[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

On the System: Bromine–Water

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Measurements have been made of the distribution of bromine between carbon tetrachloride and water, of the vapor pressures of bromine from carbon tetrachloride solutions and the *p*H of aqueous solutions of sodium hypobromite and hypobromous acid at 15, 25, 35 and 45°. From these data the following have been calculated: (a) the activity coefficient of bromine in aqueous solutions as a function of both concentration and temperature; (b) the ionization constant of hypobromous acid as a function of the temperature; and (c) the changes in heat content, free energy and entropy for the processes for the distribution of bromine between carbon tetrachloride and water, of the evaporation of bromine from aqueous solutions and of the ionization of hypobromous acid. The equilibrium constants for these processes and the corresponding changes in heat content have been expressed as functions of the temperature.

Introduction

When bromine is added to water several reactions occur giving various equilibria. The equilibrium constants as functions of the temperature have been determined for two of these reactions, the hydrolysis of bromine[1] and the formation of the tribromide ion.[2] The constant for pentabromide ion formation at 25° has been estimated[3] to be 40.

The earlier work on the calculation of the ionization constant of hypobromous acid from kinetic measurements[4–6] gave diverse results, the value of the constant varying from 2.5×10^{-8} to 2×10^{-11}. These estimates necessarily involve the uncertainties and assumptions used with data of this type. Furthermore, the results were obtained using buffered solutions in which the ionic strength must have considerable effect.

The determination of the ionization constant by the potentiometric titration method[7–11] has given more concordant results. The findings of Shilov and of Farkas and Lewin appear to be the most accurate and give a value of K_i to be 2.1×10^{-9} at 20–22°. No systematic study of the ionization constant as a function of the temperature has been reported.

The work presented herein was completed during World War II. Publication has been delayed because additional experiments were contemplated to broaden its scope. The demands of other investigations, however, have prevented the consummation of the original plan.

An investigation has been made over a range of temperature (14.5 to 45°) of the ionization of hypobromous acid and the activity coefficient of the principal non-ionic species in the system, molecular bromine.

The determination of the ionization of hypobromous acid was by the titration method[8,10,11] using a glass electrode. For the evaluation of the activity coefficients a more involved method was employed. First the distribution ratios of molecular bromine between carbon tetrachloride and water were determined, using much the same procedure as Lewis and Storch[12] except for the introduction of hydrobromic acid in the aqueous phase to repress the hydrolysis of bromine. This was followed by the measurement of the vapor pressure of bromine from its solutions in carbon tetrachloride to determine directly the activity of bromine in this phase.

Experimental

The reagents used were of "reagent analyzed" quality. The bromine and carbon tetrachloride were found free of interfering impurities and were used without further treatment. The sodium chloride and potassium dichromate, used as primary standards, were recrystallized twice from water, dried, powdered and redried. The potassium hydrogen phthalate was recrystallized first from a dilute solution of potassium carbonate and then from distilled water before drying. All other reagents were found to be free of interfering impurities.

The distribution of bromine between carbon tetrachloride and water was carried out in glass tubes, diameter 3.8 and length 21.6 cm. Into these were introduced 50 ml. of a solution of bromine in carbon tetrachloride and 100 ml. of 0.001 *N* solution of hydrobromic acid in water. They were then sealed, set in a submerged rocker in a water thermostat and rocked at constant temperature for 1.5 to 3 days, the rocking cycle being approximately 2 seconds. Equilibria were obtained at four temperatures, 14.33, 24.94, 34.50 and 45.90°. At the higher temperatures the rocking was for the shorter time. Preliminary experiments indicated approximately the time required to reach equilibrium at each temperature and this was exceeded as little as possible while yet ensuring equilibrium for the distribution of bromine between the phases. Long continued rocking especially at the higher temperatures and concentrations involved the formation of appreciable quantities of bromate ion from hypobromite ion.

