DEPENDENCE OF THE REDOX POTENTIAL OF BROMIDE-BROMATE MIXTURES ON THE CONCENTRATION OF HYDROCHLORIC ACID

Ts. G. Raikhinshtein

Ivanov Institute of Chemical Technology, Department of Analytical Chemistry

During titration with bromate as reducing agent we found that the oxidation-reduction potential falls [1] at the equivalent point of the reaction with increasing acid concentration. One of the possible explanations of this phenomenon is that with increasing acid concentration the oxidation of the reducing agent takes place at the expense of the bromine evolved during reaction of bromate with the bromide formed in the initial stage of the reaction.

Nevertheless, it appears desirable to undertake a study of the dependence of the oxidation-reduction potential of bromide-bromate mixtures on the concentration of hydrochloric acid, since in most cases both direct titration with bromate and oxidation with excess of bromate are carried out in a hydrochloric acid medium.

The normal oxidation-reduction potentials of the systems bromate-bromine, bromine-bromide, and bromate-bromide have been determined with great care by a number of authors [2]. These data, however, do not provide any evidence as to the possible changes in potential during change of acid concentration, particularly in presence of hydrochloric acid. Moreover, the experimental conditions of previous workers differed considerably from those applied when using bromate in volumetric analysis. Thus, for example, the normal potential of the system bromate-bromine has been determined for the equilibrium state of bromate-saturated bromine solution; that of the system bromine-bromide has been determined for the equilibria: liquid bromine-bromide, saturated bromine solution-bromide, and gaseous bromine-bromide.

During titration with bromate, bromine ions are formed at the very start of the reaction, so that the following intermediate reaction is unavoidable:

$$BrO_3^- + 5Br^- + 6H^+ \rightleftarrows 3Br_2 + 3H_2O, \qquad (I)$$

and three equilibria must therefore be considered:

$$2BrO_3^- + 10\underline{e} + 12H^+ \rightleftarrows Br_2 + 6H_2O, \qquad (A)$$

$$BrO_3^- + 6\underline{e} + 6H^+ \rightleftarrows Br^- + 3H_2O, \qquad (B)$$

$$Br_2 + 2\underline{e} \rightleftarrows 2Br^-. \qquad (C)$$

It has been shown by Sammet [2] that the oxidation-reduction potentials of the systems (A), (B), and (C), which are represented by the equations:

$$E_A = E_{oA} + \frac{RT}{10F} \ln \frac{[BrO_3^-]^2[H^+]^{12}}{[Br_2]},$$

$$E_B = E_{oB} + \frac{RT}{6F} \ln \frac{[BrO_3^-][H^+]^6}{[Br^-]},$$

$$E_C = E_{oC} + \frac{RT}{2F} \ln \frac{[Br_2]}{[Br^-]^2},$$

are correlated at the equilibrium position of all of the three components of reaction (I) by the expressions:

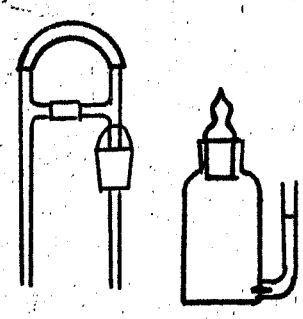
$$(1)\ E_{oB} - E_{oA} = \frac{RT}{30F} \ln K, \quad (2)\ E_{oC} - E_{oB} = \frac{RT}{6F} \ln K, \quad (3)\ E_{oC} - E_{oA} = \frac{RT}{5F} \ln K,$$

where K is the equilibrium constant of reaction (I).

Having determined E_{oC} and E_{oA}, Sammet obtained the value of $K = 0.73 = 0.73(\pm 0.21) \cdot 10^{33}$, from equation (3). This value of the constant shows that with sufficiently high acid concentration the reaction bromate – bromide proceeds to completion with substantially complete removal from the sphere of the reaction of one of the two components of the mixture.

