

CXVII.—*Bromine in Solutions of Potassium Bromide.*

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ALTHOUGH it has long been known that bromine is much more soluble in water containing potassium bromide than in pure water, practically no determinations of the extent of this increased solubility appear to have been made, and little has been done with the view of ascertaining its exact cause. Wildermann (*Zeit. physikal. Chem.*, 1893, 11, 407) describes a single experiment in which he found the solubility of bromine in a solution of potassium bromide containing one gram-molecule per litre. By considering the vapour pressure of the bromine above the solution, he was able to arrive at the concentration of the free bromine in the solution. The remainder of the dissolved bromine he considered to be combined with the potassium bromide, and in this way found that for every molecule of potassium bromide there were more than one and less than two molecules of combined bromine in solution. He assumed that KBr_3 and other more complex polybromides were formed, but without justifying this assumption or taking into account the fact that the compound formed probably exists in a partly dissociated condition.

Roloff (*Zeit. physikal. Chem.*, 1894, 13, 327) approached the question of the cause of the increased solubility from the point of view of chemical equilibrium, and examined solutions of potassium bromide containing insufficient bromine for saturation. The method employed was based on the principle, propounded by Nernst, that at a given temperature the ratio of distribution of a substance between two solvents is constant, provided that the molecular weight is the same in each. Pure water and water containing different amounts of potassium bromide were shaken up with a concentrated solution of bromine in carbon disulphide, and the concentration of the bromine in the water estimated by titration. The concentration of the free bromine in the potassium bromide solutions was taken as being the same as that in the pure water. Two series of experiments were thus performed with solutions containing 0.25, 0.125, and 0.0625 gram-molecule of potassium bromide per litre. In a third series, the concentration of the potassium bromide solution was kept at 0.125 gram-molecule per litre, whilst that of the free bromine was made to vary from 0.0475 to 0.0117 by successive additions of carbon disulphide. On applying Guldberg and Waage's equation of equilibrium, the values of the constant obtained on the assumption that KBr_3 was formed were found

to be nearly constant, varying at most from 0.048 to 0.051. This was accepted as evidence of the formation of KBr_3 . In Roloff's investigations, the number of experiments was small, and the range of concentrations of the free bromine and of the potassium bromide very limited. No account was taken of the electrolytic dissociation of the dissolved salts, nor of the fact that the value of the method would appear to be considerably impaired by the solubility of carbon disulphide in water. Roloff found no indication of the formation of higher bromides than KBr_3 .

As Wildermann's experiment seems to be the only attempt which has been made to determine the solubility of bromine in aqueous potassium bromide solutions, and as his deduction is based on such slender foundations, the solubility of bromine in solutions of potassium bromide has been determined at different temperatures over a wide range of concentrations, in the manner described in part I. In part II the constitution of potassium bromide solutions containing different amounts of bromine insufficient for saturation has been examined from the point of view of chemical equilibrium.

PART I.

The total solubility of bromine in aqueous solutions of potassium bromide of different strengths was determined by shaking up excess of bromine with these solutions contained in stoppered bottles, the halogen being enclosed in small glass bulbs. The stoppers could thus be inserted in the bottles without any air being expelled by the bromine vapour, and on breaking the bulbs the total pressure of the enclosed gases was practically the same in every case. The bottles were then shaken mechanically for five hours in a water-bath of constant temperature and left there overnight. Two series of experiments were made, the first at 26.5° and the second at 18.5° . The concentrations of the potassium bromide solutions varied from 0.01 to 0.9 gram-molecule per litre in each series. Between the concentrations 0.01 and 0.1, the strengths of the solutions were increased by 0.01 gram-molecule per litre at each step, and between the concentrations 0.1 and 0.9 by 0.1 gram-molecule. Duplicate experiments were made at each concentration.

The amount of dissolved bromine in the solution was estimated indirectly, samples being removed by means of a pipette, introduced into excess of a concentrated potassium iodide solution, and titrated with standard sodium thiosulphate. Although the rapidity with which bromine vapour was liberated from the solutions rendered this means of estimation somewhat unsatisfactory, it was

found, however, that an appreciable amount of time was required for the concentration of the potassium bromide to diminish sensibly after the bottle had been opened, and two samples were taken from each bottle immediately after removing the stoppers.

