Upon the assumption that at the lowest concentration (0.0034 *M*) at which the measured electromotive forces are exact the ion activity is equal to the ion concentration, a revised series of activity coefficients for hydrochloric acid from 0.0034 to 4.5 *M* was computed (see Table VIII). These again show a divergence of about 10% from the conductance ratio (Λ/Λ_0) at 0.1 *M*. They attain a minimum value at about 0.5 *M* and increase very rapidly at concentrations above 1 *M*.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE POTENTIAL OF THE BROMINE ELECTRODE; THE FREE ENERGY OF DILUTION OF HYDOGEN BROMIDE; THE DISTRIBUTION OF BROMINE BETWEEN SEVERAL PHASES.

BY GILBERT N. LEWIS AND HYMAN STORCH.

Received September 3, 1917.

The potential of the bromine electrode has been studied in much detail by Boericke,[1] but unfortunately, as in most of the earlier investigations of electromotive force, the use of concentrated solutions, the lack of information concerning the corrected degree of dissociation, and the introduction of liquid potentials of uncertain magnitude render it difficult to make accurate calculations from the measurements. Thus, Boericke, who used various concentrations of bromine in solutions of potassium bromide between molal and tenth molal, obtained values for the normal electrode potential which varied by 0.008 volt. In this paper we shall attempt to fix the value of the normal electrode potential within a few tenths of a millivolt.

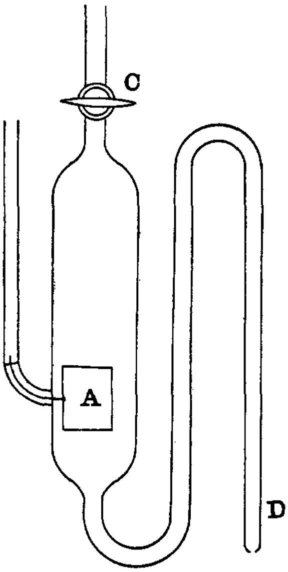

Fig. 1.

Potential Measurements in Potassium Bromide.

The first measurements were made in solutions of potassium bromide which were brought to a definite bromine content by shaking with successive portions of a known solution of bromine in carbon tetrachloride. Electrodes of platinum-iridium, faintly iridized to improve their reversibility, were contained in a vessel of about 20 cc. capacity shown in Fig. 1. In order to avoid change in concentration through evaporation, the solution of bromine in potassium bromide was introduced into the cell at D, not through suction at C, as is the common practice with

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[1] Boericke, *Z. Elecktrochem.*, 11, 57 (1905).

such cells, but by pressure applied to the vessel in which the distribution with carbon tetrachloride was obtained. The liquid was thus forced through D until the cell was completely filled. The stopcock C was well ground and left unlubricated. The connections between the cell and the distribution vessel need not be described in detail. It will suffice to point out that the liquid must not come in contact with rubber, nor with stopcock lubricant. These precautions are indispensable in the manipulation of dilute bromine solutions, if concentration changes are to be avoided.

The solution of bromine in carbon tetrachloride was kept in the vessel shown in Fig. 2. The solution was introduced at A, and covered with a layer of aqueous potassium bromide, D. It was transferred from this vessel in small portions by blowing at C, the stopcock A being so manipulated as to prevent siphoning back. The bromine itself was prepared from sodium bromide and freed from all traces of chlorine and iodine by a method analogous to that used by Baxter.[1]

The electrode cell dipped in all cases into a vessel containing potassium chloride 0.1 *M*, into which also dipped a tenth normal calomel electrode, which was repeatedly checked against a normal calomel electrode. All measurements were made at 25° in an oil thermostat.

The results of the first two series of measurements are given in Table I. The first column shows the concentration of potassium bromide. It is to be noted particularly that in addition to the potassium bromide all the solutions were made 0.001 *M* with respect to hydrochloric acid, in order to prevent the hydrolysis of the bromine.