Measurement of the Potential of Mixtures with Excess of Bromide

The measuring procedure was as follows: solutions of $KBrO_3$ of exactly 0.05 and 0.005 molar concentration were prepared, and also solutions of KBr of the same concentrations. These solutions were mixed in such proportions that after addition of hydrochloric acid two series of solutions were obtained, containing bromine and bromine ion: 1) with $[Br_2] = 0.005$ molar and with $[Br^-] = 0.01$ molar, and 2) with $[Br_2] = 0.0005$ molar and with $[Br^-] = 0.001$ molar. The reaction was carried out in the very same vessel in which the oxidation-reduction potential was subsequently measured (see drawing).



The vessel consists of a small cylindrical bottle of 38-40 ml capacity with a platinum electrode sealed into the side tube. The stopper of the bottle is of ground glass. The volume of reaction mixture was so selected that it filled the vessel almost completely, thus avoiding appreciable volatilization of bromine from the solution. The mixture was rapidly shaken and the bottle closed with the stopper. Potential measurements were performed within 24 hours after the start of the reaction between the components of the mixture; after this period, as shown in control tests, equilibrium has been established and the potential remained constant after more prolonged standing. The following chain was constituted for measuring the oxidation-reduction potential.

$$|Pt|Br_2,\ Br^-|mMHCl|HClmM|H_2|Pt|.$$

In order to prevent the development of a diffusion potential at the boundary of both half-elements, the concentration of hydrochloric acid in the vessel for measuring the redox potential and in the hydrogen electrode was identical. The electrolytic bridge and the connecting vessel were filled with acid of exactly the same molarity. We prepared the acid for the hydrogen electrode, the electrolytic bridge, and the connecting vessel in the following manner: To the same volume of acid that was introduced into the vessel with the bromate-bromide mixture was added a standard solution of potassium hydroxide in quantity equivalent to the quantity of acid consumed during the reaction of the bromate with the bromide. Thereupon the volume was made up with water to the very same volume that was occupied by the solution under investigation. A batch of this solution large enough for all of the parallel experiments was prepared and its molarity was determined by titration. In order to check whether the activity of the hydrogen ions was the same in both half-elements, the pH values of the hydrogen electrodes were measured in a series of solutions connected to a saturated calomel electrode, and other measurements were made in corresponding solutions, which had contained the system $Br_2 - 2Br^-$, with the aid of the glass electrode after the redox potential of these had been determined. Good agreement was obtained in nearly all cases. Results are given

in Table 1. In the fourth column the pH values calculated from the hydrochloric acid activity on the basis of Linhart's data [3] are shown for comparison.

All of the measurements were performed in a thermostat at 30°. Before the vessel used for measurement of the redox potential was place in the thermostat, its ground glass stopper was rapidly replaced by an electrolytic bridge, one of the limbs of which was sealed into a similar ground glass stopper.

TABLE 1

Molarity of HCl	pH		
	By hydrogen electrode	By glass electrode	Calculated from activity of HCl
0.0458	1.38	1.41	1.37
0.0803	1.11	1.08	1.17
0.1822	0.73	0.82	0.81
0.2211	0.74	0.71	0.77
0.3562	0.51	0.55	0.56
0.5082	0.29	0.44	0.40
0.6493	0.23	0.26	0.30
0.8604	0.12	0.14	0.16
1.0177	0.11	0.01	0.07
1.2300	0.00	-0.07	-0.02
1.2592	-0.07	-0.11	-0.04
1.7935	–	-0.26	-0.25
2.4735	-0.42	-0.46	-0.46
3.7496	-0.73	-0.72	-0.80

