

INFLUENCE OF THE CONCENTRATION OF
POTASSIUM IODIDE
ON THE RATE OF DIFFUSION OF IODINE
in
POTASSIUM IODIDE SOLUTION.

A Dissertation
Presented to the Faculty of the University of Virginia,
as a part of the requirements for
the Degree of Doctor of Philosophy.

By
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OUTLINE.

The purpose of this work was to discover, if possible, why the concentration of potassium iodide should affect the rate of solution of metals in iodine, the concentration of the latter being constant.

This fact, that the concentration of potassium iodide does influence the reaction, had been established by the work of Van Name and Edgar, and was in a way a serious objection to the "Diffusion Theory of Reaction Velocity" which their work in all other respects completely confirmed.

The following is a brief outline of the present work:

PART I. The Diffusion Theory of Reaction Velocity, What it is, and why it was advanced.

PART II. Determination of the Rate of Diffusion - Apparatus used by Stefan and Ohlm - Modification used by Edgar - Apparatus used in this work - Advantages and disadvantages.

Mathematics involved - Solution of the differential equation

Complete solution for the present case.

PART III. EXPERIMENTAL DATA. - Diffusion of iodine in solutions of potassium iodide of varying concentrations - Viscosity of potassium iodide solutions - Density of potassium iodide solutions. CURVES.

PART IV. DISCUSSION OF RESULTS. What is Diffusion- Nernst's "Reststrom" - Work of

Harry Heymann - Relation of density and viscosity to the rate of diffusion.

General confirmation of the Diffusion Theory of Reaction Velocity - Summary.

ACKNOWLEDGEMENT.

PART I.

The Diffusion Theory of Reaction Velocity in Heterogeneous systems.

Work of Noyes & Whitney - 1897. In 1897 Noyes and Whitney carried out a series of experiments for the purpose of discovering, if possible, the laws governing the rate of solution of salts in water and other solvents. From the results of their work, and those of others the theory has been advanced by Nernst that reaction velocity in heterogeneous systems is controlled largely, and in some cases entirely, by the rate of diffusion of the reacting or dissolving substances through a thin unstirred layer of the saturated solution adhering to the surface of the solid. (1 - 2 - 3) That is, we conceive of a thin film of saturated solution adhering to the dissolving solid somewhat as a film of water adheres to the inside of a pipette. This film is always saturated on the inside, because the rate of solution is very rapid in comparison with the rate of diffusion, which latter in liquids is very slow.

This if we assume the thickness of the layer to be

approximately constant, as seems reasonable with uniform stirring, it should follow that solution, or reaction velocity, varies directly as the rate of diffusion. This latter is usually assumed to be proportional to the difference in concentration on the opposite sides of the thin unstirred layer. This theory was suggested by Noyes and Whitney, and further elaborated by Nernst.

The rate of reaction for first order reactions in homogeneous systems is expressed by the "Unimolecular formula",

$$\frac{dx}{dt} = k(a - x)$$

where k is the reaction velocity constant, that is a number depending on the so called "affinity" of the reacting particles for each other. (a is the amount of reacting material originally present, and x the amount transformed)

The rate of reaction in heterogeneous systems is expressed by the formula,

$$\frac{dx}{dt} = k.O.(a - x)$$

where O is the surface of the reacting solid. It would seem natural to suppose that k had the same significance as in the first case, but according to the "Diffusion theory" this is not true. k is a constant depending on the rate of diffusion of the reacting, or dissolving, substance and is independent of the

"affinity" of the reacting substances. (k is also independent of the "order" of the reaction.)

Numerous investigations have been made which seem to support this hypothesis, and it has been accepted as a working basis by many writers, but criticism of it has been very vigorous by others. In testing its validity we should choose such reagents as will react to produce only soluble bodies under the conditions of the experiment. Thus we should not expect the theory to hold for metals reacting with acids to liberate hydrogen, or for metals reacting with soluble salts to yield insoluble salts. These facts should be remembered in evaluating the criticisms advanced by Marc, Wildermann, and others. (4,5,6,7,8,9).