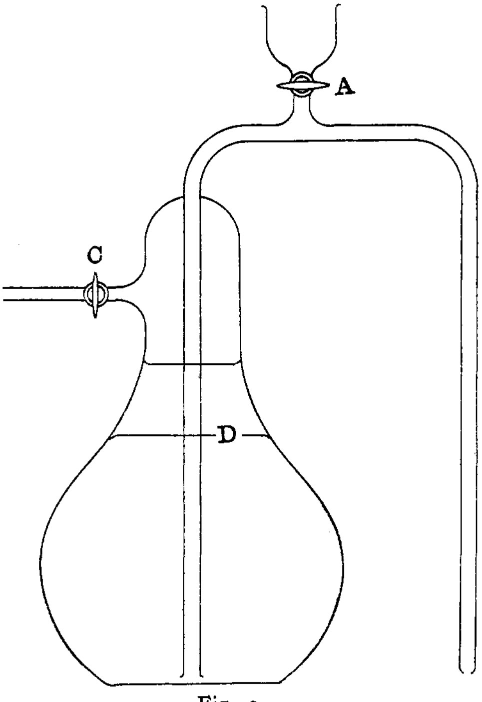

Fig. 2.

The second column shows the actual composition, as determined by analysis, of the carbon tetrachloride layer which was last shaken with the bromide solution. The composition is here expressed as mol fraction of bromine.

The third column gives the observed electromotive force against the

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[1] Baxter, This Journal, 28, 1325 (1906).

normal calomel electrode, or the sum of the potential against the tenth normal calomel electrode and the potential of the latter against the normal. Each reading is the average from four electrodes prepared with the same solution. The four rarely showed deviations as great as 0.0001 v.

Col. 4 gives the concentration of free bromine, obtained by multiplying the values of Col. 2 by 0.371 which we shall show later to be the distribution coefficient between carbon tetrachloride and water.

Of the original potassium bromide a considerable part will be in the form of potassium tribromide. Lewis and Randall,[1] in a paper on the free energy of bromine compounds, obtain, from a review of the data of Jakowkin and others, the equilibrium constant $(KBr_3)/(Br_2)(KBr) = 16.2$. The figures for potassium tribromide and potassium bromide in Cols. 5 and 6, are, therefore, obtained from those in Cols. 1 and 2 and from this constant.

TABLE I.

KBr. Original concentration.	Br_2. Mol fraction in CCl_4 layer = N.	—E. Observed. E. M. F. *vs.* N. E.	Br_2(aq.) "Free bromine."	KBr_3.	KBr.	Br^-.	—E°. Normal bromine electrode *vs.* N. E.
0.1003	0.01222	0.8008	0.00453	0.00686	0.09344	0.0729	0.8028
0.1003	0.01227	0.8009	0.00455	0.00689	0.09341	0.0729	0.8028
0.03009	0.01241	0.8276	0.00460	0.00209	0.02800	0.0242	0.8014
0.03009	0.01251	0.8276	0.00464	0.00211	0.02798	0.0242	0.8013
0.01003	0.01274	0.8519	0.00473	0.000714	0.009316	0.00866	0.7987
0.01003	0.01274	0.8519	0.00473	0.000714	0.009316	0.00866	0.7987
0.01003	0.01270	0.8520	0.00471	0.000711	0.009319	0.00867	0.7989
0.01003	0.01225	0.8519	0.00454	0.000688	0.009342	0.00869	0.7990
0.1003	0.004600	0.7885	0.00171	0.00270	0.09760	0.0761	0.8041
0.1003	0.004667	0.7887	0.00173	0.00274	0.09756	0.0761	0.8041
0.1003	0.004432	0.7885	0.00164	0.00260	0.09770	0.0762	0.8047
0.03009	0.004590	0.8163	0.00170	0.000806	0.029284	0.0253	0.8040
0.03009	0.004760	0.8163	0.00177	0.000839	0.029251	0.0253	0.8035
0.03009	0.004855	0.8163	0.00180	0.000853	0.029237	0.0253	0.8033
0.01003	0.004930	0.8421	0.00183	0.000289	0.009741	0.00906	0.8022
0.01003	0.005110	0.8426	0.00190	0.000300	0.009730	0.00905	0.8022
0.01003	0.005100	0.8423	0.00189	0.000298	0.009732	0.00905	0.8020

Having now the concentration of potassium bromide as such, and assuming that the corrected degree of dissociation α is the same at the same total salt concentration $(KBr + KBr_3)$ as in the case of potassium chloride,[2] namely, 0.780 at 0.1 *M*, 0.865 at 0.03 *M*, 0.930 at 0.01 *M*, we find the concentration of Br^- given in Col. 7.

