[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Standard Potential of the Bromine Electrode

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The standard potential of the bromine electrode is defined as the potential of an inert electrode immersed in an aqueous solution which is saturated with liquid bromine and contains bromide ion at unit activity, measured against a hydrogen electrode at 1 atmosphere pressure and with hydrogen ion at unit activity and with all liquid junction potentials eliminated. Since the bromine electrode forms the positive pole in this cell, according to the convention used in Lewis and Randall's "Thermodynamics" it must be given a negative sign. To avoid confusion we have marked the actual polarity of the electrodes of all cells mentioned by signs in parentheses.

The exact conditions stated in the definition are, however, not realizable experimentally and therefore the standard potential, E^0, is computed from the equation

$$E + E_j = -E^0 - \frac{RT}{F}\ln a_1 - \frac{RT}{2F}\ln\frac{a_w}{a_2}$$

where E is the measured positive potential against the hydrogen electrode; E_j is the liquid junction potential; a_1 and a_2 are the activities of the bromide ion, Br^-, and of the free bromine Br_2, respectively; a_w is the activity of the free bromine in water or in a solution of a bromide which is saturated with liquid bromine. a_w may be taken as equal to the concentration of free bromine, Br_2, in a saturated solution of bromine in pure water, since the ionic strength of such a solution is very nearly zero.

The experimental determination of this standard potential is complicated by the fact that free bromine in the presence of water or of solutions of bromides undergoes hydrolysis and forms a complex tribromide ion, Br_3^-, and probably also a pentabromide ion, Br_5^-. An experimental study of these equilibria was carried out for the purpose of obtaining the data needed to make proper allowance for these side reactions, and is described in the preceding paper.

If concordant results for the computed normal potential can be obtained in spite of wide variations in the concentration of the bromide ion and of the free bromine, it may be taken as evidence that difficulties due to the side reactions have been overcome successfully.

Many measurements of the potential of cells containing bromine electrodes have been made but in the early work the concentrations and activities were not accurately known or the reference electrodes not well defined, so that they do not permit a precise calculation of the standard potential.

The most recent and clearly the best measurements are by Lewis and Storch,[1] who measured the cells: Pt(+), KBr + Br_2 + 0.001 *M* HCl, 0.1 *N* KCl, HgCl, Hg(−); and Pt(+), HBr + Br_2, HBr, Pt(−), H_2.

The first type of cell gave less concordant and reliable results than the second type of cell, in which they used solutions of hydrobromic acid from 0.01 to 0.1 *M* with free bromine up to about 0.6% of saturation, measured directly against a hydrogen electrode in hydrobromic acid of the same concentration. The free bromine was controlled and determined by distribution with carbon tetrachloride. The allowance for tribromide was made by computation based on a value of 16.2 for the tribromide equilibrium constant taken from Jakowkin's work. No corrections for liquid junctions were applied. The values of the activity coefficients required for the calculations were determined by special measurements on the cell: Ag(+), AgBr, HBr, H_2, Pt(−). The extreme variation in the ten measurements was only 0.001 volt. The accepted average from this series is −1.0872 volts. They add a correction of +0.0211 volt, based on vapor pressure measurements to obtain −1.0661 volts as the standard potential of liquid bromine.

The value −1.0659 volts is given in the book "Thermodynamics" by Lewis and Randall based on the same data recomputed by the use of different values of the activity coefficients.

The "International Critical Tables" (Vol. VI, p. 333) gives the figure −1.0648 volts with a reference to Lewis and Randall "Thermodynamics" only.

Experimental

The Bromine Cell and the Free Energy of Formation of Silver Bromide

The cell measured was Pt-Ir(+), KBr(c) + Br_2, KBr(c), AgBr, Ag(−). Two independent bromine elec-

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[1] G. N. Lewis and H. Storch, THIS JOURNAL, **39**, 2544 (1917).

trodes and two independent silver–silver bromide electrodes were mounted in the same apparatus as shown in Fig. 1. The glass tube, a, with the well-ground but ungreased stopper, b, tightly in place was filled completely with a solution of potassium bromide and bromine of known composition. The electrode consisted of a foil (4 × 8 mm.) of platinum-iridium alloy (50% Ir), which is unattacked by bromine. The outer vessel contained two silver bromide electrodes immersed in a solution of potassium bromide of the same concentration as that in the inner vessel, a, but no free bromine. The junction between the two solutions occurred in the ground joint of the stopper, b.