Let us briefly survey the chief of these objections that have been advanced against the diffusion theory of reaction velocity.

I. That it is unnecessary, as the same equation for reaction velocity in heterogeneous systems can be, and has been (9) deduced from other and better established premises.

II. That the temperature coefficient of reaction velocity is found by experiment to be very different from the temperature coefficient for diffusion in many cases.
(4)

III. That if the diffusion theory were correct metals

having widely different solution pressures should dissolve in a given solution at the same rate; likewise, that such substances as marble, dolomite, and magnesite, should dissolve in acids at the same rate; which conclusions, it is urged, are manifestly not in accord with the well known facts.

The above list of objections, while not by any means exhaustive, embody the most important arguments against the theory.

A type of reaction that seemed to lend itself well to this investigation was the rate of solution of certain metals in a solution of iodine in potassium iodide. The advantages were: (1) that no gaseous product was formed which might disturb the "Unstirred" layer; (2) the ease with which the materials might be obtained pure and in the desired form; (3) the ease and accuracy with which iodine can be estimated in solutions of all concentrations. A little work along this line had been done as early as 1891 by Schükarew, who worked with various metals in solutions of halogens. (10). (This work was done about six years before the diffusion theory of reaction velocity had been advanced by Noyes & Whitney.) In 1905 Brunner worked with zinc in solutions of hydrochloric acid, and also in iodine solutions. (11). This work, while on the whole confirming the theory of reaction velocity given above, is very far from satisfactory. The most systematic

and definite work thus far done along this line was done by Van Name and Edgar in 1910.

Work of Van Name & Edgar. In 1910 R.G. Van Name and Graham Edgar undertook a series of experiments for the purpose of determining more exactly reaction velocities between metals and dissolved halides for the purpose of testing the validity of the diffusion theory of reaction velocity. Having a very definite end in view Van Name and Edgar took all possible precautions against such sources of error as were likely to invalidate in any way their work for the particular end in view. All of their work was done at the temperature of 25°; the stirring was thoroughly and uniformly accomplished by means of an eighth horse power motor. Samples of iodine solution were withdrawn at desired intervals and titrated. The velocity constant k could be determined as many times as desired from the same materials. The following from Van Name & Edgar will make clear the method of calculation. (12).

"From the point of view of the diffusion theory the mechanism of the reaction is as follows: The weight of iodine which reaches and reacts with the surface of the metal in the time interval dt is the amount which can diffuse through the adherent layer of liquid in that time, that is according to Fick's law, it is proportional to the concentration fall across the layer. Owing to the rapidity of chemical reaction the concentration of the iodine at the surface of the metal is always practically zero. At the outer surface of the layer it is equal to c , the concentration of the main solution. Hence the concentration fall is c , and if m is the total weight of available halogen in the solution,

$$-\frac{dm}{dt} = -\frac{d(cv)}{dt} = k.c.$$

where K is the velocity constant. Integration for constant volume gives

$$K = \frac{v}{t_2 - t_1} \cdot \frac{\ln \frac{c_1}{c_2}}{c_2} "$$

Van Name and Edgar worked with Hg, Cu, Cd, Zn, and Ag. Though most of their work was done in iodine solution, some was also done in bromine solution. Some attention was paid to the effect of stirring at different rates, and to temperature effects.

As was to be expected the rate of reaction was increased in all cases by increasing the rate of stirring. This is in perfect accord with the diffusion theory, for we should expect the unstirred layer to be thinner when the stirring was rapid than when slow.

The following sample table taken from the work of Van Name & Edgar will serve to illustrate the high degree of accuracy of their work.