The potential of the system $Br_2 + 2\underline{e} \rightleftarrows 2Br^-$ is represented by the equation:

$$E_{Br_2/2Br^-} = E_o + 0.030 \log \frac{a_1}{a_2^2} =$$

$$= E_o + 0.030 \log \frac{\gamma_1}{\gamma_2^2} + 0.030 \log \frac{c_1}{c_2^2},$$

where a_1 is the activity, γ_1 is the activity coefficient, and c_1 is the concentration of bromine; a_2 is the activity, γ_2 is the activity coefficient, and c_2 is the concentration of bromine ion. On measuring the emf of the chain constituted according to the scheme given on p. 2024, we obtain:

$$E_{meas.} = E_{Br_2/2Br^-} - 0.060 \log a_H = E_{o\,Br_2/2Br^-} + 0.030 \log \frac{\gamma_1}{\gamma_2^2} +$$

$$+ 0.030 \log \frac{c_1}{c_2^2} + 0.060 \text{ pH}.$$

Denoting $E_o + 0.030 \log \frac{\gamma_1}{\gamma_2^2}$ by E_o' (the "apparent" normal oxidation-reduction potential) we find:

$$E'_{oBr_2/2Br^-} = E_{meas.} - 0.030 \log \frac{c_1}{c_2^2} - 0.060 \text{ pH}$$

when $C_1 = 5 \cdot 10^{-3}$ mole and $C_2 = 1 \cdot 10^{-2}$ mole, $0.030 \log \frac{c_1}{c_2^2} = 0.051$

and $E'_{oBr_2/2Br^-} = E_{meas.} - 0.051 - 0.060$ pH (4)

when $C_1 = 5 \cdot 10^{-4}$ mole and $C_2 = 1 \cdot 10^{-3}$ mole, $0.030 \log \frac{c_1}{c_2^2} = 0.081$

and $E'_{oBr_2/2Br^-} = E_{meas.} - 0.081 - 0.060$ pH. (5)

In Table 2 are given the results of measurements of the potential of the system $Br_2 + 2\underline{e} \rightleftarrows 2Br^-$, carried out in solutions with $C_1 = 5 \cdot 10^{-3}$ mole and $C_2 = 1 \cdot 10^{-2}$ mole; in the fourth column are the values of $E_{o\,Br_2/2Br^-}$ calculated from equation (4). All of the results are the mean of several values differing from each other by 2-3 mV.

In Table 3 are presented the results of measurements of the potential of the same system for $C_1 = 5 \cdot 10^{-4}$ mole and $C_2 = 1 \cdot 10^{-3}$ mole; $E_{o\,Br_2/2Br^-}$ was calculated from Equation (5).

These two tables show that the value of the "apparent" normal oxidation-reduction potential of the system $Br_2 + 2\underline{e} \rightleftarrows 2Br^-$, and consequently also the magnitude of $0.030 \log \frac{\gamma_1}{\gamma_2^2}$ at first increases with increasing concentration of hydrochloric

TABLE 2

$[Br_2] = 5 \cdot 10^{-3}$ mole. $[Br^-] = 1 \cdot 10^{-2}$ mole

Molarity of HCl	pH*	$E_{meas.}$	$E'_{oBr_2/2Br}$
0.0362	1.53	1.206	1.06_3
0.0894	1.12	1.200	1.08_2
0.1747	0.84	1.188	1.08_7
0.2211	0.77	1.191	1.09_4
0.3595	0.55	1.177	1.09_3
0.5111	0.40	1.160	1.08_5
0.6595	0.29	1.144	1.07_6
0.8604	0.16	1.135	1.07_4
1.0177	0.07	1.123	1.06_8
1.2592	-0.04	1.115	1.06_6
1.7804	-0.25	1.094	1.05_8
2.5286	-0.48	1.066	1.04_4
3.7496	-0.80	1.045	1.04_2