When the rocking was sufficient, the tubes were opened and samples of each phase were forced by pressure into weighing bottles containing potassium iodide solution. The immediate transformation of the bromine into bromide ion with the formation of triiodide ion minimized evaporation losses while weighing. The samples were then diluted to 100 ml. and titrated with standard sodium thiosulfate solution using starch indicator.

The vapor pressures of bromine from its solutions in carbon tetrachloride were determined using a series of four horizontal, glass, tubular saturators, diameter 4.2 cm. and length 25.4 cm., similar in operation to those proposed by Bichowsky and Storch.[13] These saturators had all-glass connections to form a single unit.

Three of the saturators contained solutions of bromine in carbon tetrachloride which had been shaken in contact with 0.001 *N* hydrobromic acid for several days in order that they correspond exactly to the solutions used in the distribution measurements. Tests showed that there was no

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(1) H. A. Liebhafsky, THIS JOURNAL, **56**, 1500 (1934).

(2) R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).

(3) G. Jones and S. Baeckstrom, THIS JOURNAL, **56**, 1517 (1934).

(4) H. A. Liebhafsky and B. Makower, *J. Phys. Chem.*, **37**, 1037 (1933).

(5) R. M. Chapin, THIS JOURNAL, **56**, 2211 (1934).

(6) A. Skrabal and R. Skrabal, *Monatsh.*, **71**, 251 (1938).

(7) M. Kiese and A. B. Hastings, THIS JOURNAL, **61**, 1291 (1939).

(8) E. A. Shilov and J. N. Gladtchikova, *ibid.*, **60**, 490 (1938).

(9) G. Sourisseau, *Compt. rend.*, **230**, 2100 (1950); *Ann. chim.* (*Paris*), **8**, 349 (1953).

(10) E. A. Shilov, *Zhur. Fiz. Khim.*, **24**, 702 (1950).

(11) L. Farkas and M. Lewin, THIS JOURNAL, **72**, 5766 (1950).

(12) G. N. Lewis and H. Storch, *ibid.*, **39**, 2544 (1917).

(13) F. R. v. Bichowsky and H. S. Storch, *ibid.*, **37**, 2695 (1915).

appreciable transfer of water to the carbon tetrachloride phase.

The fourth saturator contained a solution of potassium iodide and was used to absorb bromine vapor. Preliminary experiments revealed the concentration of potassium iodide which would remove all the bromine; this was always greatly exceeded in the solutions used. A check was made from time to time on the efflux gases; no loss of bromine was found.

Dry nitrogen from a glass container (1.5 liters) was bubbled through the train of saturators. Approximately a liter of vacuum pump oil, exactly measured, was introduced dropwise into the container to force the nitrogen through the system. Possible entrainment of small droplets in the gas stream was prevented by glass wool plugs at appropriate locations in the line.

The entire apparatus was submerged in the water thermostat, brought to temperature equilibrium and the internal pressure adjusted. The oil was then dropped at a rate that required approximately 3 hours for a run. When completed, the content of the absorber was titrated with standard sodium thiosulfate solution. Samples were taken from the final saturator and analyzed as in the distribution experiments. In the beginning, samples were taken from all three saturators and compared with the original solution. No appreciable change was found in either the second or third saturator during a run.

The ionization constant of hypobromous acid was determined by the measurement of the *p*H of various mixtures of hypobromous acid and sodium hypobromite by means of a glass electrode in the cell

$$\mathrm{Ag, AgCl, HCl}(0.1\ N)\mathrm{, glass, soln.\ X, satd.\ KCl,}\quad \mathrm{KCl}(N)\mathrm{, Hg_2Cl_2, Hg}$$