The results of the experiments are given in the following tables. Column I gives the concentrations of the potassium bromide solutions in gram-molecules per litre; columns II and III contain those of the dissolved bromine in the duplicate experiments in gram-atoms per litre; the means of the results tabulated under II and III are given in column IV. The increased concentration of the dissolved bromine, due to the presence of the potassium bromide, is given in column V, being found by deducting the concentration of bromine in pure water from the numbers in column IV. Column VI shows the ratio of these increased concentrations to those of the potassium bromide given in column I.

The results have also been shown graphically, with the concentrations of the potassium bromide solutions (column I) as ordinates, and those of the dissolved bromine (column IV) as abscissæ (Figs. 1, 2, and 3).

Series A. Temperature 26.5°.

Gram-molecules of potassium bromide per litre.	Gram-atoms of dissolved bromine per litre.			Total dissolved bromine, minus that dissolved by pure water.	The ratio V : I.
	A.	B.	Mean of A and B.		
I.	II.	III.	IV.	V.	VI.
0.00	Six experiments		0.4282	—	—
0.01	0.4485	0.4495	0.4490	0.0208	2.08
0.02	0.4672	0.4670	0.4671	0.0389	1.94
0.03	0.4948	0.4902	0.4925	0.0643	2.14
0.04	0.5085	0.5117	0.5101	0.0819	2.05
0.05	0.5307	0.5296	0.5301	0.1019	2.04
0.06	0.5513	0.5547	0.5530	0.1248	2.08
0.07	0.5636	0.5636	0.5636	0.1354	1.93
0.08	0.5920	0.5920	0.5920	0.1638	2.06
0.09	0.5930	0.6033	0.5981	0.1699	1.89
0.1	0.6496	0.6481	0.6488	0.2206	2.21
0.2	0.8580	0.8602	0.8591	0.4309	2.15
0.3	1.0769	1.0805	1.0787	0.6505	2.17
0.4	1.2710	1.2698	1.2704	0.8422	2.11
0.5	1.4841	1.4621	1.4731	1.0449	2.09
0.6	1.6979	1.6457	1.6717	1.2435	2.07
0.7	1.9216	1.9179	1.9197	1.4915	2.13
0.8	2.0885	2.1174	2.1029	1.6747	2.09
0.9	2.3240	2.3458	2.3349	1.9067	2.12

Series B. Temperature 18.5°.

Gram-molecules of potassium bromide per litre.	Gram-atoms of dissolved bromine per litre.			Total dissolved bromine, minus that dissolved by pure water.	The ratio V : I.
	A.	B.	Mean of A and B.		
I.	II.	III.	IV.	V.	VI.
0.00	Five experiments		0.4448	—	—
0.01	0.4647	0.4621	0.4634	0.0186	1.86
0.02	0.4819	0.4828	0.4823	0.0374	1.87
0.03	0.5059	0.5040	0.5049	0.0601	2.00
0.04	0.5238	0.5249	0.5243	0.0795	1.99
0.05	0.5419	0.5443	0.5431	0.0983	1.97
0.06	0.5668	0.5668	0.5668	0.1220	2.03
0.07	0.5910	0.5880	0.5895	0.1447	2.07
0.08	0.6089	0.6029	0.6059	0.1611	2.01
0.09	0.6315	0.6287	0.6301	0.1853	2.06
0.1	0.6587	0.6480	0.6533	0.2085	2.08
0.2	0.8718	0.8718	0.8718	0.4270	2.13
0.3	1.0572	1.0527	1.0549	0.6101	2.03
0.4	1.3123	1.3126	1.3124	0.8676	2.17
0.5	1.5462	1.5410	1.5436	1.0988	2.20
0.6	1.7749	1.7675	1.7712	1.3264	2.21
0.7	2.0073	1.9941	2.0006	1.5558	2.22
0.8	2.2515	2.2194	2.2354	1.7906	2.23
0.9	2.4825	2.4877	2.4851	2.0403	2.27

An examination of the tables shows that for concentrations of potassium bromide under 0.1, both at 26.5° and 18.5°, the increased solubility of bromine in the water, due to the presence of the potassium bromide, is proportional to the concentration, being equivalent to two atoms of bromine for every molecule of the dissolved salt. For concentrations above 0.1 the same relation holds fairly closely for the higher temperature, but at the lower the ratio shows a steady increase with increasing concentration of the potassium bromide solution. The curves for concentrations of potassium bromide below 0.1 gram-molecule per litre are perfectly straight, and correspond exactly to an additional absorption of two atoms of bromine for every additional molecule of potassium bromide (Fig. 1). The curves for concentrations above 0.1 deviate slightly on the side of greater solubility of bromine. The dotted lines correspond to the additional absorption of two atoms of bromine for every molecule of potassium bromide in solution. This deviation is more noticeable at the lower temperature.