TABLE 3

$[Br_2] = 5 \cdot 10^{-4}$ mole. $[Br^-] = 1 \cdot 10^{-3}$ mole

Molarity of HCl	pH	$E_{meas.}$	$E'_{oBr_2/2Br}$
0.0458	1.37	1.211	1.04_8
0.0918	1.12	1.207	1.05_9
0.1713	0.85	1.201	1.06_9
0.2234	0.76	1.198	1.07_2
0.3551	0.57	1.186	1.07_1
0.5082	0.40	1.174	1.06_9
0.6493	0.30	1.165	1.06_8
0.8762	0.15	1.150	1.06_0
1.0216	0.07	1.145	1.06_0
1.2300	0.00	1.134	1.05_4
1.7613	-0.24	1.116	1.04_9
2.4735	-0.46	1.086	1.03_3
3.7630	-0.80	1.047	1.01_4

acid and then falls. A consideration of the factors capable of influencing the activity coefficients of bromine and bromine ion during increase in the concentration of hydrochloric acid suggests that the following are concerned: 1) the increase in the ionic strength of the solution; 2) the presence in the solution of the equilibrium $Br_2 + Cl^- \rightleftarrows Br_2Cl^-$; and 3) the existence of the equilibrium $Br_2 + Br^- \rightleftarrows Br_3^-$.

Influence of the Magnitude of the Ionic Strength of the Solution

There are no data in the literature about the influence of this factor upon the activity coefficient of bromine; regarding the activity coefficient of the bromine ion, this falls with increasing ionic strength of the solution, according to the data of Lewis and Randall [4], to a value of $\mu = 0.1$.

Influence of the Equilibrium $Br_2 + Cl^- \rightleftarrows Br_2Cl^-$

It is obvious that displacement of the equilibrium $Br_2 + Cl^- \rightleftarrows Br_2Cl^-$ to the right must reduce the activity coefficient of bromine. Jakowkin [5] found, $K = \frac{[Br_2][Cl^-]}{[Br_2Cl^-]}$, values in the range of 0.69-0.76. This constant, however, is equal to 0.708 according to Ray and Sarkar [6].

Influence of the Equilibrium $Br_2 + Br^- \rightleftarrows Br_3^-$

This equilibrium is bound to have an effect both upon the activity coefficient of bromine and that of bromine ion. Jakowkin [7] found that $K = \frac{[Br_2][KBr]}{[KBr_3]} = 0.063$ (0.061-0.066); similar results were obtained by Lewis and Storch [2]; Griffith, McKeown, and Winn [8] obtained approximately the same values for the equilibrium constant, and according to their data K increases with increasing ionic strength of the solution.

Nevertheless, the foregoing equilibrium can scarcely be expected to exercise a great influence upon the magnitude of $0.030 \log \gamma_1/\gamma_2^2$, since if the activity of Br_2 increased in consequence of the formation of Br_3^-, then the activity coefficient of Br^- should be correspondingly reduced. Lewis and Randall [9] consider that the activity coefficient of Br_3^- is 8% smaller than the activity coefficient of Br^-. Hence, the chief factor influencing the magnitude of the "apparent" normal oxidation-reduction potential of the system $Br_2 + 2e \rightleftarrows 2Br^-$ on increase of concentration of hydrochloric acid may be assumed to be the equilibrium $Br_2 + Cl^- \rightleftarrows Br_2Cl^-$.

*The pH values in this table and the later tables are calculated from the values of the activity of HCl.

Measurement of Redox Potential in Solutions of Mixtures with Excess of Bromate

In practice such mixtures are formed during the oxidation of reducing agents with excess of bromate. In a hydrochloric acid medium in presence of an excess of bromate the reactions:

$$BrO_3^- + 5Br^- + 6H^+ \rightleftarrows 3Br_2 + 3H_2O; \quad Br_2 + Cl^- \rightleftarrows Br_2Cl^-, \qquad (I)$$

may be accompanied by the reactions:

$$2BrO_3^- + 10Cl^- + 12H^+ \rightleftarrows Br_2 + 5Cl_2 + 6H_2O, \qquad (II)$$

$$6BrO_3^- + 5Cl^- + 6H^+ \rightleftarrows 3Br_2 + 5ClO_3^- + 3H_2O, \qquad (III)$$