The silver–silver chloride electrodes were prepared by the second method of Harned[14] and the glass electrodes were of the type suggested by MacInnes and Dole.[15] The e.m.f. of the cell was measured with a type K potentiometer and a vacuum type amplifier similar to that used by Kiehl and Ellis[16]; the only changes made were the replacement of the 5000 ohm resistance, R_2, by a 50,000 ohm rheostat and of the 22.5 volt battery in the plate circuit of the final tube by a 45 volt battery. The two glass electrodes each contained two silver–silver chloride electrodes for check readings. The solution vessel first contained the standard buffer 0.05 *M* potassium hydrogen phthalate. After the e.m.f. of this system was determined the buffer was replaced by the hypobromite solutions for another set of readings. Finally the buffer was reintroduced and the original value checked. From the difference in the e.m.f. between the buffer and the hypobromite solution, the *p*H of the latter was computed. A series of McIlvaine's buffers was used to check the behavior of the glass electrodes over a range of *p*H.

The preparation of the hypobromite solutions was accomplished by the following procedure. A solution of bromine in carbon tetrachloride was shaken for several hours with water. The aqueous layer was separated and shaken for 15 minutes with less than an excess of silver oxide. The finely divided solid silver bromide and the remaining silver oxide were removed as completely as possible by centrifugation and decantation, yielding an aqueous solution containing hypobromous acid, molecular bromine and small amounts of bromic acid already formed. A small quantity of colloidal silver bromide remained suspended in the solution. A rapid titration with silver nitrate solution indicated approximately the amount of molecular bromine remaining in solution. Sodium hydroxide equivalent to all of the hydrobromic and bromic acids and part of the hypobromous acid was then added to give a solution containing hypobromous acid and sodium hypobromite with small amounts of the neutral salts, sodium bromide and bromate. Rapid operation was necessary to limit the formation of bromate.

The solution was analyzed for bromate, bromide and total hypobromite ions before the determination of *p*H and afterwards for bromate and hypobromite ions. This analysis was carried out essentially by the method suggested by Rupp and others.[17–19] To a 25-ml. sample of the solution was added an excess of potassium iodide, 25 ml. of water and 5 ml. of 6 *N* hydrochloric acid. The free iodine, titrated with standard thiosulfate solution, corresponded to the total content of hypobromite and bromate ions. To another 25-ml. sample was added a slight excess of 0.1 *N* sodium hydroxide solution and 5 ml. of 3% hydrogen peroxide. Shaking this mixture intermittently for 5 minutes completely destroyed the hypobromite without removing the bromate. Sufficient sodium hydroxide to give an excess of approximately 5 ml. was next added and also a small crystal of potassium iodide. The solution was then boiled for ten minutes to destroy the excess peroxide, the iodide acting as a catalyst. Finally the solution was cooled and diluted to 50 ml. Excess potassium iodide and 5 ml. of 6 *N* hydrochloric acid were added, and the liberated iodine titrated with thiosulfate; this corresponds to the bromate content of the solution.

Finally by the addition of hydrogen peroxide under acidic conditions all the bromate and hypobromite ions were changed to bromide ion. A gravimetric bromide determination was then made which included the bromine from all three sources. This also included the silver bromide left suspended in the solution. A precipitation under the same conditions as the gravimetric bromide determination, except that the addition of silver nitrate was omitted, gave the amount of suspended silver bromide. The difference between these determinations represented the summation of bromide, hypobromite and bromate in the solution. From the results of these processes, the amount of bromine in each form originally present could be calculated.

Results

To calculate the distribution ratio it was necessary to correct the titrated oxidant in the aqueous layer for the presence of hypobromous acid and tribromide ion. Jones and Baeckstrom[3] report for pentabromide formation the equilibrium constant

$$K = \frac{(\mathrm{Br_5^-})}{(\mathrm{Br^-})(\mathrm{Br_2})^2} = 40$$

computations showed that the correction for the pentabromide ion present could be disregarded. These solutions, like the hypobromite solutions prepared by Chapin,[5] contained only negligible amounts of bromous acid. The correction for the hydrolysis of bromine was based on the values of the equilibrium constant, K_2, obtained by Liebhafsky.[1] The data on the formation of the tribromide ion were taken from Griffith, McKeown and Winn.[2] From their results for the reaction: $\mathrm{Br^- + Br_2 \rightleftarrows Br_3^-}$, Liebhafsky has obtained the equation

$$\log K_1 = \frac{340}{T} + 0.0900$$

From these equations and the amount of added bromide ion (hydrobromic acid) the amounts of tribromide ion and hypobromous acid could be calculated by the following procedure.