If now there were no liquid potentials present, we could proceed at once to the calculation of the normal potential of bromine. Between potassium bromide (0.01 *M*) and potassium chloride (0.1 *M*) the liquid

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[1] THIS JOURNAL, 38, 2348 (1916).

[2] Lewis, Sebastian and Brighton, *Ibid.*, 39, 2249 (1917).

potential is less than one millivolt; but, unfortunately, as we have explained before, it was necessary to make each solution 0.001 *M* with respect to hydrochloric acid in order to prevent the hydrolysis of bromine. This probably introduces, especially in the more dilute solutions, an appreciable liquid potential, and one which cannot be readily calculated. For this reason we have been obliged to calculate the normal potential as though these liquid potentials were absent, by means of the familiar formula

$$\mathbf{E} = \mathbf{E}^\circ + 0.05915 \log \frac{(\mathrm{Br}^-)}{(\mathrm{Br}_2)^{1/2}},$$

where $\mathbf{E}^\circ$ is the e. m. f. of the cell, $\mathrm{Br_2}$ (aq., 1 *M*), Br^- (1 *M*) || N. E.

The results, which are given in the last column, show considerable variation, undoubtedly due in large measure to the liquid potentials which we have neglected, but in part also to a magnification of errors which enter into the determination of the concentration of potassium bromide. These errors should be at a minimum when the concentration of potassium bromide is large and that of bromine is small. The average value of $\mathbf{E}^\circ$, if we eliminate those at 0.01 *M* in the first set, is —0.8030. If, however, we average only the first six values of the second set, where the liquid potential is doubtless very small, and the concentration of bromine is small enough to prevent any serious error in the calculation of potassium bromide, we obtain the average —0.8039. We shall regard this, however, only as a preliminary result and proceed to the discussion of another more accurate method.

Potential Measurements in Hydrobromic Acid.

Owing to the difficulty in the preceding work of eliminating the hydrolysis of bromine, without at the same time producing liquid potentials of uncertain magnitude, we decided to undertake an entirely new series of measurements, using solutions of hydrobromic acid instead of potassium bromide, and the hydrogen electrode instead of the normal calomel electrode. Having in the meantime, through experiments which will be described in a later section, become convinced of the reliability of the dissociation constant of the tribromide used in the previous calculation and its applicability to hydrobromic acid solutions, we made in the new series of measurements no attempt to fix the bromine concentration by shaking with carbon tetrachloride solution, but instead calculated from the total bromine, as determined by iodimetric analysis, the concentration both of bromine as such and of the tribromide.

A solution of hydrobromic acid to which a certain amount of bromine had been added, was placed in a separatory funnel, well mixed, and then, transferred in such a way as to avoid loss of bromine, into four electrode vessels of the type already described, two samples being also removed for analysis.

These four bromine electrodes were connected in the oil thermostat with another electrode vessel, of the type described by Lewis, Sebastian and Brighton, containing HBr of the same concentration, and the hydrogen electrode.

The four bromine electrodes of one set usually gave identical values and never in the final series of measurements differed by more than 0.0001 volt. Only one value is, therefore, given for each concentration of hydrobromic acid and bromine in Table II, which summarizes all of the measurements.

Table II.

HBr.	Total bromine.	Free bromine.	Tribromide.	Bromide.	Bromide ion.	Barom. pressure.	Observed E. M. F.	E°.
0.10	0.03021	0.01291	0.01730	0.0827	0.0680	755.5	1.1639	1.0870
0.10	0.02332	0.00972	0.01360	0.0864	0.0710	752.3	1.1592	1.0870
0.10	0.01053	0.00419	0.00634	0.0937	0.0770	752.3	1.1465	1.0871
0.10	0.00339	0.00131	0.00208	0.0979	0.0804	758.5	1.1308	1.0872
0.03	0.00775	0.00535	0.00240	0.0276	0.0243	761.6	1.2087	1.0873
0.03	0.003463	0.002359	0.001104	0.0289	0.0255	761.6	1.1971	1.0874
0.03	0.001393	0.000942	0.000451	0.0295	0.0260	761.0	1.1848	1.0873
0.01	0.005683	0.004941	0.000742	0.00926	0.00861	760.3	1.2618	1.0880
0.01	0.002098	0.001813	0.000285	0.00972	0.00904	759.4	1.2472	1.0874
0.01	0.001573	0.001358	0.000215	0.00979	0.00910	759.4	1.2438	1.0879

The first column gives the concentration of HBr throughout the cell, and the second the total concentration of bromine, as determined by analysis.