$$ClO_3^- + 5Cl^- + 6H^+ \rightleftarrows 3Cl_2 + 3H_2O. \qquad (IV)$$

The hydrochloric acid concentration at which reaction (II) commences was established as approximately 0.2 molar for a BrO_3^- concentration of 0.001 molar. The following procedure was used for determination of the foregoing hydrochloric acid concentration. Into flasks with ground glass stoppers were introduced 1 ml of a 0.02 molar solution of $KBrO_3$ and 20 ml of hydrochloric acid of varying concentration; a small piece of paper moistened with indigo carmine was suspended in the flask and then the flask was tightly closed. At hydrochloric acid concentrations of 0.17 and 0.22 molar, decolorization of the edges of the paper was observed only after 24 hours; at a hydrochloric acid concentration of 0.35 molar, decolorization of the paper set in rapidly. In precisely the same manner the minimum concentration of acid required for initiation of reaction (IV) was established. After 24 hours traces of chlorine were detected at hydrochloric acid concentrations of 0.88 molar and 1.08 molar; at a HCl concentration of 1.25 molar and higher, appreciable decolorization of the indigo carmine was observed only after 24 hours.

For confirmation of formation of chlorate ion in a hydrochloric acid solution of bromate-bromide mixture on prolonged standing, we applied the method of Fichter and Tschudin [10] for quantitative determination of bromates in presence of chlorates. The basis of the method is that the reaction between bromate ions and iodine ions proceeds almost instantaneously, whereas that between chlorate ions and iodine ions proceeds extraordinarily slowly. In our case bromate ions participate in the reaction with iodine ions (if not all of the bromate has decomposed towards the end of the reaction), as well as free bromine and free chlorine; consequently the difference between the quantity of bromate taken and that found after reaction with hydrochloric acid should correspond to the amount of chlorate formed. Into a flask with a ground glass stopper were measured various amounts of bromate and hydrochloric acid; after standing for 24 hours, the sum of the bromate, bromine and chlorine was determined iodometrically. Results are shown in Table 4. In Expt. 3 the solution was diluted twice before the addition of potassium iodide; in Expt. 4 it was diluted 4 times.

TABLE 4

Expt. No.	Volume of HCl (ml)	Molarity of the $KBrO_3$	Volume of $KBrO_3$ (ml)	Amount of $KBrO_3$ taken, g	Amount of $KBrO_3$ found, g	Note
1	20	0.15	1.00	0.0027	0.0021	In the last column the amount of $KBrO_3$ comprises the sum of $KBrO_3$, Br_2 and Cl_2, computed as $KBrO_3$
2	20	0.37	1.00	0.0027	0.0018	
3	40	0.50	10.00	0.0283	0.0208	
4	40	2.50	10.00	0.0283	0.0158	

The slowness of reaction (III) is demonstrated by the fact that bromate in hydrochloric acid solutions can be quantitatively determined with great accuracy. The low speed of this reaction may be explained by the fact that there is a very slight difference between the oxidation-reduction potentials of the systems:

$$2BrO_3^- + 10\underline{e} + 12H^+ \rightleftarrows Br_2 + 6H_2O$$

and $$ClO_3^- + 6\underline{e} + 6H^+ \rightleftarrows Cl^- + 3H_2O.$$

The normal oxidation-reduction potentials are $E_{oBrO_3^-/\frac{1}{2}Br_2} = 1.50$ V and $E_{oClO_3^-/Cl^-} = 1.44$ V. The equilibrium constant of the reaction, according to these data, is 10^{30} (at 30°).

From the foregoing observations it follows that the following systems must be present in hydrochloric acid solutions of bromate-bromide mixtures with an excess of bromate: bromate–bromine, chlorine–chlorine ion, chlorate–chlorine ion, and chlorate–chlorine, their amounts depending upon the hydrochloric acid concentration.