Let n represent the concentration of hydrobromic acid, m' that of the titrated oxidant (includes $\mathrm{Br_3^-}$ and HOBr) as bromine, x the concentration of tribromide ion and $x + y$ that of the hypobromous acid. Then $x + y$ represents the extent of the hydrolysis. The concentration of the hydrogen ion will equal $n + (x + y)$, that of the bromide ion $n + y$, that of molecular bromine m

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[14] H. S. Harned, This Journal, **51**, 416 (1929).

[15] D. A. MacInnes and M. Dole, *Ind. Eng. Chem., Anal. Ed.*, **1**, 57 (1929).

[16] S. J. Kiehl and S. B. Ellis, *Rev. Sci. Inst.*, **4**, 131 (1933).

[17] E. Rupp, *Z. anal. Chem.*, **56**, 580 (1917); **57**, 16 (1918).

[18] H. Kretzschmar, *Z. Elektrochem.*, **10**, 789 (1904).

[19] F. Foerster and F. Jorre, *Z. anorg. Chem.*, **23**, 181 (1900).

$= m' - (2x + y)$. The two equilibrium constants can be expressed

$$K_1 = \frac{x\gamma_{\mathrm{Br_3^-}}}{(n + y)(m' - 2x - y)\gamma_{\mathrm{Br^-}}\gamma_{\mathrm{Br_2}}} \qquad (1)$$

$$K_2 = \frac{(n + x + y)(n + y)(x + y)\ \gamma_{\mathrm{H^+}}\gamma_{\mathrm{Br^-}}\gamma_{\mathrm{HOBr}}}{(m' - 2x - y)\gamma_{\mathrm{Br_2}}} \qquad (2)$$

The activity coefficients of the ionic species may be estimated in accordance with the Debye and Hückel formulation. The value taken for D, the dielectric constant, as a function of t (centigrade) is that given by Lange and Robinson[20] as the Drude interpolation formula.

Rearranging equations 1 and 2 we obtain the more convenient forms for use

$$x = \frac{K_1\gamma_{\mathrm{Br_2}}(n + y)(m' - y)}{1 + 2K_1\gamma_{\mathrm{Br_2}}(n + y)} \qquad (3)$$

$$y = \frac{\gamma_i^{-2}K_2\gamma_{\mathrm{Br_2}}(m' - 2x) - (n + x + y)(n + y)x}{\gamma_i^{-2}K_2\gamma_{\mathrm{Br_2}} + (n + x + y)(n + y)} \qquad (4)$$

In starting the solution of these equations for numerical values of x and y it was not possible to estimate a value for γ_{Br2}; consequently a value of unity was assumed. A method of successive approximations for x and y was followed. First, a value was assumed for y and from it a value was calculated for x. Using these two values in the right hand side of equation 4, y was recalculated. From this a better value of y could be estimated. This procedure was continued until the calculated and assumed values of y agreed.

From the data for x, y and m' the concentration of bromine in the aqueous layer was determined and then the desired distribution ratios. From these data and the vapor pressure measurements, an evaluation of $\gamma_{\mathrm{Br_2}}$ was accomplished with which a recalculation of x and y was made in cases where the error was greater than 0.05%.

