained from the electromotive force measurements of the latter. In order to determine the coefficients in the working range of our experiments it was necessary to plot the two sets of data and extend the curves until a single one was obtained. To convert the vapor pressure results into activity coefficients the free energy data of Lewis and Randall[5] were used. The activity coefficients at 100° (the temperature of the reaction tubes) were then calculated by the use of the heat data given in the "International Critical Tables."[6]

The solution of simultaneous equations containing different values for the activities of hydrobromic acid and different concentrations of octavalent osmium, reduced osmium and of bromine showed n, the power of the hydrobromic acid activity, to be about four.

A reaction scheme which would require a value of one-half for m and approximately four for n seemed to be one of the following.

(1) A single reaction of the type

$$\mathrm{OsO_4 + H^+ + 5/2\,Br^- = Os(OH)O_3Br^- + {}^1/_2Br_3^-}$$

(2) A pair of reactions, the first of which is very rapid, producing a complex with a coördination number of eight and the second of which is the slower and equilibrium-determining step

$$\mathrm{OsO_4 + 7HBr = Os(OH)Br_7 + 3H_2O}$$
$$\mathrm{Os(OH)Br_7 + H^+ + 5/2\,Br^- = OsBr_8^- + {}^1/_2Br_3^- + H_2O}$$

In accordance with these proposed reactions it is assumed that septivalent osmium and tribromide ion are the products of the reduction of the octavalent osmium. The presence of septivalent osmium seems to be the most reasonable assumption to make in order that the tribromide-ion concentration appear in the equilibrium expression to the one-half power.

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[3] Bates and Kirschman, THIS JOURNAL, **41**, 1991 (1919).

[4] Livingston, *ibid.*, **48**, 45 (1926).

[5] Lewis and Randall, "Thermodynamics and Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, Chapt. 36.

[6] "International Critical Tables," Vol. V, p. 177.

In preliminary calculations of equilibrium constants using different exponents for the hydrogen and bromide ion activities, the best agreement was obtained when the combined exponent was 3.5 and that of the hydrogen ion was unity. Both in the cases where it was assumed that hydrogen ion had no part in the reaction and in those in which it was assumed that it appeared as the second power, non-concordant constants were obtained. In order to satisfy these requirements the presence of $Os(OH)Br_7$ and of $OsBr_8^-$ are not necessarily the only forms that might be postulated in scheme (2). Such octavalent forms as those ranging in composition from $OsO_3(OH)Br$ to $Os(OH)Br_7$ and such septivalent forms as those ranging in composition from $OsO_3(OH)Br^-$ to $OsBr_8^-$ might also be possible.

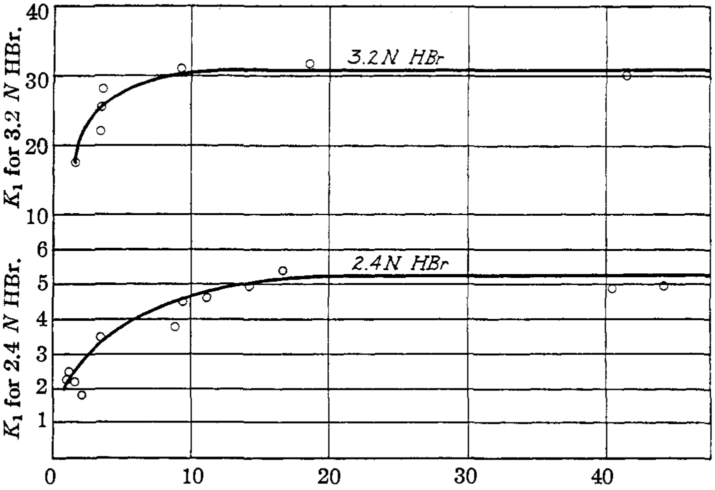

Fig. 1.