The silver-silver bromide electrodes were prepared as follows. A platinum wire about 6 cm. long was fused into the ends of glass tubes and coiled into spirals. Silver was deposited on the spirals by making them cathodes in potassium silver cyanide. The anode was a silver wire and was kept in a separate vessel, connected by a glass siphon to the cathode vessel. The current employed was 1 milliamp. per electrode for one hour. The electrodes were then thoroughly rinsed and allowed to stand for at least twenty-four hours in distilled water. They were coated with a paste of silver oxide, prepared from carefully recrystallized silver nitrate and barium hydroxide, by filtering a dilute solution of the latter directly into a dilute solution of excess of silver nitrate during constant stirring. The silver oxide was washed free from barium and made into a paste with water. The coated electrode was heated to bright cherry red which coated it with "thermal silver" by the decomposition of the silver oxide. The silver electrodes prepared in this way were given an electrolytic coating of silver bromide by making them anodes in 0.1 *N* potassium bromide with a current of 0.1 to 0.12 milliamp. per electrode for four to six hours. The cathode was a platinum spiral, kept in a separate vessel. The electrodes were then kept short circuited in 0.1 *N* potassium bromide. Electrodes that agreed within a few hundredths of a millivolt were used. They could be kept in 0.1 *N* potassium bromide for a week or longer, without any measurable change in their relative potential. If they were to be used in any other concentration of potassium bromide than 0.1 *N*, they were equilibrated with the solution to be employed in the measurements by soaking overnight in the solution. The solutions of bromine and potassium bromide used in the inner tube were identical with those that were used for the equilibrium studies described in the preceding paper and were taken directly from the equilibrator and may be identified by the corresponding numbers. The activity of the free bromine and the concentration of each ion were determined by the methods described and are recorded in Table III of the preceding paper.

The cell was left in the 25.00° thermostat for one hour, for the establishment of equilibrium. The potentials were then measured on a Wolff potentiometer, used in conjunction with a ballistic galvanometer of high sensitivity and a standard Weston cell, certified by the U. S. Bureau of Standards. Since the cell was of the ground stopper type and consequently had a high internal resistance (about half a million ohms) a condenser of 44 microfarads' capacity was shunted across the contact key in the galvanometer circuit, as recommended by Jones and Kaplan[2] for cells with high internal resistance. By the aid of this device the potentiometer was sensitive to 0.00001 volt.

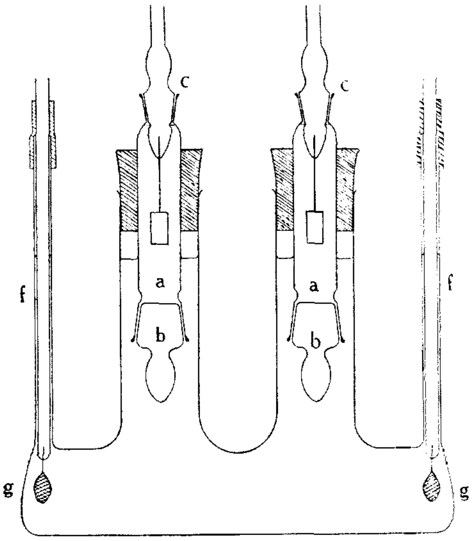

Fig. 1.

Each of the two bromine cells was measured against each of the two silver–silver bromide electrodes. The electromotive forces usually agreed to at least 0.0001 volt and the accepted value represents the average. Measurements were repeated at intervals of one hour to ensure constancy of the potentials. The cells were constant, often within a few hundredths of a millivolt if the solutions were dilute in bromine. More concentrated bromine solutions (about 17% saturated, or more) gave inconstant cells, the potentials falling with time. In this concentrated range supposedly identical cells often disagreed, sometimes as much as a millivolt. Since dilute solutions also offer theoretical advantages, due to less formation of complexes and hydrolysis, all accepted results are based on solutions not more than 10.3% saturated and usually considerably more dilute.

On long standing the potentials of the cells decreased due to diffusion of bromine to the silver electrodes. It was often possible to keep them for six or seven hours without appreciable change, however, which was more than ample time to ensure temperature adjustment and the establishment of a constant liquid junction potential in the ground stopper.

The results of the potential measurements of these cells are given in Table I.

As the first step in the calculation of the normal potential we will calculate the potential, E_s, corresponding to the reaction $Br_2(l) + 2Ag = 2AgBr$ and the free energy of this reaction. For each of our cells: Pt(+), $KBr + Br_2$, KBr, AgBr, Ag(−), three corrections must be computed and applied.

(1) There will be a potential at the liquid junction because the composition of the solution

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[2] Grinnell Jones and B. B. Kaplan, THIS JOURNAL, **50**, 1853 (1928).

