[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF VIRGINIA.]

THE DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTIONS.[1]

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A few years ago a series of papers appeared in the American Journal of Science, by Van Name and his co-workers,[2] dealing with the rates of reaction of metals with halogens dissolved in solutions of metallic halides. In these papers it was shown that numerous metals react with a given solution of, say, iodine dissolved in potassium iodide solution, at a rate which is independent of the nature of the metal. This is in harmony with the diffusion theory of heterogeneous reaction,[3] according to which the rate of such reactions is determined by the rate of diffusion of the iodine to the metal and is independent of the metal. In the above papers, however, a fact was brought out which seemed to merit further investigation. This was the unexpected result that the rate of reaction of iodine with metals was markedly influenced by the concentration of the potassium iodide in which the iodine was dissolved, an increase in the concentration of the potassium iodide producing a marked increase in the rate of the reaction. This would be in accord with the diffusion theory only if iodine *diffuses* more rapidly in a concentrated solution of potassium iodide than in a dilute one. No reliable data on this point were available, and the present paper deals with the experimental investigation of the subject.

Apparatus and Technique.

The first determinations were made in a diffusion cylinder similar to that employed by Scheffer,[4] and Stefan,[5] using a four-layer system, and calculating the diffusion constant with the aid of the tables of Stefan. This method proved unsatisfactory in the case of the solutions investigated, partially because of the very slight difference in specific gravity of the layers, and partially because of the length of time necessary for the completion of a single experiment (about 8 days), during which any variation of temperature, or any jarring would cause a complete loss. The method finally employed was a two-layer system, and the method of employing it will be described in some detail. Glass diffusion cylinders were used, of a capacity about 35 cc., and a length about 8 cm. They

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[1] The data given in this paper are taken from *Bull. Philosophical Soc.*, University of Virginia, Scientific Series, Vol. 1, pp. 477–512 (1914).

[2] Van Name and Edgar, *Am. J. Sci.*, **29**, 237; Van Name and Bosworth, *Ibid.*, **32**, 207; Van Name and Hill, *Ibid.*, Jan., 1914.

[3] Nernst and Brunner, *Z. phys. Chem.*, **47**, 52 and 56; Van Name and Edgar, *loc. cit.*

[4] *Z. physik. Chem.*, **2**, 390.

[5] Wiener, *Akad. Ber.*, **79**, 161.

were made with very flat bottoms and true cylindrical sides. These cylinders were fitted with tightly fitting corks, through which passed a separatory funnel terminating in a fine capillary, and a bent capillary tube through which to remove the layers. Fig. 1 is self explanatory. A determination was carried out as follows: The cylinder was rigidly supported in a sensitive thermostat and allowed to reach the temperature of the bath (usually 25°). About 15 cc. of pure potassium iodide solution was then carefully introduced through the separatory funnel and run into the cylinder. After a few minutes, exactly the same amount of a solution of iodine in potassium iodide was introduced in the same way, being run in under the first layer. The concentration of potassium iodide in the two layers was identical. After three or four days the two layers were removed for analysis. This was accomplished by very carefully running a concentrated solution of potassium iodide into the cylinder under the two layers and gradually raising the level until the top layer had just appeared at the mouth of the exit tube at *a*. Any liquid remaining in the separatory funnel was then carefully removed with a roll of filter paper, and an amount of concentrated potassium iodide solution exactly equal to the volume of the first layer was measured into the funnel and run into the cylinder, thus displacing at *a* the liquid in the top layer. This was then analyzed for iodine by titration with dilute sodium thiosulfate solution. The iodine in the bottom layer was determined by subtracting that in the top layer from the total amount originally introduced (also determined by titration). The diffusion constant is calculated from these data with the aid of the following formula:

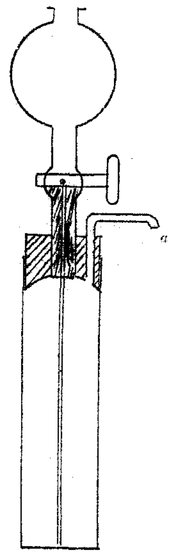

Fig. 1.—Diffusion cylinder.

$$K = \frac{r^2}{t} \frac{2.30}{\pi} \log \frac{8.}{\pi^2} \frac{V_0}{V_0 - V_1}$$

where r is the total length of the liquid column in the cylinder; t the time of diffusion, in days; V_0 the total amount of iodine in the cylinder, and V_1 the iodine in the top layer. The derivation of this formula is given in full in *Bull. Philosoph. Soc.*, U. Va., referred to above.