The results shown in columns 7, 8 and 9 of Table I were calculated under the assumption that the osmium in the equilibrium mixtures is reduced to a septivalent form and that during the titration with hydrazine sulfate it is further reduced to a quadrivalent form with the liberation of three equivalents of bromine per mol of osmium reduced. Consequently a correction amounting to one and one-half times the molar concentration of the reduced osmium was deducted from the titrated value of the bromine (in column 6) in order to obtain the equilibrium concentration of the tribromide ion. In column 10 are the calculated values of K_I using the equilibrium concentrations of Os_7, Os_8 and of Br_3^- expressed in millimoles per liter at 25°. It was noted that in the runs at 2.4 and 3.2 N in which the bromine and osmium concentrations were varied over a wide range, the constants seemed to depend upon the concentration of bromine present. Accordingly, the values of K_I were plotted against bromine concentrations at equilibrium and the curves shown in Fig. 1 were obtained. It will be seen that at the lower bromine concentrations the constants are also lower, but with increasing concentration of bromine they increase and reach a constant value. The values corresponding to the horizontal portion of the curves were used in the final calculation of the equilibrium constants. In the runs at other acid concentrations the average values for the constant K_I were used.

If the activity coefficient of the osmium tetroxide is assumed to be unity and that of the septivalent osmium and the tribromide ion assumed to be equal to the mean ion activity coefficient of the hydrobromic acid, we may write for the equilibrium constant in either of the above cases

$$\frac{(\mathrm{Os_7}^-)(\mathrm{Br_3}^-)^{1/2}\,\gamma_{\pm}{}^{3/2}}{(\mathrm{Os_8})(\mathrm{H}^+)(\mathrm{Br}^-)^{5/2}\,\gamma_{\pm}{}^{7/2}} = K = \frac{K_{\mathrm{I}} \times g^{-0.5}}{(\mathrm{H}^+)(\mathrm{Br}^-)^{5/2}\,\gamma_{\pm}{}^{2}}$$

where $\mathrm{Os_7}^-$, $\mathrm{Br_3}^-$, $\mathrm{Os_8}$, H^+ and Br^- represent the concentrations of these substances in mols per thousand grams of water, g the number of grams of water per liter of solution at 25°, $\gamma_{\pm}$ the mean ion activity coefficient of the hydrobromic acid at 100°, and K the equilibrium constant at 100° when the concentrations of all the constituents are expressed in mols per thousand grams of water.

In Table II are given the average values of the equilibrium constants as calculated according to the above expression. The results for experiments in which potassium bromide and hydrobromic acid were used are shown in runs 37–41, inclusive. As the literature does not contain data on the activity coefficients of hydrobromic acid in solutions of potassium bromide at the concentrations used in our work, these values at 25° were estimated by use of the results of Harned[7] on the activity coefficients of hydrochloric

TABLE II

CALCULATION OF EQUILIBRIUM CONSTANTS AT 100°

Runs	Concentration in mols per 1000 g. of water HBr	KBr	K_I	g	Log $\gamma_{\pm}^2$ at 100°	K × 10^6
1	0.825		0.0450	977	2.7390	5.2
2	1.24		0.192	967	2.8143	4.5
3– 6 incl.	1.66		0.780	958	2.9544	4.8
8–13 incl.	2.10		1.20	954	3.0443	2.6
14–27 incl.	2.55		5.30[a]	945	3.1917	4.2
28–34 incl.	3.50		31.0[a]	916	3.5343	3.7
			Average of all HBr runs except 8–13			4.5
37	1.26	0.84	0.846	952	2.7677	5.8
38	1.70	0.85	1.30	940	2.8151	3.7
39	2.14	0.86	1.87	934	2.8572	2.6
40	2.62	0.88	3.96	915	2.8471	3.1
41	1.75	1.75	5.96	915	2.9280	5.8

[a] These values were taken from the curves of Fig. 1. The remaining values are averages.