TABLE I

THE STANDARD POTENTIAL (E_s) OF THE CELL REACTION $^1/_2$ $Br_2(l) + Ag(s) = AgBr(s)$ AT 25° FROM MEASUREMENT OF THE CELL (Pt(+) KBr + Br_2, KBr, AgBr, Ag(−)

No. of solution	K^+	$a_2 = [Br_2]f_2$	% satd.	$+E$	$+E_j$	$+E_2$	E_1	E_s
1	0.99961	0.007533	3.7	+0.95396	+0.00067	+0.04273	−0.00300	−0.9944
2	.99961	.006505	3.2	.95195	.00055	.04401	− .00254	− .9940
3	1.00007	.003994	3.0	.94422	.00035	.05088	− .00157	− .9939
4	1.00007	.001801	0.9	.93433	.00017	.06111	− .00074	− .9949
5	0.50026	.010355	5.1	.95851	.00084	.03864	− .00394	− .9940
6	.50480	.008219	4.0	.95461	.00069	.04161	− .00321	− .9937
7	.50477	.006538	3.2	.95185	.00057	.04455	− .00261	− .9944
8	.19825	.021325	10.3	.97015	.00169	.02936	− .00776	− .9934
9	.20193	.011823	5.8	.96083	.00100	.03693	− .00468	− .9941
10	.20193	.008764	4.3	.95601	.00077	.04078	− .00355	− .9940
11	.10096	.03642	17.5	.9801	.00238	.02248	− .01212	(− .9928)
12	.10096	.01473	7.1	.96382	.00119	.03411	− .00562	− .9935
13	.10096	.005649	2.8	.94957	.00053	.04642	− .00239	− .9941
14	.10095	.004975	2.5	.94717	.00046	.04806	− .00207	− .9936
15	.10095	.004927	2.5	.93136	.00040	.04818	+ .01406	− .9940
16	.050506	.006872	3.4	.95242	.00073	.04391	− .00323	− .9938
17	.050480	.006159	3.0	.95058	.00061	.04532	− .00261	− .9939
18	.019999	.005984	3.0	.95035	.00068	.04569	− .00252	− .9942
19	.019999	.004819	2.4	.94710	.00057	.04847	− .00210	− .9940
20	.009995	.006626	3.3	.95078	.00098	.04438	− .00282	− .9933
21	.009995	.004815	2.4	.94677	.00077	.04848	− .00212	− .9939
							Accepted average	− .9940

at the bromine electrode is changed by the addition of bromine due to hydrolysis and the formation of tribromide and pentabromide. The concentration of each ion has been determined for this purpose and is recorded in Table III of the preceding paper. The liquid junction potential, E_j, was computed by the Henderson equation using the ion mobilities given in that paper.

(2) The solutions used were all unsaturated with respect to bromine but the activity of the free bromine in each was determined by the equilibrator. Our experiments recorded in the preceding paper show that the activity of free bromine in a saturated aqueous solution is 0.2098. Therefore the correction for a solution having activity a_2 as shown in column 2 of Table I is

$$E_2 = +\frac{0.05915}{2} \log \frac{0.2098}{a_2}$$

(3) The bromide-ion concentration is not identical on both sides of the cell due to hydrolysis and complex formation. However, the ionic strength is not changed significantly by these side reactions and therefore the activity coefficients of the bromide ion may be taken as identical on the two sides and therefore the correction is $E_1 = +0.05915 \log c_1''/c_1'$, where c_1' is the concentration of the bromide ion around the silver bromide electrode and c_1'' is the concentration of the bromide ion around the bromine electrode taken from Table III of the preceding paper. However, in Experiment 15 the bromine was measured against a 0.05 *N* KBr, AgBr, Ag electrode. In this case the activity coefficients of the bromide ion around the two electrodes are different but due allowance for this difference based on Harned's measurements was made in the computation of E_1.

Adding these corrections to the measured potential, E, and changing the sign to conform to the Lewis and Randall correction, gives E_s, the potential of the cell Pt(+), $Br_2(l)$, KBr(*c*), KBr(*c*), AgBr, Ag(−), in which the electromotively effective reaction is $Br_2(l) + 2Ag(s) = 2AgBr(s)$. The results are shown in Table I. In Experiment 11 the potential readings varied with time to an abnormal extent and the computed standard potential came out abnormally low. The bromine concentration was 17.5% of saturation in this experiment, which was much higher than in any other experiment. This result was omitted in computing the average.

This corrected potential, E_s, should be independent of the concentration of the potassium bromide used. Any systematic trend with change in the concentration of the potassium bromide would indicate that some systematic error is present in the data or in the calculation of the corrections. As will be seen there is no systematic trend. The average value is −0.9940 volt. The free energy of formation of silver bromide per mole from liquid bromine and solid silver at 25° is therefore $\Delta F = -0.9940 \times 96{,}494 = -95{,}915$ joules = −22,935 calories.