Even with the improved method, numerous determinations came to grief through accidental errors of technique, fluctuations of the thermostat temperature caused by breaks in the city electric current, vibration of the building, and other sources. The tables give all of the results which the authors believe to be free from other than average experimental error. In all cases duplicate results were obtained, usually four cylinders being run at the same time. This is quite necessary, as a two-layer system gives no check with the lower layer, while the four-layer system should give three checks on each determination.

In addition to the diffusion data, the fluidity of the potassium iodide solutions used was measured for purposes of comparison. The measurements of fluidity were carried out in the usual Ostwald viscosity tube, no especial care being taken to achieve the highest degree of accuracy, since the purpose of the measurements was purely for comparison.

The diffusion of iodine (about 0.05 *N* in all cases) was measured in potassium iodide solutions of concentrations 0.25 *N*, 0.5 *N*, *N*, 2 *N*, 3 *N*, and 4.5 *N*. The fluidity of all of the potassium iodide solutions was also measured. The results follow.

TABLE I.—DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTION (25°).

Normality of KI_3, $^1/_{20}$. Normality of KI, 0.25.

*	*l* (length of liquid layer). Cm.	l^2.	*t* (time in days).	V_o (vol. of $Na_2S_2O_3$ equiv. to I_2 in both layers), cc.	V_1 (vol. of $Na_2S_2O_3$ equiv. to I_2 in top layer), cc.	K @ 25° (diffusion constant).
c	7.60	58.0	3.70	49.05	14.40	1.083
d	7.57	57.3	3.70	49.05	14.50	1.080
e	7.57	57.3	3.70	49.05	14.50	1.080
					Mean,	1.08

TABLE II.—DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTION (25°).

Normality of KI_3, $^1/_{20}$. Normality of KI, 0.5.

*	*l*.	l^2.	*t*.	V_o.	V_1.	K.
a'	7.48	56.2	3.68	39.00	11.80	1.10
e	7.57	57.3	3.69	39.00	11.50	1.09
d	7.57	57.3	3.75	39.40	11.70	1.07
e	7.57	57.3	3.75	39.40	11.70	1.07
c	7.60	58.0	3.73	42.00	12.40	1.07
d	7.57	57.3	3.73	42.00	12.50	1.08
e	7.57	57.3	3.73	42.00	12.50	1.08
					Mean,	1.08

TABLE III.—DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTION.

Normality of KI_3, $^1/_{20}$. Normality of KI, 1.

*	*l*.	l^2.	*t* days.	V_o.	V_1.	Temp.	K.	K @ 25°.
a	7.54	56.9	3.72	26.20	8.18	25.0°	1.20	1.20
b	7.56	57.2	3.73	26.20	8.18	25.0°	1.19	1.19
a	7.54	56.9	4.01	26.50	8.51	24.8°	1.175	1.18[1]
b	7.56	57.2	4.02	26.50	8.54	24.8°	1.183	1.19[1]
c	7.60	58.0	4.02	26.50	8.52	24.8°	1.194	1.20[1]
							Mean,	1.195

TABLE IV.—DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTION (25°).

Normality of KI_3, $^1/_{20}$. Normality of KI, 2.

*	*l*.	l^2.	*t*.	V_o.	V_1.	K @ 25°.
a'	7.48	56.2	2.94	35.32	10.20	1.25
c	7.60	58.0	2.94	35.32	10.15	1.26
d	7.57	57.3	2.94	35.32	10.26	1.27
					Mean,	1.26

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* Asterisk refers to the particular cylinder used.

[1] Calculated by extrapolation, with the aid of the formula of Nernst.

TABLE V.—DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTION (25°).

Normality of KI_3, $^1/_{20}$. Normality of KI, 3.

*	l.	l^2.	t.	V_0.	V_1.	K @ 25°.
c	7.60	58.0	3.21	48.30	14.30	1.255
a′	7.48	56.2	3.74	48.60	15.85	1.285
c	7.60	58.0	3.74	48.60	15.75	1.300
d	7.57	57.3	3.74	48.60	15.50	1.250
a′	7.48	56.2	3.06	48.90	14.45	1.275
c	7.60	58.0	3.06	48.90	14.30	1.286
d	7.57	57.3	3.06	48.90	14.30	1.275
e	7.57	57.3	3.06	48.90	14.30	1.275
a′	7.48	56.2	2.92	51.00	14.95	1.268
					Mean,	1.275

TABLE VI.—DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTION (25°).

Normality of KI_3, $^1/_{20}$. Normality of KI, 4.5.

*	l.	l^2.	t.	V_0.	V_1.	K @ 25°.
a′	7.48	56.2	3.15	44.75	13.50[1]	(1.29) 1.28
c	7.60	58.0	3.15	44.75	13.20	1.27
d	7.57	57.3	3.15	44.75	13.30	1.27
					Mean,	1.275

[1] In this case 2 drops too much were drawn off with the layer titrated. Making the correction, we obtain the unbracketed value for K given above.