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(7) Harned, THIS JOURNAL, **48**, 329 (1926).

acid in solutions of potassium chloride. The coefficients at 100° were calculated by use of the conversion factors employed in the salt-free hydrobromic acid runs. The density-percentage composition data required to convert mols per liter into moles per 1000 g. of water were obtained from the "International Critical Tables."[8]

Since in the absence of direct data on the activity coefficients of the constituents involved it has been necessary to make certain assumptions concerning these coefficients in the calculation of the equilibrium constants; no doubt the latter will be modified to some extent when these data are obtained. The agreement of our results among themselves in most cases is surprising. In a qualitative way, at least, they indicate that at low concentrations of acid and of osmium and at high tribromide concentrations the tendency is for the osmium to be reduced to the septivalent form. At higher acidities and lower tribromide concentrations it is possible that other lower valence forms of osmium, such as sexivalent and quadrivalent compounds, are also present. Due to the instability of the osmium compounds present in the equilibrium mixture, we have not yet been able to isolate them in the original state. It might be recalled in this connection that in the potentiometric titration of octavalent osmium with titanous chloride in hydrobromic acid solutions a double inflection in the curve was obtained when the determination was made at 25° (Ref. 2a, p. 1697). This behavior was not explained at the time but it might be due to the presence of septivalent osmium whose reduction potential might be very near that of octavalent osmium but whose rate of reduction might be somewhat slower.

The color changes of the solutions do not afford much help in the interpretation of results, although at the lower acid concentrations the shade is more toward a brownish-red, while in the more concentrated acid solutions the color is a deeper red. Quadrivalent osmium formed in concentrated hydrobromic acid solutions produces crimson colored solutions and it may be that the deep red color of the equilibrium mixture at the higher acidities is due to the presence of small amounts of the quadrivalent form.

The results of the experiments in which hydrogen bromide and potassium bromide were used show clearly that the hydrogen and bromide ions each have their separate effects upon the equilibrium. Because the method of estimating the activity coefficients in these runs involved greater approximations than in the runs in which potassium bromide was absent, the individual equilibrium constants were not considered in obtaining the final average value. The agreement with the other values, however, is probably as good as could be expected.

In the experiments with 2.00 *N* hydrobromic acid the constants are much lower than in the runs at lower acidities but are of the same order of magni-

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[8] "International Critical Tables," Vol. III, pp. 55 and 87.

tude as those for 1.60, 2.40 and 3.20 *N* acid at low tribromide concentrations. This is probably due to the low concentrations of tribromide in all the runs at 2.00 *N* acid and to the tendency to form lower valence compounds of osmium at this acid concentration. For these reasons, this constant was also omitted in the calculation of an average value. Using 4.5×10^{-6} for the constant, calculations of the ratios of concentrations of octavalent to septivalent osmium in solutions 0.10 and 8.0 *N* in hydrobromic acid containing equivalent amounts of tribromide ion are in agreement with previous statements[2c] that the conversion of octavalent into reduced osmium in 8.0 normal acid is practically complete and that the reverse reaction is likewise practically complete in 0.1 normal acid.

In conclusion, we take this opportunity to thank Dr. Don M. Yost for the very many helpful suggestions made during the course of this work.

Summary

A study of the equilibrium involved when octavalent osmium reacts with hydrobromic acid in a closed tube at 100° with the formation of bromine and lower oxidation states of osmium has been made. The results indicate that at low concentrations of osmium and of acid and high bromine concentrations the osmium was reduced to the septivalent form.

The mass action expression was found to have the form

$$\frac{(\mathrm{Os}_7{}^-)(\mathrm{Br}_8{}^-)^{1/2}}{(\mathrm{Os}_8)(\mathrm{H}^+)(\mathrm{Br}^-)^{5/2}\,\gamma_\pm{}^2} = K$$

where $\gamma_\pm$ represents the mean ion activity coefficient of the hydrobromic acid; and on the basis of this expression two possible types of reactions were suggested.

The average value for the equilibrium constant K when the concentrations are expressed in moles per 1000 grams of water is 4.5×10^{-6}.

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