To compute the potential of the bromine electrode referred to the standard hydrogen electrode as zero it is necessary to add the potential of the cell: Ag(+), AgBr, HBr, H_2, Pt(−), with HBr at unit activity.

This cell has not been measured directly with sufficient precision for this purpose but the hydrogen electrode has been compared with both the mercury–calomel electrode and with silver–silver chloride electrode with care and precision, and it therefore seemed desirable to connect our measurements on the bromine electrode to the hydrogen electrode through these well studied electrodes. We have therefore measured the cells: Ag(−), AgBr, 0.1 *N* KBr, 0.1 *N* KCl, HgCl, Hg(+); and Ag(−), AgBr, 0.1 *N* KBr, 0.1 *N* KCl, AgCl, Ag(+).

The calomel electrode was prepared from carefully purified materials in the usual manner. The silver–silver chloride electrodes were prepared in a manner entirely analogous to the silver–silver bromide electrodes described above. The maximum difference between the highest and lowest of a set of seven such electrodes was only 0.00003 volt. The cells used were of the flowing junction type. The junction was formed inside the key of a three-way glass stopcock. Two or three electrodes of each type were used in each cell, connected through a common flowing junction. The maximum difference between any pair of electrodes in the same cell when first measured was only 0.00003 volt. Constant potentials were quickly established and were not influenced by considerable variations in the rate of flow. The values given in the following tables are the averages for all the electrodes in a given cell. The silver bromide–calomel cell showed a slight tendency to decrease in voltage with time at a rate of about 0.0003 volt per hour in the worst cases although this rate of change varied erratically from cell to cell and with the age of any given cell. The initial values of freshly prepared cells were more reproducible than the values after aging and were accepted. The silver bromide–silver chloride cells on the other hand showed no variations of more than a few hundredths of a millivolt over many hours. Our experience indicates that the silver chloride electrode is more reliable and convenient as a reference electrode than the calomel electrode. The liquid junction potential between 0.1 *N* KCl and 0.1 *N* KBr may be computed by the Henderson equation to be 0.00022 volt, which must be added to the measured potentials. According to the careful measurements of Harned[3] the activity coefficient of 0.1 *M* KBr is 0.765 and of 0.1 *M* KCl, 0.764. The correction due to this slight difference is only −0.00003. It is therefore only necessary to correct our measured potentials on these cells by +0.00022 − 0.00003 = +0.0002 to obtain the voltage of our cells at unit activity.

TABLE II

ELECTROMOTIVE FORCE OF THE CELLS AT 25°

Ag (−), AgBr, 0.1 *N* KBr, 0.1 *N* KCl, HgCl, Hg (+)			Ag (−), AgBr, 0.1 *N* KBr, 0.1 *N* KCl, AgCl, Ag (+)		
E obs., volt	E_j calcd., volt	*E* corr., volt	E. m. f. obs., volt	E_j calcd., volt	E. m. f. corr., volt
0.1963	0.0002	0.1965	0.1509	0.0002	0.1511
.1964	.0002	.1966	.1509	.0002	.1511
.1964	.0002	.1966	.1508	.0002	.1510
.1964	.0002	.1966	.1509	.0002	.1511
Accepted mean *E* = 0.1966			Accepted mean *E* = 0.1511		

The difference between these values, 0.1966 − 0.1511 = +0.0455 agrees exactly with the value for the cell: Ag(−), AgCl, 0.1 *N* KCl, 0.1 *N* KCl, HgCl, Hg(+) found by Gerke[4] and confirmed by Randall and Young.[5]

Randall and Young have demonstrated that calomel electrodes containing hydrochloric acid are sensitive to oxygen and that since this fact was overlooked by earlier experimenters, the previous comparisons of the calomel electrode and hydrogen electrode are in error by more than a millivolt.

According to Randall and Young for the cell Hg(+), HgCl, $Cl^- + H^+$ ($a = 1$), H_2, Pt(−); $E^0 = -0.2676$. Our measurements give for Ag(−), AgBr, Br^- ($a = 1$), Cl^- ($a = 1$), HgCl, Hg(+): $E^0 = +0.1966$. Therefore Ag(+), AgBr, Br^- ($a = 1$), H^+ ($a = 1$), H_2, Pt(−) = −0.0710. In 1926 Güntelberg[6] discovered that the silver–silver chloride electrode in acid solution is sensitive to air so that even minute traces of dissolved oxygen increase the potential of the cell. This has been confirmed

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[3] H. S. Harned, THIS JOURNAL, **51**, 424 (1929).