The third, fourth and fifth columns are obtained simultaneously from the first two through the use of the constant $(HBr_3)/(HBr)(Br_2) = 16.2$, which we shall discuss in a later section.

In order to determine the corrected concentration, or the activity, of Br^- and H^+, which may be taken as equal, the corrected degree of dissociation must be known. Observations with hydrochloric acid have indicated a corrected degree of dissociation at tenth molal considerably higher than that of potassium chloride. We have, therefore, made a separate series of measurements, which will be discussed in the following section, and which shows the corrected degree of dissociation of HBr to be 0.930, 0.882 and 0.822 in 0.01 *M*, 0.03 *M* and 0.1 *M*, respectively. The figures of Col. 5 are, therefore, multiplied by these fractions to obtain Col. 6. The figures of Col. 1 multiplied by these same fractions give the corrected concentration or activity of H^+.

Col. 7 gives the barometric pressure, from which the actual pressure of the hydrogen is obtained by subtracting the vapor pressure of water at 25°, namely, 23.8 mm.

Col. 8 gives the observed e. m. f. It is to be noted that even in this type of cell there is a slight liquid potential, for on one side is pure hydrobromic acid, on the other a mixture of hydrobromic acid and hydrogen tribromide of the same total concentration. If the conductivity of Br_3^- were the same as that of Br^- there would be no liquid potential, but Bray and MacKay[1] have shown that the tri-iodide ion has only a little more than half the mobility of iodide ion. In order to make the very small correction for liquid potential we have assumed, for want of better information, that the mobility of Br_3^- is the same as that of I_3^-, and that the degree of dissociation of hydrogen tribromide is the same as that of hydrobromic aid. Applying then the formula of Lewis and Sargent[2] for liquid potentials, $\mathbf{E} = 0.05915 \log \Lambda_1/\Lambda_2$, where Λ_1 and Λ_2 are the conductances of the two solutions with a common ion, we find that in order to obtain the e. m. f. exclusive of liquid potential we must add 0.0004 v. in the first case, 0.0003 in the second, 0.0001 in the third, 0.0002 in the fifth, 0.0001 in the sixth, and 0.0001 in the eighth.

Representing the process occurring in the cell by the equation $^1/_2H_2 + {}^1/_2Br_2 = H^+ + Br^-$, $\mathbf{E} = \mathbf{E}^\circ - 0.05915 \log (H^+)(Br^-)/[H_2]^{1/2}(Br_2)^{1/2}$, where E is the observed e. m. f. corrected for liquid potential, $\mathbf{E}^\circ$ is the normal e. m. f. of the reaction, (H^+) and (Br^-) are the corrected concentrations of the ions, (Br_2) the concentration of free bromine, and $[H_2]$ the pressure of hydrogen in atmospheres.

It is evident that the values obtained in 0.01 *M* hydrobromic acid are not completely concordant and might well be repeated. It is, of course, almost invariably true that in measurements of this character it is more difficult to obtain constant and reproducible results the lower the concentration of electrolyte. With the exception of two out of the three measurements at this concentration, the values of $\mathbf{E}^\circ$ obtained with a tenfold variation in the concentration of HBr and a more than tenfold variation in the concentration of bromine show a maximum difference of only 0.0004 v.

We shall take, therefore, the mean of the first seven data as the final value of the bromine potential, with Br_2 and Br^- at (hypothetical) molal concentration, measured against the normal hydrogen electrode, $\mathbf{E}^\circ = -1.0872$ v.

According to Lewis, Sebastian and Brighton, the difference in potential between the normal hydrogen and normal calomel electrodes is 0.2828, whence the corresponding potential of bromine against the normal calomel electrode is —0.8044. This differs by only 0.0005 from the best value obtained in our preliminary measurements with potassium bromide.

The Free Energy of Dilution of Hydrobromic Acid.

In order to determine the free energy of dilution, and thence the activity of the ions and the corrected degree of dissociation at the several concentrations of HBr, measurements were made of the cell H_2, HBr,

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[1] Bray and MacKay, THIS JOURNAL, 32, 914 (1910).

[2] Lewis and Sargent, *Ibid.*, 31, 363 (1909).