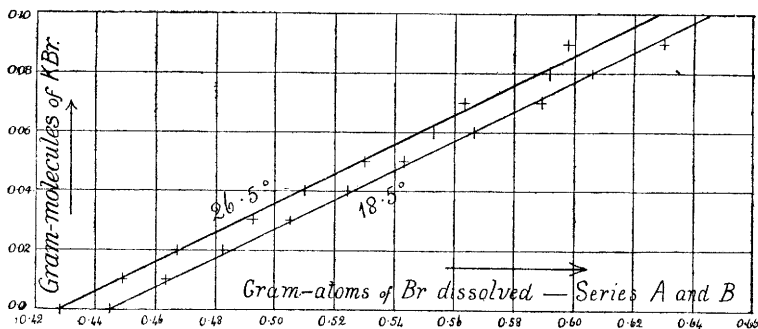


FIG. 1.

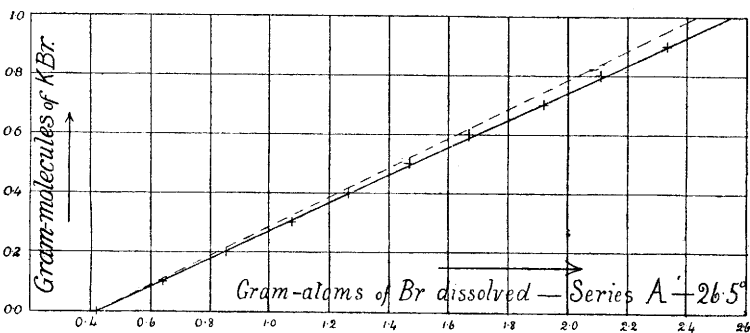


FIG 2.

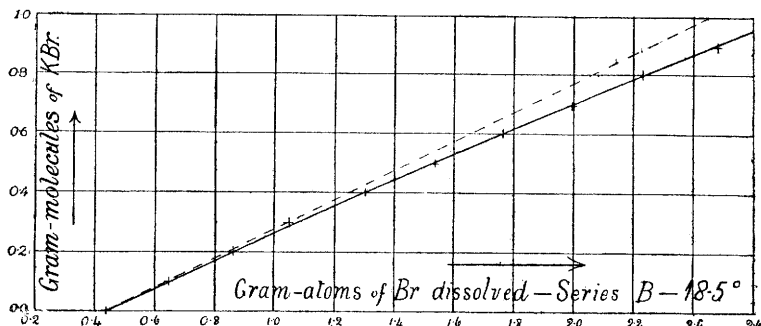


FIG 3

Investigation of the Cause of the Increased Solubility.

There appears to be little doubt, as Roloff has shown, that the increased solubility of bromine in potassium bromide solution is due to combination of part of the dissolved bromine with potassium bromide to form a polybromide. Moreover, Wildermann has shown that the density of bromine vapour over a solution of potassium

bromide saturated with bromine is the same as that over water saturated with bromine. It follows that the concentration of the free bromine in the potassium bromide solution and in the water is the same, and the remainder of the bromine in the potassium bromide solution must be combined with potassium bromide. In order, however, to account for the fact that the dissolved bromine can be entirely removed by a stream of air or by successive shakings with carbon disulphide, it must be assumed that the compound formed is unstable, and except in the presence of free bromine is dissociated into potassium bromide and bromine. If the free bromine is removed as it is formed, the dissociation will proceed until all the polybromide is decomposed. If, however, the bromine is allowed to remain in the solution, a state of equilibrium will result between the concentrations of the various substances present. Now in the presence of the great excess of free bromine in solutions saturated with bromine, the polybromide may not be dissociated to an appreciable extent. Practically the whole of the potassium bromide in the solution may have combined with bromine to form a polybromide. This would be quite in accordance with the observed fact that the increased solubility of the bromine is exactly proportional to the amount of potassium bromide in solution, if we consider for the present only dilute solutions of potassium bromide. If now the polybromide were dissociated to an appreciable extent, we should expect the degree of dissociation to be greater the higher the temperature. In other words, for any particular concentration of potassium bromide, a smaller proportion of potassium bromide will be in combination with dissolved bromine at the higher of two temperatures. Two similar samples of water, A and B, are each saturated with bromine at the temperatures t_0 and t_1 respectively, t_0 being the lower. The concentration of the bromine in A will be greater by a certain amount, say x , than that in B. If equal amounts of potassium bromide are added successively to each, the solutions being always kept saturated with bromine, then, if a polybromide exists in the solution in a partly dissociated state, one should expect the degree of dissociation to be greater at the temperature t_1 than at t_0 . Thus, for every concentration of potassium bromide there will be a greater proportion of polybromide in A than in B. Now the concentration of the free bromine in each does not alter, as was shown above, and the difference is always x . Consequently, the difference between the total amounts of bromine dissolved in A and B becomes greater as the concentration of the potassium bromide increases. If the solubilities of bromine in A and B are plotted side by side, the solubility curves will thus diverge with increasing concentration of