[4] R. H. Gerke, *ibid.*, **44**, 1684 (1922).

[5] M. Randall and L. E. Young, *ibid.*, **50**, 992 (1928).

[6] E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

by Carmody.[7] On the other hand, the silver chloride electrode with potassium chloride as electrolyte is uninfluenced by dissolved oxygen. Randall and Young have demonstrated that the calomel electrode acts similarly. Since the determination of the value for E^0 depends on an extrapolation to infinite dilution, it is especially important to have accurate data at extreme dilutions. The work of Carmody is especially important for this purpose because he used more dilute solutions than any of the others and was the only experimenter to use quartz apparatus to avoid neutralization of the acid by attack on the glass, which may be important at extreme dilution. We shall accept Carmody's result for the cell Ag(+), AgCl, $Cl^- + H^+$ (a = 1), H_2, Pt(−); $E^0 = -0.2223$ volt. This value has been confirmed within 0.0001 volt by Scatchard,[8] by Roberts,[9] by Harned and by Ehlers.[10] Our measurements give for Ag(−), AgBr, Br^- (a = 1), Cl^- (a = 1), AgCl, Ag(+); $E^0 = +0.1511$ volt. Therefore Ag(+), AgBr, Br^- (a = 1), H^+ (a = 1), H_2, Pt(−); $E^0 = -0.0712$ volt. We believe that this value −0.0712 is more reliable than the value −0.0710 based on the calomel electrode discussed above and therefore combine it with our value for the cell Pt(+), Br_2(l), Br^- (a = 1), AgBr, Ag(−); $E^0 = -0.9940$ volt to obtain Pt(+), Br_2(l), Br^- (a = 1) || H^+ (a = 1), H_2, Pt(−); $E^0_{298} = -1.0652$ volt. Therefore the free energy of reaction

$$^1/_2H_2 \text{ (1 atm.)} + {}^1/_2Br_2\text{(l)} = H^+ + Br^- \ (a = 1)$$

is $\Delta F = -1.0652 \times 96{,}494 = -102{,}785$ joules = −24,578 calories.

If the standard bromine electrode is defined as having both bromide and free bromine present at unit activity, it is necessary to add the quantity −0.05915/2 log 0.2098 = −0.0200 volt. This gives

$$\text{Pt}(+),\ Br_2\ (a = 1)\ Br^-\ (a = 1)\ ||\ H^+\ (a = 1),\ H_2\ \text{(1 atm.) Pt}(-);\ E^0_{298} = -1.0852 \text{ volt.}$$

This figure does not depend on the experimental data for the solubility of free bromine (Br_2) in water and is therefore more reliable than the figure −1.0652 volts for the potential of liquid bromine.

Grateful acknowledgment is made for an appropriation from the Milton Fund of Harvard University for use in this investigation.

Summary

1. The electromotive force of galvanic cells of the type

$$\text{Pt}(+),\ \text{KBr}(c) + Br_2,\ \text{KBr}(c),\ \text{AgBr, Ag}(-)$$

were measured at 25°. The potassium bromide concentration varied from 0.01 to 1.0 N and the bromine concentration from 0.9 to 10.3% of saturation. E^0_{298} for this cell was found to be −0.9940 volt, which gives for the free energy of formation of silver bromide $\Delta F_{298} = -22{,}935$ cal.

2. The silver–silver bromide electrode was compared with the calomel and silver–silver chloride electrodes. The results were

$$\text{Ag}(-),\ \text{AgBr, 0.1 } N \text{ KBr}\ ||\ \text{0.1 } N \text{ KCl, HgCl Hg}(+) \quad E^0_{298} = 0.1966 \text{ volt}$$

$$\text{Ag}(-),\ \text{AgBr, 0.1 } N \text{ KBr}\ ||\ \text{0.1 } N \text{ KCl, AgCl Ag}(+) \quad E^0_{298} = 0.1511 \text{ volt}$$

3. These results were combined with recent determinations of the standard electrode potential of the silver–silver chloride electrode to give the value −1.0652 volt for the standard electrode potential of liquid bromine and the value −1.0852 volt for the standard electrode potential of bromine at unit activity.

CAMBRIDGE, MASS.

RECEIVED APRIL 21, 1934

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[7] W. R. Carmody, THIS JOURNAL, **54**, 188 (1932).

[8] G. Scatchard, *ibid.*, **47**, 641, 2098 (1925).

[9] E. J. Roberts, *ibid.*, **52**, 3877 (1930).

[10] H. S. Harned and R. W. Ehlers, *ibid.*, **54**, 1354 (1932).