The concentrations in the aqueous layer are expressed as molalities, m and those in the carbon tetrachloride as mole fraction, N_2, giving the distribution ratio $D_m = m/N_2$, as used by Lewis and Storch.[12] The data for D_m as a function of m at the four temperatures used are presented graphically in Fig. 1.[21] The data for values of m greater than 0.023 are not considered of sufficient agreement to warrant inclusion in the graph. Below this concentration the error is probably less than 0.2%. For comparison the results obtained at 25° in the early work of Jakovkin[22] (as estimated from his data by the authors) are included in the graph.

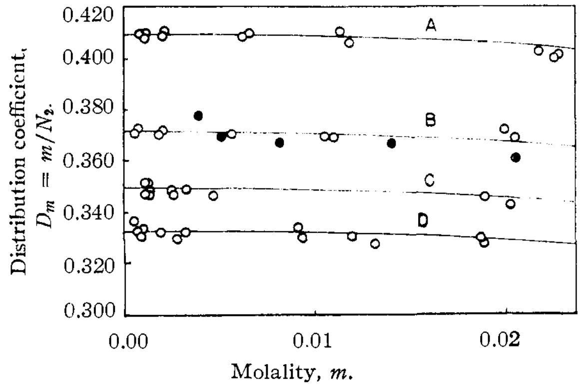

Fig. 1.—Distribution ratios: A, 14.33°; B, 24.94°; C, 34.50°; D, 45.90°; ●, Jakovkin, 25°.

It is of interest to note that the curvature shown in Fig. 1 is of the form predicted by Liebhafsky[23] for aqueous halogen solutions. Unfortunately, the data are insufficient to permit a definite correlation.

The extrapolated values of D_m to $m = 0$, designated D_0, were found to satisfy the following function of the temperature

$$\log D_0 = -55.061 + \frac{2676.6}{T} + 18.450 \log T$$

Log D_0 as a function of $1/T$ is given in Fig. 2. D_m as a function of m follows very closely the curve, $\log D_0/D_m = 16.7m^2$, at all temperatures and at molalities up to 0.023.

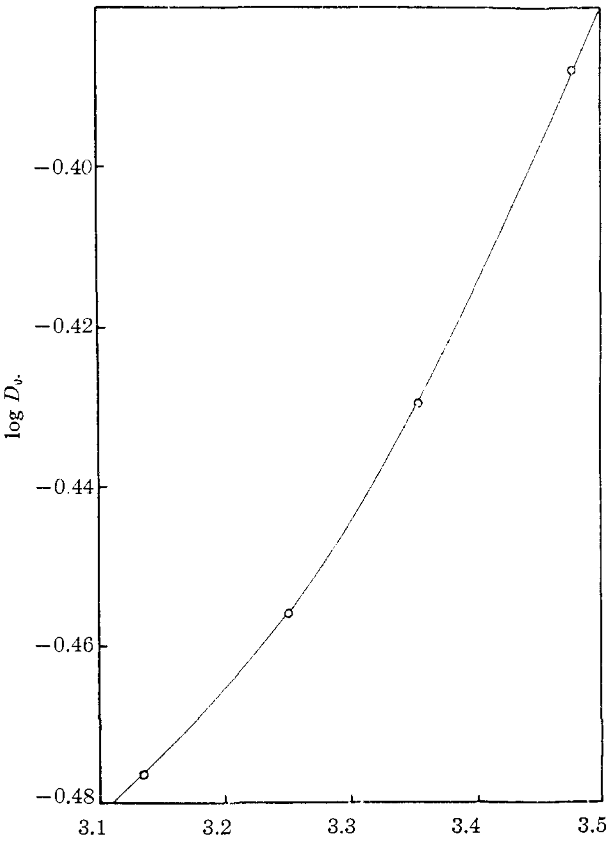

Fig. 2.—Distribution ratios as a function of the temperature.

The vapor pressures were measured at four temperatures: 14.54, 25.22, 35.32 and 44.94° and through the concentration range 0.003 to $0.130N_2$. The amount of bromine in the vapor was measured directly but the volume was calculated. The vol-

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[20] E. Lange and A. L. Robinson, THIS JOURNAL, **52**, 2811 (1930).