AgBr, Ag with three different concentrations of HBr. The silver bromide electrodes were prepared by electroplating silver upon platinum gauze, and then covering with a slight anodic deposit of silver bromide by electrolysis in HBr. Of five electrodes so prepared, one differed from the others by several tenths of a millivolt and was discarded. The others were used throughout the whole series of measurements. They did not always give identical values, but the average deviation of the individual electrodes from the mean was less than 0.0001 v. Table III gives the results of these measurements in the order in which they were obtained. The first column gives the concentration of hydrobromic acid; the second, the observed e. m. f.; the third, the barometric pressure; the fourth, the e. m. f. calculated to one atmosphere of hydrogen; the fifth, the increase in free energy upon dilution to 0.01 *M*,[1] where $\Delta F = F'(E_1 - E_2) = 23074 (E_1 - E_2)$, E_2 being the e. m. f. in 0.01 *M* hydrobromic acid. The last column gives the corrected degree of dissociation, calculated from the equation $\Delta F = R'T \ln [(\alpha_2 c_2)^2/(\alpha_1 c_1)^2]$, where α_2, the corrected degree of dissociation in 0.01 *M* hydrobromic acid, is taken to be 0.930. It is to be noted that αc is the activity of each ion if they are both alike, otherwise it is the geometrical mean of the two activities. There is no question that they are essentially equal at 0.01 *M* and it seems probable that they are nearly so at 0.1 *M*.

TABLE III.

Conc.	E.	*p*.	E corr.	ΔF.	α.
0.10	0.2018	757.8	0.2022	—2582	0.822
0.03	0.2600	760.8	0.2604	—1239	0.882
0.01	0.3137	759.8	0.3141	......	0.930

In order to make sure that there had been no change in the silver bromide electrodes the four electrodes which had been used successively in 0.1 *M*, 0.03 *M*, and 0.01 *M* hydrobromic acid were once more measured against the hydrogen electrode in 0.1 *M* hydrobromic acid. The e. m. f. was identical with the previous value.

These values of α are extremely close to those found by Lewis, Sebastian and Brighton for HCl at the same concentrations, namely, 0.816, 0.884, 0.930 (assumed).

The Distribution of Bromine between Water and Carbon Tetrachloride, and between Aqueous Hydrogen Bromide and Carbon Tetrachloride.

The otherwise reliable measurements of Jakowkin[2] on the partition coefficient of bromine between water and carbon tetrachloride were vitiated

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[1] The reader who is not familiar with the notation and the point of view here employed is referred to the following papers: Lewis, THIS JOURNAL, 34, 1631 (1912); 35, 1 (1913); Lewis and Randall, *Ibid.*, 36, 1969 (1914).

[2] Jakowkin, *Z. physik. Chem.*, 20, 19 (1896).

in the very dilute solutions owing to the hydrolysis of the bromine in the aqueous phase. For this reason we determined the partition between carbon tetrachloride, and water which was made 0.001 *N* with respect to hydrochloric acid. This acid gives a sufficient concentration of hydrogen ion to prevent any appreciable hydrolysis of the bromine, as may be readily calculated from the work of Bray and Connolly,[1] but is presumably too dilute to affect the true solubility. The mean of two concordant experiments at 25° gave $m/\mathrm{N} = 0.3705$, where m is the number of mols of bromine to 1000 g. of water, and N is the mol fraction of the bromine in the carbon tetrachloride.

Since there seemed to be a possibility that bromine might form a complex with chloride ion, two similar determinations were made, using thousandth normal sulfuric instead of hydrochloric acid. These led to an almost identical value, namely, $m/\mathrm{N} = 0.3710$. In all of these measurements the concentration in the aqueous phase was only about 0.005 *M*. We may take, therefore, 0.371 as the partition coefficient at infinite dilution.

It seemed possible that the dissociation constant of hydrogen tribromide might for some reason be different from that of potassium tribromide. In order to test this point some partition measurements were made between carbon tetrachloride and 0.1 *M* hydrobromic acid, and the results are given in Table IV. The first column gives the total bromine in the aqueous phase determined by iodimetric analysis; the second, the mol fraction of bromine in the carbon tetrachloride, the third, the concentration of free bromine obtained by multiplying the figures of the second column by 0.371; the fourth, the concentration of tribromide obtained by subtracting the third from the first column; the fifth, the concentration of hydrobromic acid obtained by subtracting the preceding column from 0.10; the sixth, the equilibrium constant, $\mathrm{K} = (\mathrm{HBr_3})/(\mathrm{HBr})(\mathrm{Br_2})$.