The nature of the changes of redox potential of solutions of this type was studied by the same method as for the system $Br_2 + 2\underline{e} \rightleftarrows 2Br^-$. The initial solutions of bromate and bromide were mixed in the ratio of 7:5 and diluted fivefold with solutions of hydrochloric acid; the reaction mixture was left for 24 hours and then the oxidation-reduction potential was measured. Results for two series of solutions are presented in Tables 5 and 6.

TABLE 5

Initial conc. of $KBrO_3$ and KBr = 0.05 molar

Molarity of HCl	pH	$E_{meas.}$	Redox potential
0.0362	1.53	1.361	1.26_9
0.0894	1.12	1.381	1.31_4
0.1747	0.84	1.407	1.35_5
0.2211	0.77	1.411	1.36_5
0.3595	0.55	1.401	1.36_8
0.5111	0.40	1.386	1.36_2
0.6595	0.29	1.369	1.35_2
0.8604	0.16	1.342	1.33_2
1.0177	0.07	1.338	1.33_4
1.2592	-0.04	1.325	1.32_7
1.7804	-0.25	1.297	1.31_2
2.5286	-0.48	1.267	1.29_6
3.7496	-0.80	1.225	1.27_3

TABLE 6

Initial conc. of $KBrO_3$ and KBr = 0.005 molar

Molarity of HCl	pH	$E_{meas.}$	Redox potential
0.0458	1.37	1.352	1.27_0
0.0913	1.12	1.368	1.30_1
0.1822	0.81	1.377	1.32_8
0.2234	0.76	1.383	1.33_7
0.3551	0.57	1.400	1.36_6
0.5082	0.40	1.383	1.35_9
0.6493	0.30	1.373	1.35_5
0.8762	0.15	1.354	1.34_5
1.0216	0.07	1.322	1.31_8
1.2300	0.00	1.296	1.29_7
1.7613	-0.24	1.266	1.28_0
2.4735	-0.46	1.236	1.26_4
3.7630	-0.80	1.183	1.23_1

These tables reveal that with increasing concentration of hydrochloric acid from 0.04 to 3.75 molar, the oxidation-reduction potential of the mixture at first rises fairly rapidly up to a concentration of 0.35 mole of hydrochloric acid and thereafter falls gradually.

This influence of the hydrochloric acid concentration may be ascribed to the fact that at low concentrations of hydrochloric acid the system bromate-bromine predominates in the solution, and the potential of this system increases with increasing hydrogen ion concentration. At the same time in the solution there is formed, according to reaction (III), the system chlorate-chlorine ion, the potential of which, on the one hand, must increase with increasing hydrogen ion concentration, and, on the other hand, must fall sharply with increasing concentration of chlorine ions. Finally, at a hydrochloric acid concentration higher than 0.2 molar, the rapid reaction (II) takes place, i.e., the predomina-

ting influence upon the potential of the mixture will be exercised by the system $Cl_2 + 2\underline{e} \rightleftarrows 2Cl^-$.

SUMMARY

1. A study was made of the influence of the hydrochloric acid concentration upon the oxidation-reduction potential of the system $Br_2 + 2\underline{e} \rightleftarrows 2Br^-$ within the concentration range of 0.04-3.75 moles HCl.

2. Up to 0.22 molar concentration of HCl the potential was found to increase, and subsequently to fall.

3. The cause of the fall in the redox potential is the reaction $Br_2 + Cl^- \rightleftarrows \rightleftarrows Br_2Cl^-$.

4. The reactions taking place in hydrochloric acid solutions in bromate – bromide mixtures containing excess of bromate were investigated.

5. The oxidation-reduction potential of bromate – bromide mixtures containing excess of bromate was studied in dependence on the hydrochloric acid concentration in the range of 0.04 to 3.75 moles HCl.

6. The potential is found to increase with increase of hydrochloric acid concentration to 0.35 molar, and then falls.

7. The cause of the fall in the redox potential is the predominance in strong hydrochloric acid solutions of the system $Cl_2 + 2\underline{e} \rightleftarrows 2Cl^-$.

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