[21] A more detailed form of this paper (material supplementary to this article) has been deposited as Document number 4884 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

[22] A. A. Jakovkin, *Z. physik. Chem.*, **18**, 585 (1895).

[23] H. A. Liebhafsky, *Chem. Revs.*, **17**, 89 (1935).

ume of the nitrogen was known and its pressure was calculated from the barometric pressure and the hydrostatic head through the saturators. The volume was redetermined at each temperature. The liquid head was found to be 8.06 mm. The increase in volume due to the bromine vapor was calculated on the assumption that bromine at these pressures obeys the ideal gas law. The estimation of the volume added by gaseous carbon tetrachloride involved the same assumption as well as that of Raoult's law.

Other than these assumptions, the calculations were made directly from the sensitive and reproducible experimental measurements. The pressures are expressed in mm. of mercury, and the concentrations as mole fractions.[21] P is the observed vapor pressure at the mole fraction N_2 and the term $(P/N_2)_0$ is the limit of this ratio as N_2 approaches zero. The activity coefficient for bromine, γ_i, in carbon tetrachloride is the quotient $(P/N_2)/(P/N_2)_0$. The data are well represented by the equation $\log (P/N_2) = -AN_2 + \log(P/N_2)_0$ where $A = 3.253 - 0.009533T$; also $\log(P/N_2)_0 = -2.473 + 0.01701T$. The smoothed solid line for each isotherm in Fig. 3 is a plot of the equation for $\log(P/N_2)$ against $\log N_2$. The activity coefficients of bromine in carbon tetrachloride, γ_1, are given by the relation, $\log \gamma_i = -AN_2$. The activity coefficients of bromine in the aqueous phase, γ_2, can then be expressed by the equation

$$\log \gamma_2 = \log \left(\frac{D_0}{D} \gamma_1\right) = 16.7m^2 - AN_2$$

Since each of these quantities is known from previous equations as a function of the temperature within the range measured, the activities can be calculated at even molalities and temperatures.

By a combination of the equations given for $\log D_0$ and $\log(P/N_2)_0$ the variation with temperature of $\log P'$ for bromine above an aqueous solution containing bromine at unit activity is expressed by the equation

$$\log \frac{P'}{m\gamma_1} = \log \left(\frac{P}{N_2}\right)_0 \left(\frac{1}{760D_0}\right) = 49.707 + 0.01701T - 18.450 \log T - \frac{2676.6}{T}$$

with the pressure P' expressed in atmospheres.

Unfortunately, the reproducibility of the data for the ionization constant K_i of hypobromous acid did not warrant an extrapolation of the values to zero concentration of any of the molecular species present. Owing to the relatively rapid decomposition of hypobromite under the conditions of the experiment, only solutions of small concentration could be used. Extending the measurements to even lower concentrations would have greatly increased the error in the determination of the concentrations of the various molecular and ionic species which was probably the greatest source of error in the results. To obtain the hypobromite coexistent with the *p*H determination, an estimation was made from the data on the hypobromite before and after the determination and the time which elapsed. The findings showed that even at the highest temperatures the error in this calculation did not exceed 2.5% and the variation of log K_i from this uncertainty was ± 0.001 and ± 0.01 at the lowest and highest temperatures, respectively.

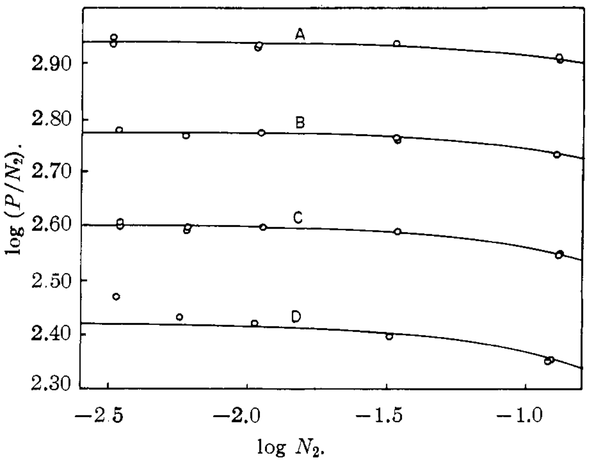

Fig. 3.—Vapor pressure relations: A, 44.94°; B, 25.32°; C, 25.22°; D, 14.54°.