TABLE IV.

Total bromine.	N.	Free bromine.	$\mathrm{HBr_3}$.	HBr.	K.
0.04348	0.0521	0.01932	0.02416	0.07584	16.47
0.04332	0.0521	0.01932	0.02400	0.07600	16.35
0.02370	0.0265	0.00984	0.01386	0.08614	16.35
0.02361	0.0267	0.00991	0.01370	0.08630	16.02
0.01624	0.0176	0.00653	0.00971	0.09029	16.45
0.01645	0.0175	0.00649	0.00996	0.09004	17.04

These measurements which were regarded as of somewhat preliminary character are evidently not of the highest accuracy, but seem to indicate that no important error can be introduced by the assumption that the equilibrium constant is the same as in the case of potassium tribromide, namely, 16.2.

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[1] Bray and Connolly, THIS JOURNAL, 33, 1485 (1911).

The Vapor Pressure of Bromine from Solutions in Carbon Tetrachloride.

In order to obtain the potential of gaseous and liquid bromine, when that of molal aqueous bromine is known, we have investigated the partial vapor pressure of bromine from solutions in carbon tetrachloride. The method adopted was a dynamical one, consisting in passing a known volume of air through the solution in a series of absorption vessels, and then determining iodimetrically the amount of bromine evaporated.

The vessels for gas absorption, specially designed for this purpose, have already been described.[1] They have the advantage of producing rapid saturation and of avoiding an excess of hydrostatic pressure. Five or six of these vessels were placed in series and sealed together hermetically. The first four were filled with the same carbon tetrachloride solution, through a side tube, by means of the apparatus which we have already shown in Fig. 2, and the side tubes were then sealed off. The last vessel was filled with a 10% aqueous solution of recrystallized potassium iodide for the absorption of the bromine. At first two such vessels were used in series, but it soon became apparent that the bromine was always completely absorbed by the first.

Through this chain dry air was bubbled at the rate of one-half to one-sixth of a liter per hour. Within these limits the results were independent of the rate. The air was driven through the apparatus from a calibrated one-liter flask by allowing concentrated sulfuric acid[2] to drop slowly into the flask until the liquid reached a definite mark. Before beginning the experiment 50 cc. of acid were allowed to stand in the flask to ensure the dryness of the air.

Between the flask and the carbon tetrachloride bulbs, and between the latter and the potassium iodide bulbs, plugs of glass wool were inserted in order to remove all spray. This was not done, however, until we had assured ourselves through a series of experiments that no appreciable amount of bromine vapor was adsorbed upon the glass wool. The whole apparatus, including the flask, was kept in a thermostat at 25°.

After the termination of the experiment, the potassium iodide bulb was cut off and its contents analyzed; the side tube of the last carbon tetrachloride bulb was cut off, a pipet with a long capillary was inserted through this tube, and into this pipet a portion of the solution was blown and then analyzed. This analysis never differed materially from that of the original solution.

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[1] Bichowsky and Storch, THIS JOURNAL, 37, 2695 (1915), Fig. 2.

[2] In the first experiments a heavy petroleum oil was used instead of the sulfuric acid, but this apparently gave off an appreciable amount of vapor, which in the presence of the bromine produced hydrobromic acid.

The total volume of gas emerging from the carbon tetrachloride cells is composed of air, carbon tetrachloride and bromine. The vapor pressure of carbon tetrachloride at 25° we have obtained as 113.9 mm. by interpolating the values given at 0°, 10°, 20° and 30° by Rex.[1] From the measured barometric pressure, the initial volume of the air, and the amount of bromine evaporated, a simple application of the gas law gives the vapor pressure of the bromine.

Our final series of measurements is summarized in Table V, in which the first row gives the mol fraction of bromine in carbon tetrachloride; the second, the vapor pressure of bromine in mm. of mercury.

TABLE V.

N.......	0.00394	0.00420	0.00599	0.0102	0.0130	0.0236	0.0238	0.0250
P.......	1.52	1.60	2.39	4.27	5.43	9.57	9.83	10.27

This table is also represented in Fig. 3 in which each vertical division is 1 mm. of pressure, and each horizontal division represents a change of 0.001 in the mol fraction. It is evident that the vapor pressure in this range is proportional to the mol fraction, although at high concentrations there must be a departure from Raoult's law, since an extrapolation of our curve to N = 1 would give for the vapor pressure of pure bromine 410 mm., whereas it is in fact only 213 mm.