RATE OF SOLUTION OF Hg in IODINE
at 25°.

c	Δt	v	K
0.0381		500	6.51
0.0356	5	480	6.51
0.0328	6	460	6.30
0.0304	5.3	440	6.36
0.0279	5.7	420	6.25
0.0257	5	400	6.55
0.0236	5	380	6.59
Average K ...			6.43

100 gms KI to the litre, rate of stirring 170.

Collecting all of the constants obtained by Van Name & Edgar for a given rate of stirring (say 240)

we have the following table:

		"K"
Hg	400 gms KI per litre	10.48
Cu	9.98 <u>mean 10.13</u>
Ag	9.93
Hg	200 gms KI per litre	9.55
Cd	9.56 <u>mean 9.58</u>
Zn	9.64
Hg	100 gms KI per litre	8.81
Cd	8.69 <u>mean 8.71</u>
Zn	8.64

In the above tables c represents concentration, Δt the time interval, v the volume of solution, and K the reaction velocity constant. There are three points to be particularly noted:

(1) That the results are of a high order of accuracy for this kind of work, and that therefore we can put more reliance on the results than we can on the rather uncertain results of previous investigators.

(2) That the reaction velocity constant is approximately the same for all metals used, and that this constant increases very decidedly with increase of the potassium iodide.

(3) That the reaction velocity constant increases, as was to be expected, with the rate of stirring.

The fact that the reaction velocity increases so markedly with increasing concentration of potassium iodide at once aroused interest, for it was not to be expected, and it did not accord with the diffusion theory of reaction velocity in so far as known facts went. (This point gives us the starting point for our

When we remember how far apart the metals in question are in the potential series it becomes impossible to ascribe the foregoing results to purely local cell effects, as has been done by Wildermann and other critics of this theory. We should bear in mind that the close duplication of results constantly shown by the data of Van Name and Edgar remove the possibility of merely accidental coincidence, which has been claimed to be the explanation of some data given by previous investigators to prove the same theory. Van Name & Edgar thus summarize their work:-

(1) "The rates of solution of the metals Hg, Cd, Zn, Cu, and Ag, in aqueous iodine solutions containing a large excess of potassium iodide have been measured at 25° and shown to be practically equal, a slight difference observed with copper and silver being in all probability due to accumulation of the solid iodide at the contact surface."

(2) "The temperature coefficient for 10° (between 25° and 35°) is about 1.3 ."

(3) "An increase in the concentration of the potassium iodide produces a marked acceleration of the reaction."

(4) "Mercury dissolves in bromine in the presence of potassium bromide slightly faster than in iodine, but in cupric bromide much more slowly. *****"

(5) "The reaction was found to be proportional, on the average, to the $4/5$ power of the rate of stirring."

(6) "So far as can be decided from the data at present available, the diffusion theory of Noyes, Whitney, and Nernst, gives a satisfactory explanation of the results obtained."

It will be noted that the fact hardest to reduce to terms of the diffusion theory is that an increase in in the concentration of the potassium iodide causes marked acceleration in the rate of reaction.

Work of Van Name & Bosworth. (13) Later Van Name and Bosworth worked with iron, nickel, and cobalt, in addition to those metals used by Van Name & Edgar. The fact that these metals also react with iodine at very nearly the same rate as those previously discussed adds greatly to the probability of the diffusion theory. The following quotation from the work of Van Name and Bosworth is of interest here.

"The agreement between the metals Cd, Fe, Ni, and Co, is very striking, and clearly proves that under like conditions these metals dissolve in iodine at the same rate. In the earlier investigation a like result was obtained with the five metals, Hg, Cu, Ag, Zn, and Cd. Eight metals in all have, therefore, been shown to possess the same rate of solution in iodine, a result for which there seems to be no satisfactory explanation other than that furnished by the diffusion theory."