potassium bromide. Now it is found that the lines representing the solubilities at 18.5° and 26.5° respectively are perfectly parallel for dilute solutions of potassium bromide of varying concentrations, the difference in solubility at any concentration being the same as the difference of solubility in pure water at those two temperatures. It follows that either the degree of dissociation is not altered by a considerable change of temperature, or that one is dealing with a substance which is not appreciably dissociated at the temperatures considered. The latter alternative seems to be by far the more likely explanation.

On the assumption that the polybromide is not dissociated to an appreciable extent, the amount of bromine dissolved corresponds exactly with the amount required to convert all the potassium bromide into KBr_3 in dilute solutions. The assumption that the compound was dissociated would necessitate the formation of a more complex compound than KBr_3 , with a very high degree of dissociation. In the case of KBr_5 , the degree of dissociation would be fifty per cent., and in this case we should expect a considerable alteration in the degree of dissociation with a change of temperature.

The deviation of the curves for concentrations of potassium bromide above 0.1 gram-molecule per litre on the side of greater solubility of bromine seems to indicate a tendency to the formation of a more complex compound than KBr_3 at high concentrations of potassium bromide. This explanation is rendered more probable by the fact that the deviation is greater at the lower temperature.

It appears probable, then, that in very dilute solutions of potassium bromide saturated with bromine, practically all the potassium bromide has united with bromine to form KBr_3 , and that in more concentrated solutions small quantities of a more complex compound are also formed. Although the foregoing experiments have in no way led to a proof of this, yet it has been shown that this explanation of the cause of the increased solubility of bromine in the solutions considered is quite in accordance with all the experimental results. Moreover, other explanations do not account for all the facts.

PART II.

It would seem that definite knowledge of the constitution of solutions of potassium bromide containing dissolved bromine might be obtained by applying the principle of mass action. We have seen that it is highly probable that such solutions contain some compound of potassium bromide and bromine in a partly dis-

sociated condition, and if, by assuming some definite formula for this compound, we can show that the relative amounts of the various substances present are always in accordance with the principle of mass action, very strong evidence in favour of the actual existence of the assumed compound will have been obtained, provided, of course, that no other assumption leads to a similar result. The equation of equilibrium between a polybromide, $\text{KBr}, n\text{Br}_2$, and its decomposition products, $\text{KBr} + n\text{Br}_2$, is

$$k(\text{KBr}, n\text{Br}_2) = (\text{KBr}) \times (\text{Br}_2)^n,$$

where k is a constant and the remaining symbols represent the concentrations of the respective substances.

Unfortunately, however, the application of the principle of mass action to the foregoing experiments leads to no knowledge of the composition of the compound formed. In this case the concentration of the free bromine is constant, and the equation consequently becomes

$$k(\text{KBr}, n\text{Br}_2) = (\text{KBr}).$$

That is to say, the concentration of the polybromide is simply proportional to that of the potassium bromide left uncombined. It readily follows that it must also be proportional to the original concentration of the potassium bromide. Now the experimental results show that for dilute solutions the concentration of the bromine combined with potassium bromide is proportional to that of the dissolved salt. As the concentration of the polybromide formed is necessarily proportional to that of this combined bromine, it must also be proportional to that of the potassium bromide, no matter how many molecules of bromine are combined with one of potassium bromide. The values of k in the above equation will thus remain equally constant whatever value we give to n .