The determination of bromate, of hypobromite and bromate and of hypobromite, bromate and bromide afforded the data within the errors of these determinations and the additive errors of the subtractions for the evaluation of the amount of each form of bromine-containing ionic constituent in the solutions. From the volume and molality of sodium hydroxide solution added, the concentration of sodium ion, Na^+, was computed. It was then necessary only to subtract the amount of bromate and bromide from the total sodium ion and consider the system to consist of a mixture of the remainder as sodium hydroxide and the hypobromous acid, not considering the neutral salts, sodium bromide and bromate, except insofar as they affect the activity coefficients of the ionic species.

The system can be represented by (a) $NaOH \rightarrow Na^+ + \bar{O}H$ and the equilibria (b) $HOBr \rightleftarrows H^+ + \bar{O}Br$ and (c) $H_2O \rightleftarrows H^+ + \bar{O}H$. It is easily seen that $(\bar{O}Br) = (Na^+)\text{-}(\bar{O}H) + (H^+)$. The hydrogen ion activity was measured directly by the *p*H determination; $(\bar{O}H)$ was obtained from $K_w = (H^+)(\bar{O}H)\ \gamma_{H^+}\ \gamma_{OH^-}$ and (Na^+) equivalent to $(\bar{O}H)$ and (OBr^-) computed. When $(\bar{O}Br)$ had been estimated, $(HOBr)$ was obtained by subtraction from the total hypobromite content of the solution, and the ionization constant

$$K_i = \frac{(H^+)(\bar{O}Br)\gamma_{H^+}\gamma_{OBr^-}}{(HOBr)\gamma_{HOBr}}$$

was calculated. In these calculations, the activity coefficients of the ionic species, on a molarity basis, were estimated from the Debye and Hückel equation; the activity coefficient of the hypobromous acid was assumed to be unity. The ionic strengths of the solutions are equal to the total sodium ion concentration. The experimental values obtained for the ionization constant at the various temperatures are presented in Table I.

From the behavior of the glass electrodes, it was estimated that the error in the determination of (H^+) could not be greater than 2% in any case.

However, the agreement of the results shows that in some cases the error due to the method of obtaining the ratio $(OBr^-)/(HOBr)$ was considerably greater. Any estimate of total error must be from the fluctuation in numerical results at each temperature.

TABLE I

IONIZATION CONSTANT OF HYPOBROMOUS ACID

Temp., °C.	Ionization constant, $K_i \times 10^9$
15.65	1.57 ± 0.22
25.28	2.53 ± .28
35.55	3.43 ± .18
45.55	4.33 ± .003

The ionization constant may be expressed as a function of the temperature as

$$\log K_i = 2802.49 + 0.7335T - 80670/T - 1115.1 \log T$$

From the equilibrium constants expressed as functions of the temperature the values were calculated for the thermodynamic relations; change in heat content, free energy and entropy of the three processes: distribution of bromine from carbon tetrachloride to water, evaporation of bromine from aqueous solutions and the ionization of hypobromous acid. The data are reported in Table II.