TABLE VII.—FLUIDITY OF POTASSIUM IODIDE SOLUTION.

Normality. KI.	Time of flow.	Fluidity (rel. 25°).	Density.
0.125	44.4	1.010	1.0125
0.250	43.8	1.010	1.0275
0.500	41.8	1.025	1.0580
0.750	40.2	1.035	1.0890
1.000	38.6	1.050	1.1180
1.500	36.2	1.060	1.1760
2.000	34.2	1.070	1.2360
2.500	32.6	1.070	1.2950
3.000	31.4	1.070	1.3520
3.500	....	1.060	1.4165
4.000	....	1.042	1.4680
4.500	....	1.020	1.5260
5.000	....	0.996	1.5830

TABLE VIII.

Normality. KI.	Fluidity (rel. 25°). KI.	Diff. const. I_2 in KI.	React. vel. constants.[1]
0.250	1.010	1.080	.....
0.500	1.025	1.080	.....
0.600	.....	.....	8.75
1.000	1.050	1.195	.....
1.200	.....	.....	9.58
2.000	1.070	1.260	.....
2.400	.....	.....	10.15
3.000	1.070	1.280	.....
4.500	1.020	1.280	.....

[1] Mean for Hg, Cu, Cd, and Zn. Taken from Van Name, Edgar, *loc. cit.*

Discussion of Results.

Tables I to VI contain diffusion data for iodine diffusing in KI solutions 0.25 *N*, 0.5 *N*, *N*, 2 *N*, 3 *N* and 4.5 *N*. Table VII contains measurements of fluidity of KI solutions. Table VIII contains a summary of the data obtained, and a comparison of the rates of diffusion and of reaction of iodine solutions, with their fluidity.

(1) **The Relation of the Reaction Velocity of Iodine Solutions to Their Rates of Diffusion.**—A brief survey of Table VIII shows that the results obtained for the rate of diffusion of iodine in solutions of KI of different concentrations are quite in accord with the results for reaction velocity of these solutions obtained by Van Name and his co-workers. The rate of diffusion increases with the concentration of the KI during the range of concentrations through which Van Name worked, and furthermore, the amount of in-

crease is distinctly of the same order of magnitude as the increase in the velocity constants, so that we can say that the results are thoroughly in accord with the diffusion theory of heterogeneous reactions, insofar as this theory applies to the reaction between iodine solutions and the metals studied by Van Name.

(2) **The Reasons for the Influence of KI on the Rate of Diffusion of Iodine.**—This subject must be considered much more carefully, and will be treated under several heads.

(*a*) **The Condition of the Dissolved Iodine.**—The work of Leblanc and Noyes,[1] Jakowkin,[2] A. A. Noyes[3] and others has shown that practically no iodine is present as such in potassium iodide solutions, practically all of it combining with the KI to form KI_3. In solutions containing a large excess of KI, such as were dealt with in this investigation the free iodine in the solution may be neglected, as having no influence on the change in the rate of diffusion.

KI_3 in dilute solution is probably largely dissociated into K^+ and I_3^-, and this dissociation must necessarily be somewhat less in the concentrated solutions of KI than in the more dilute ones, due to the effect of the excess of the common K ion. We are therefore dealing with the diffusion of KI_3 and I_3^- ions, and not with free iodine.

(*b*) **The Influence of KI on the Diffusion of KI_3 and I_3^-.**—Concerning the influence of KI on the rate of diffusion of undissociated KI_3 we can say very little, though it seems most probable that it must be indirect—as for example, by influencing the fluidity of the solution, a factor which will be treated later. Concerning the actual rate of diffusion of undissociated KI_3 as compared with that of I_3^- ions and K^+ ions, we can only say that, in general, the rate of diffusion of an un-ionized molecule is considerably less than that of its ions. Any increase in the relative amount of KI_3 in the more concentrated KI solutions would therefore have the effect of *decreasing* the total rate of diffusion of the iodine, all other forces being equal.

The influence of KI on the rate of diffusion of I_3^- ions may be discussed according to the principles laid down by Abegg and Bose[4] on the subject of the influence of a common ion on the rate of diffusion of an electrolyte. The authors show that for many substances the rate of diffusion of an electrolyte is *decreased* by the addition of an electrolyte containing a common ion *if the common ion is the faster of the two,* and *increased* if the common ion is the *slower* of the two. In our case the common K^+ ion with its migration velocity[5] of about 74.8 is much faster than the I_3^-

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[1] *Z. physik. Chem.*, 6, 401.