This difficulty, however, will not occur in the case of solutions of potassium bromide unsaturated with bromine, where the concentration of the bromine is made to vary. The difficulty in this case will be to determine how much of the bromine is free and how much is combined with the potassium bromide. All chemical methods of estimating free bromine are based on its removal as such from the solution. The removal of free bromine from a system containing bromine, potassium bromide, and polybromide in equilibrium results in a further decomposition of the polybromide. Consequently, any chemical method for estimating dissolved bromine indicates only the total amount dissolved. In the experiments to be described, the difficulty was overcome in the following simple manner. Two solutions of bromine, one in pure water and the other in a solution of potassium bromide of known concentration,

were simultaneously shaken up, without being allowed to mix, in an apparatus providing a common vapour space for the two solutions. When the system had attained equilibrium, the concentrations of the bromine in the two solutions were estimated by titration. Now Nernst has shown (*Zeit. physikal. Chem.*, 1891, **8**, 110) that "at a given temperature for every molecular species there exists a constant ratio of distribution of a dissolved substance between a solvent and its vapour space," and that "this is independent of the presence of other molecular species, it being a matter of indifference whether the particular molecular species is reactive with the other or not." It follows that the ratio of the concentrations of bromine in the water and in the vapour space is the same as that of the free bromine in the potassium bromide solution and

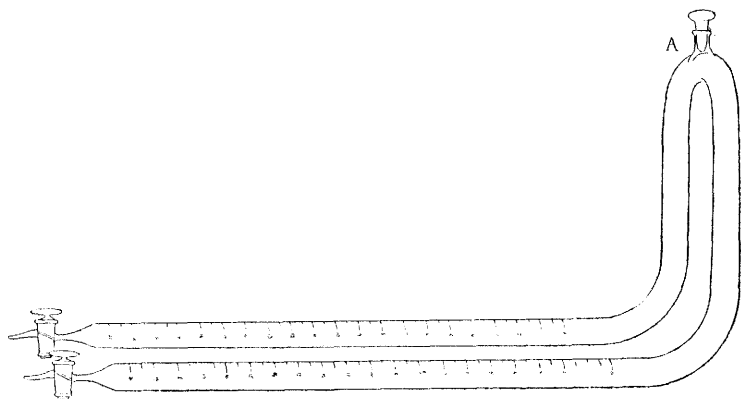


FIG 4

in the vapour space, and that consequently the concentration of the bromine in the water is the same as that of the free bromine in the potassium bromide solution. The difference between the concentrations of the total dissolved bromine in the solution and that which is free gives the concentration of the combined bromine. It is thus possible to obtain in this way the data necessary to calculate the active masses of all the substances in solution.

The apparatus employed is shown in Fig. 4. It is in the form of a long U-tube bent at right angles at about a third of the distance from the doubled end. The two straight limbs are graduated in centimetres and half-centimetres, and to their ends are attached burette taps; a short neck of thinner tubing containing a stopper was affixed at A. With this apparatus it is possible to determine by the foregoing method, without the presence of any foreign

substance such as carbon disulphide, the concentrations of both the free and the combined bromine in a solution of potassium bromide containing bromine. Water can be drawn up into one limb and potassium bromide solution containing bromine into the other, and the whole apparatus immersed in a water-bath of the required temperature and kept in motion until equilibrium has been attained between the two solutions. The apparatus has also the great advantage of rendering unnecessary the use of pipettes for measuring the quantity of solution taken for titration. This quantity is measured directly by the graduations on the limbs of the tube as the solution is drawn off.

Preliminary experiments had first to be made in order to determine the interval of time required for equilibrium to be attained. For this purpose pure water was drawn up into one limb and water containing bromine into the other, and the apparatus kept in motion in a water-bath of constant temperature. It was observed that the concentration of the bromine was not the same in both limbs until after forty-eight hours. It was found, however, that by partially exhausting the air space between the two limbs the time required could be reduced to considerably under twenty-four hours.

While in the bath the apparatus was fastened to a horizontal frame, one end of which was fixed to a rod fitting into loose sockets at the ends, while the other could be alternately raised and lowered by a string attached to a water engine. In this way the liquid could be made to flow from end to end of each limb without any passing from one to the other. The two positions of the tube are shown in Fig. 5.

Detailed Description of Experiments.

An aqueous solution of bromine was drawn up into one limb. The stopper was then inserted and the apparatus exhausted by attaching the tap of the other limb to a pump. Potassium bromide solution of the required concentration, and containing bromine, was then drawn up into this limb by gently turning the tap, while the end was immersed beneath the surface of the solution. The amount of bromine in each limb was so regulated, by means of the colour of the solutions, that the system might attain equilibrium with as little change as possible. The concentration of the potassium bromide was the same throughout one series of experiments. The concentration of the dissolved bromine in each limb was varied by admitting, in varying proportions, water or potassium bromide solution, as the case may be, partly without bromine

and partly saturated with the halogen. The apparatus was then kept in motion for twenty hours in the water-bath; air was then admitted by removing the stopper for a moment, and the motion in the bath continued for another three hours.