TABLE II

THERMODYNAMIC PROPERTIES OF AQUEOUS BROMINE SOLUTIONS

Temp., °C.	log K	ΔH, cal.	ΔF^0, cal.	ΔS^0, cal./°K.
Distribution from carbon tetrachloride				
15.00	−0.391	−1900	516	−8.5
25.00	− .430	−1600	587	−7.2
35.00	− .457	−1200	645	−6.0
45.00	− .474	− 850	690	−4.8
Evaporation of bromine				
15.00	−0.061	8400	80	28.8
25.00	+ .148	8500	−202	29.1
35.00	.345	8600	−487	29.5
45.00	.532	8700	−775	29.9
Ionization of hypobromous acid				
15.00	− 8.83	9300	11600	− 8.2
25.00	− 8.60	6800	11700	−16.6
35.00	− 8.47	5000	11900	−22.6
45.00	− 8.37	3800	12200	−26.2

The values for ΔH in calories per mole expressed as functions of the temperature are

$$\Delta H_d = -12250 + 35.84T$$

$$\Delta H_v = 12250 - 35.84\ T + 0.0779T^2$$

$$\Delta H_i = 3.69 \times 10^5 - 2215T + 3.355T^2$$

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Oxidation of Ferrous Sulfate by Ionizing Radiations from (n, α) Reactions of Boron and Lithium[1a]

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The high degree of reproducibility of irradiations carried out in the thermal-neutron facility of the Brookhaven reactor makes possible detailed study of chemical reactions produced by the very densely ionizing radiations from (n,α) activation of boron and lithium. The respective 100 e.v. yields for oxidation of ferrous ion by these radiations have been found to be 4.22 ± 0.08 and 5.69 ± 0.12 for 1 mM ferrous sulfate in aerated 0.8 N sulfuric acid solution and 3.77 ± 0.10 and 4.10 ± 0.10 in deaerated solution. From the above values, a yield of 6.7 in aerated solutions is estimated for the 2.7 Mev. tritium recoil produced in the neutron activation of lithium. The yields of ferric ion are increased slightly by saturating the solutions with oxygen and also by increasing the concentration of ferrous sulfate from 1 to 10 mM.

The over-all effects of radiation on aqueous systems can be described in terms of the formation of radicals H· and ·OH and molecular products H_2 and H_2O_2. It has long been evident[2] that, while for sparsely ionizing radiations such as fast electrons the predominant effect is radical production, very densely ionizing radiations tend to produce high yields of molecular products. Although cyclotron beams provide a convenient tool for quantitative studies of the effect of ionization density on the yields of radiation-chemical reactions,[3] these measurements do not give accurate yields for α particle energies less than ~10 Mev. and deuteron energies less than ~5 Mev. For the purpose of establishing limiting values, independently determined yields for particles of high ionization density are desirable. Pertinent data are provided from studies of chemical reactions induced by the recoil particles from (n,α) activation of boron and lithium salts in solution. Such measurements also eliminate difficulties inherent in particle-beam experiments due to the presence of zones of high local radiation intensity.

Absolute radiation yields[4] for the oxidation of aerated ferrous sulfate have previously been determined by McDonell and Hart[5,6] as 4.2 for the radiations from the reaction B^{10} (n,α)Li^7 and 5.2 for the

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(1) (a) Research performed under the auspices of the U. S. Atomic Energy Commission. Presented at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 20, 1956; (b) Department of Radiation Research, Mellon Institute, Pittsburgh, Pa.; (c) Department of Biophysics, Sloan-Kettering Institute, New York, N. Y.

(2) A. O. Allen, (a) *J. Phys. Colloid Chem.*, **52**, 479 (1948); (b) *Radiation Research*, **1**, 85 (1954).

(3) R. H. Schuler and A. O. Allen, THIS JOURNAL, **77**, 507 (1955).

(4) All radiation yields are expressed as molecules reacting per 100 e.v. of absorbed energy (G). The symbols G_B and G_{Li} are used to represent the yields of the chemical reactions induced by heavy particle recoils from the nuclear reactions B^{10}(n,α)Li^7 and Li^6(n,α)H^3.

(5) W. R. McDonell, A.E.C. Document ANL-4949 (1952).

(6) W. R. McDonell and E. J. Hart, THIS JOURNAL, **76**, 2121 (1954).