[2] *Ibid.*, 20, 19.

[3] *Ibid.*, 27, 357.

[4] *Z. physik. Chem.*, 30, 545.

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

ion with its migration velocity of about 41.0, so that the influence of increasing the concentration of the KI should *decrease* that rate of diffusion of the I_3^-, if Abegg and Bose's theory be correct.

(*c*) **The Influence of the Fluidity of the Solution.**—That fluidity has a marked effect upon rates of diffusion is well known, and since solutions of potassium salts in general have high fluidity, it might be expected that this influence alone would account for the observed increase in the rate of diffusion of the iodine with increasing KI concentration. An examination of Table VIII, however, will show that this is not the case. The fluidity of 0.25 *N* KI is 1.010 at 25°, and this increases steadily until a maximum is reached at about 2.5 *N*, where the value is 1.070. After this the fluidity drops rapidly, so that at 4.5 *N* the value is 1.020, and at 5 *N* only 0.996. On the other hand, the diffusion constant rises much more rapidly and becomes uniform at about 2.5 *N*. The value of the diffusion constant at 3 *N* is nearly 20% higher than that at 0.50 *N*, while the corresponding rise in the fluidity curve is only about 5%. A still more striking illustration of the fact that fluidity alone will not account for the increasing diffusion rate is found by comparing the figures for fluidity and diffusion in concentrations of KI 0.5 *N*, and 4.5 *N*. The fluidities are almost *identical*, the more dilute solution being slightly higher, while there is an *increase* in the diffusion constant of almost 20%. It is thus obvious that the effect of increasing KI concentration on the rate of diffusion of iodine cannot be explained by the increase in fluidity alone. Recapitulating, we may say that factors *b* and *c*, treated above, seem entirely inadequate to explain the *increase* in the rate of diffusion of iodine with increasing KI concentration which is shown in Tables I to VII. Factor *b* should work in the opposite direction, if at all, and factor *c* seems entirely inadequate to account for the results. The authors do not, at the present time, attempt to offer any explanation for the observed facts. It would be interesting to investigate other metallic iodides in a similar way, and perhaps sufficient data might be obtained in this way to enable a sound theory to be advanced to account for the facts given in this article.

Summary.

1. The rate of diffusion of iodine dissolved in potassium iodide solutions of different concentrations has been measured at 25°. Increase in the concentration of the KI causes, in general, a marked increase in the rate of diffusion of the iodine. The fluidity curve of KI has also been determined at 25° for a wide range of concentration.

2. The results bear on the work of Van Name and others on the rate of solution of metals in iodine solutions, and entirely corroborate the conclusions of these writers that these reactions are governed by the rate of diffusion of the iodine, under the conditions of their experiments.

3. No satisfactory explanation of the influence of the KI on the diffusion of iodine, is offered, though several possible explanations are considered.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE DENSITIES AND CUBICAL COEFFICIENTS OF EXPANSION OF THE HALOGEN SALTS OF SODIUM, POTASSIUM, RUBIDIUM AND CESIUM.

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For purposes of computation in the preceding paper upon "Changes in Volume upon Solution in Water of the Halogen Salts of Alkalis" it was necessary to know the densities of the solid salts at different temperatures. Since neither these values nor the coefficients of expansion of the salts have been found with accuracy, the problem of determining the densities over the necessary range in temperature, and thus the coefficients of expansion, was undertaken.

The method employed was that of displacement of toluene. In order to reduce the effect of the errors of experiment, a very considerable quantity of salt was used. Furthermore, especial pains were taken, first in drying the salt, and second, in freeing it as far as possible from entangled air when immersed in toluene in the pycnometer.

The pycnometer itself, instead of being of the ordinary stoppered form for solids, was merely a 25 cc. graduated flask, the neck of which was very much constricted at one point to increase accuracy in adjusting the volume of its contents. The diameter of the constriction was about 2.5 mm. which secured an accuracy in setting of about 0.3 mg. of toluene. This form of pycnometer has the advantages, first that the ground surface is not wet with liquid and hence there is no difficulty from evaporation, second that the neck of the flask serves as a reservoir when used at low temperatures.

The volume of the flask at different temperatures was found by weighing it full of water after the liquid had been set at the mark in the thermostats used for finding the densities of the solutions in the preceding paper. The neck of the flask was dried before the meniscus was set. Preparatory to being weighed, the outside of the flask was washed with dilute ammonia solution, wiped with a clean, slightly damp, cotton coth, and was allowed to stand in the balance room for at least one hour. In order to find the densities of the different specimens of toluene, the flask was weighed after being filled with toluene at the temperatures used. No attempt was made to purify the toluene beyond drying it over metallic sodium for