For removing samples for titration, the apparatus was placed in a vertical position and the stopper taken out. After neglecting the first portions, a definite volume from each limb, measured by the graduations, was introduced into a concentrated solution of potassium iodide, the liberated iodine being then titrated with standard sodium thiosulphate. In order to prevent loss of bromine through contact of the solution with the air, the potassium iodide solution was contained in a funnel, into which a long stopper had been ground, standing over a flask (Fig. 6). In this way the end

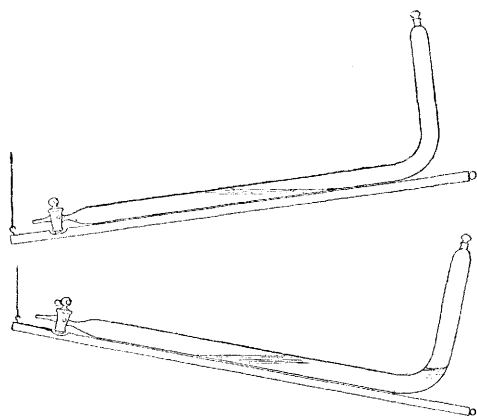


FIG. 5.

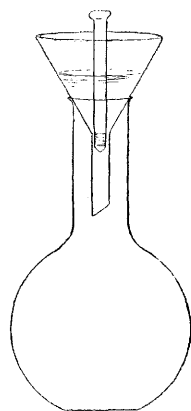


FIG. 6.

of the tap could be kept beneath the surface of the potassium iodide solution while samples were being added.

The first two series were conducted at 26.5° with potassium bromide solution containing 0.5 and 0.1 gram-molecule per litre respectively. In order to obtain results comparable with those of Roloff, a third series was conducted at 32.6° , with potassium bromide solution having a concentration 0.125.

Experimental Results, and the Application of the Principle of Mass Action.

If A, B, and C represent the concentrations in gram-molecules per litre of the potassium bromide solution, the dissolved bromine in the limb containing the potassium bromide solution, and that in

the limb containing water respectively, then, as was previously shown, the concentration of the bromine in combination with potassium bromide is represented by $B-C$. Also, if n molecules of bromine combine with one of potassium bromide, the number of gram-molecules of the compound formed will be $\frac{B-C}{n}$, and of the free potassium bromide remaining $A - \frac{B-C}{n}$.

On substituting these symbols in the equation of equilibrium,

$$k(\text{KBr}, n\text{Br}_2) = (\text{KBr}) \times (\text{Br}_2)^n,$$

one obtains for the value of the constant—

$$k = \left(A - \frac{B-C}{n} \right) C^n \div \frac{B-C}{n} = \frac{(nA - B - C)C^n}{B - C}$$

The results are tabulated in the following tables, which give the concentrations in gram-molecules per litre of the total dissolved bromine B , of the free bromine C , and of the combined bromine $B-C$. k_1 and k_2 are the values of k corresponding to $n=1$ and $n=2$, or to the formation of KBr_3 and KBr_5 respectively.

Series A.

$\text{KBr} = 0.5$ gram-molecule per litre; temperature 26.5° .

B. (Total dissolved Br_2 .)	C. (Free Br_2 .)	$B-C$. (Combined Br_2 .)	K_1 . ($n=1$.)	K_2 . ($n=2$.)
0.51829	0.12507	0.39322	0.0340	0.0241
0.48217	0.10583	0.37634	0.0348	0.0185
0.46720	0.10431	0.36289	0.0394	0.0191
0.45997	0.09712	0.36285	0.0367	0.0166
0.42581	0.08508	0.34073	0.0398	0.0140
0.42246	0.08714	0.33532	0.0428	0.0150
0.37041	0.07352	0.29689	0.0503	0.0128
0.32753	0.06008	0.26745	0.0522	0.0099
0.29450	0.04999	0.24451	0.0522	0.0077
0.28966	0.04818	0.24148	0.0516	0.0073
0.21067	0.03249	0.17848	0.0585	0.0049
0.14892	0.02000	0.12892	0.0576	0.0027
0.11400	0.01515	0.09885	0.0615	0.0021
0.05700	0.00751	0.04949	0.0684	0.0011

Series B.

KBr = 0.1 gram-molecule per litre ; temperature 26.5°.