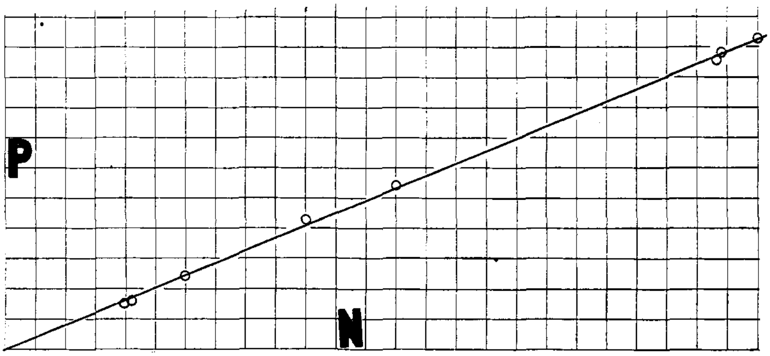

Fig. 3.

As the final result of these measurements we may take for the ratio of P in atmospheres to the mol fraction N, P/N = 0.539. We have seen that when bromine is distributed between water and carbon tetrachloride the ratio of the molal concentration in the former phase to the mol fraction in the latter phase is 0.371. From these two figures we may find the partial pressure in atmospheres of bromine over an aqueous solution in which the molal concentration is m, namely, $P/m = 1.45$.

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[1] Rex, *Z. physik. Chem.*, **55**, 363 (1906).

The Electrode Potential of Gaseous Bromine and of Liquid Bromine.

We have found that the normal electrode potential of aqueous bromine is —1.0872 v. against the normal hydrogen electrode. Now the vapor pressure of (hypothetical) molal bromine we have just seen to be 1.45 atmos. Hence, for bromine vapor at atmospheric pressure the normal potential will be numerically less by $0.05915 \times \log (1.45)^{1/2}$, and is, therefore, —1.0824 v.

The vapor pressure of liquid bromine at 25°, according to the measurements of Ramsay and Young,[1] is 213 mm. = 0.280 atmos. Therefore, the normal electrode potential of liquid bromine is $-1.0824 - 0.05915 \log (0.280)^{1/2} = -1.0661$ v.

Summary.

The potential of bromine in potassium bromide has been measured against the calomel electrode, and the potential of bromine in hydrobromic acid against the hydrogen electrode. In the latter case concordant measurements with variations in concentration of tenfold in hydrobromic acid, and of more than tenfold in bromine, fix the normal electrode potential of bromine within one- or two-tenths of a millivolt. The free energy of dilution of hydrobromic acid from 0.1 *M* and 0.03 *M* to 0.01 *M* has been measured and the corrected degrees of dissociation shown to be identical with those of hydrochloric acid. The distribution constant of bromine between carbon tetrachloride and slightly acidified water has been obtained, as well as the distribution constant between carbon tetrachloride and 0.1 *M* hydrobromic acid. The vapor pressure of bromine over solutions in carbon tetrachloride have been measured and found to be proportional to the mol fraction in the latter phase.

With the aid of these measurements we find the following normal electrode potentials against hydrogen at 25°:

$$\mathrm{Br_2\ (aq.),\ Br^-} \,\|\, \mathrm{H^+,\ H_2;\ \mathbf{E}^\circ = -1.0872}$$

$$\mathrm{Br_2\ (\mathit{l}),\ Br^-} \,\|\, \mathrm{H^+,\ H_2;\ \mathbf{E}^\circ = -1.0661}$$

$$\mathrm{Br_2\ (\mathit{g}),\ Br^-} \,\|\, \mathrm{H^+,\ H_2;\ \mathbf{E}^\circ = -1.0824}$$

BERKELEY, CALIFORNIA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE ENTROPY OF THE ELEMENTS AND THE THIRD LAW OF THERMODYNAMICS.

BY GILBERT N. LEWIS AND G. E. GIBSON.

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The concept of entropy as developed by Clausius, fundamental as it is, has always been regarded as an abstraction far less tangible than the concept of energy. The idea was rendered more concrete by Boltzmann

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[1] Ramsay and Young, *J. Chem. Soc.*, **49**, 453 (1886).