B. (Total dissolved Br ₂ .)	C. (Free Br ₂ .)	B—C. (Combined Br ₂ .)	K_1 , ($n=1$.)	K_2 , ($n=2$.)
0.23849	0.15455	0.08394	0.0296	0.0330
0.21650	0.13515	0.08135	0.0310	0.0266
0.18013	0.10647	0.07366	0.0381	0.0194
0.17761	0.10532	0.07229	0.0404	0.0196
0.16684	0.09644	0.07040	0.0406	0.0171
0.14837	0.08516	0.06321	0.0496	0.0157
0.13202	0.07215	0.05987	0.0484	0.0122
0.08416	0.04173	0.04243	0.0566	0.0065
0.06365	0.03027	0.03338	0.0604	0.0046
0.04320	0.01938	0.02382	0.0620	0.0028

Series C.

KBr = 0.125 gram-molecule per litre ; temperature 32.6°.

B. (Total dissolved Br ₂ .)	C. (Free Br ₂ .)	B—C. (Combined Br ₂ .)	K_1 , ($n=1$.)	K_2 , ($n=2$.)
0.22530	0.12800	0.09730	0.0364	0.0257
0.21711	0.12094	0.09617	0.0363	0.0234
0.18989	0.10202	0.08787	0.0431	0.0192
0.13328	0.06838	0.06490	0.0539	0.0120
0.11750	0.05446	0.06304	0.0535	0.0088
0.07974	0.03423	0.04551	0.0598	0.0053
0.04875	0.01974	0.02901	0.0653	0.0030
0.01831	0.00698	0.01133	0.0700	0.0013

It is seen that the value of the constant in each series, on the assumption that $n=1$, shows a gradual increase as the amount of free bromine is diminished, whilst on the assumption that $n=2$ it exhibits a rapid and regular decrease. The value of n corresponding to constant values of k must lie between 1 and 2 and much nearer the former. The only interpretation that this can have, in accordance with the law of mass action, is that the compound produced is chiefly KBr_3 , but that a smaller amount of some more complex compound is also formed.

The experimental results are also shown graphically in Figs. 7 and 8, where the concentrations of the bromine in the limb containing water (free bromine) have been plotted as ordinates against

those of the bromine in the limb containing the potassium bromide solution (total dissolved bromine) as abscissæ.

The curve RR was plotted from Roloff's numbers, and represents the relative concentrations of the free bromine and the total dissolved bromine in his experiments. This curve is very limited, owing to the small range of concentrations of bromine covered by his experiments; but it has been continued as a dotted

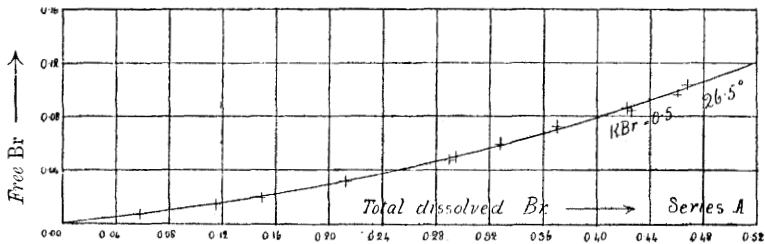


FIG. 7.

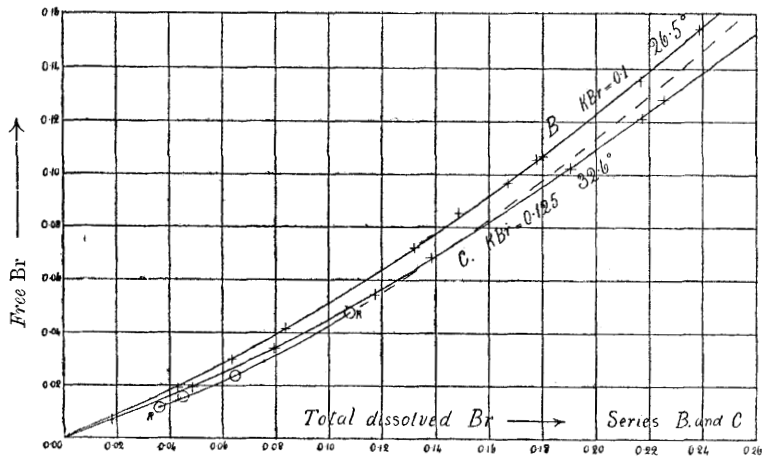


FIG. 8.

line on the assumption that his constant remains the same at higher concentrations of bromine. A comparison of this curve with that derived from my experiments at the same temperature, and with the same concentration of potassium bromide (curve C, Fig. 8), shows that for the same concentration of free bromine, Roloff's curve corresponds to a greater concentration of total dissolved bromine for small concentrations of free bromine, and if continued corresponds to a smaller concentration for higher concentrations of

free bromine. This difference cannot be due to an error in the concentrations of any of the solutions used, for such an error would always affect the result in the same sense, and could not cause the curves to cross as they do in this case. The difference must be due to the difference in method, and may possibly be explained by the presence of the carbon disulphide in Roloff's experiments.

The variation of the values of the constants given in the tables was explained by supposing that more than one compound was formed in the solution. The formation of a small amount of a more complex polybromide along with a comparatively large quantity of KBr_3 would undoubtedly cause a deviation in the constant, such as was observed; but before accepting this explanation, four other possible causes must be considered.

(1) Impurities in the materials used:—The precautions, however, taken in purifying the materials render this very unlikely.

(2) Experimental error:—It is obvious that the same error, if there is one, must be common to all three series of experiments. Now the three solutions of potassium bromide were prepared separately by weighing, and the chance of the same error occurring in each is highly improbable. The concentration of the thio-sulphate solution was tested and found to be correct.

(3) The concentration of the bromine in the limb of the apparatus containing water may not be a correct measure of that of the free bromine in the limb containing potassium bromide solution. There was no apparent means of ascertaining whether the presence of potassium bromide or a higher bromide affected the distribution ratio of the free bromine between the solution and the vapour space. Experiments were made, however, to see whether the presence of a salt, chemically inactive with bromine, affected the distribution ratio. A decinormal solution of potassium chlorate was contained in one limb of the apparatus and water in the other, with different amounts of bromine in the apparatus. Two experiments showed that the amount of bromine dissolved was unaffected by the presence of the potassium chlorate, the concentration being practically the same in both limbs, the following being the concentrations reckoned in gram-molecules per litre:

In $KClO_3$ solution	0·1289	0·0960
In water	0·1284	0·0968

There is no apparent reason why potassium bromide or a higher bromide should not act in the same way as potassium chlorate, and it must therefore be concluded that the concentration of the bromine in the limb containing water is a correct measure of that of the free bromine in the limb containing potassium bromide solution.

(4) In applying the equation of equilibrium, no account was taken of the ionisation of the potassium bromide or the polybromide. The value of the constant will be unaffected only if these substances are equally dissociated into ions; but this is probably not the case. There does not, however, seem to be any means of determining the degree of ionisation of the polybromide. Even were it known, it would be difficult to make a correction for it in the equilibrium equation on account of the observed non-conformity of highly ionised substances to the law of mass action.

The above discussion shows clearly that the only reasonable explanation of the variation of the constant obtained on applying the equation of equilibrium, other than that which assumes the formation of more than one compound in the solution, is that it is due to the degree of ionisation of potassium bromide and the polybromide formed being different. It is not improbably due to a combination of both these causes. These results, taken in conjunction with those obtained in part I of this paper, leave little room to doubt that KBr_3 is formed in the solutions, and seem to indicate that small quantities of a more complex polybromide are formed at the same time.

Summary.

1. The solubility of bromine in aqueous solutions of potassium bromide has been determined over a wide range of concentrations at 18.5° and at 26.5° .

2. The solubility curves for concentrations below 0.1 gram-molecule per litre are perfectly straight, and correspond both at 18.5° and at 26.5° to an additional absorption of two atoms of bromine for every molecule of potassium bromide in solution. In these cases the bromine probably combines with the whole of the potassium bromide present to form KBr_3 , no compounds of greater complexity being formed.

3. The curves for higher concentrations of potassium bromide deviate slightly on the side of increased solubility of bromine, and probably indicate the additional formation of small quantities of more complex compounds than KBr_3 . This explanation is supported by the fact that the deviation is seen to be greater at the lower temperature.

4. The application of the principle of mass action has been shown to lead to no knowledge of the constitution of the polybromide formed in the case of solutions saturated with bromine. Its application in the case of solutions containing varying amounts of bromine insufficient for saturation leads to results which appear to

substantiate the formation of KBr_3 along with smaller quantities of a more complex compound.

5. A simple means has been devised of determining the quantity of a volatile substance present in a system containing various substances in equilibrium, where estimation by chemical means is not possible. It has the great advantage over other methods which have been devised of avoiding the presence of a foreign substance, such as carbon disulphide, and by its simplicity reduces the chances of experimental error to a minimum.

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