Work of Van Name & Hill. Recently Van Name and

Hill (14) have measured the effect of added non-electrolytes on the reaction velocity, using metallic cadmium and iodine in potassium iodide solution as the reacting substances. The results obtained by them were not in accord with the formula deduced by Arrhenius; (15) this they attribute to the increase in the thickness of the diffusion layer caused by the greater viscosity of the solution. For our purpose the most important point in the work of Van Name & Hill is that they have shown that the reaction velocity varies approximately as the fluidity varies when the fluidity change is caused by the addition of a non-electrolyte. This, as we shall see later, certainly does not hold for the case where the decrease in fluidity is caused by increasing the concentration of the Potassium iodide beyond a certain limit.

Attention has been called to the fact that the reaction velocity increases as the concentration of the KI increases. Nernst deduces the following theoretical expression for the rate of diffusion of any electrolyte:

$$D = 2 \frac{uv}{u+v} \cdot g \cdot RT \cdot 10^{-9}$$

where D is the diffusion constant, u the velocity of migration for the cation, v that of the anion, and g is a constant. According to this simple formula we should not expect the addition of a common ion (K)

to have any effect on the rate of diffusion. (Or on the reaction velocity.) This apparently unexplained deviation from the results naturally expected from the diffusion theory of reaction velocity, becomes of great importance when we note that it is the only such deviation observed in the very careful and convincing work of the investigators quoted above. In fact it seemed that if this ^{Exception} ~~fact~~ could be cleared up in a satisfactory manner we would be in a position to definitely look upon the diffusion ^{theory} ~~of~~ reaction velocity as established in those cases, - typical of reactions in heterogeneous systems - studied by Van Name, Edgar, and Bosworth.

At the suggestion of Dr. Graham Edgar and in every way aided and guided by him, the writer undertook to measure directly the rate of diffusion of iodine in solutions of KI of various concentrations.

PART II.

Diffusion of Iodine in Potassium Iodide.

The work previously quoted showed plainly that, "An increase in the concentration of the potassium iodide produces a marked acceleration of the reaction." As no data bearing upon the rate of diffusion of iodine in KI solutions of varying concentrations were available a few rough determinations were made by Van Name and Edgar. These, however, owing to the experimental difficulties encountered and to the lack of time to push further a side investigation, only gave a rough ~~and~~ confirmation of the hypothesis. During the winter of 1911 - 12 Dr. Graham Edgar made a few determinations of the same kind at the University of Virginia. The results of these preliminary investigations showed that it was very probable that the original hypothesis was correct as to iodine diffusing more rapidly in strong than in weak KI solutions, also that the value of the diffusion constant was somewhere about 1.1 . It also developed that experimental difficulties were much greater than had been anticipated.

As previously stated Nernst has deduced an expression for the rate of diffusion of electrolytes in terms of the velocity of migration of the ions formed. This expression was deduced on purely theoretical grounds, making the assumption that the electrolyte was completely dissociated. The complete expression is:

$$D = 0.4485 \frac{uv}{u+v} \cdot (1 + 0.0034 (t - 18))$$

where D is the diffusion constant, u and v the transport numbers, and t is the temperature on the Centigrade scale.

Making the assumption that the KI_3 is completely dissociated, and that the ions would migrate at the same velocities in the KI solution as in water, and using the values given by Nernst for the K ion, and that given by Bredig for the I_3 ion we obtain for the diffusion constant 1.21. (16, 17, 18) This value is in all probability too great for the reason that the triiodide can not be completely dissociated. In fact the theoretical values thus obtained for a very large number of salts are in nearly all cases ~~very~~ much larger than the results of actual experiments performed by Scheffer and by Ohlm. (16, 19, 20) In this connection it is of interest to note that the theoretical constant similarly calculated for KI is 1.47 and that actually found by Ohlm using a solution of .01 normal was 1.46. This solution was about five times as dilute as the solution of KI_3 used by Van Name and Edgar, to say nothing of the immense excess of KI always present, the effect of which would certainly be to drive the dissociation still further back. (21)

In the case of acetic acid Ohlm found that the constant was 0.93 as against 1.37 theoretical, using 0.01 N solution. (Acetic acid is, of course, a very weakly dissociated acid.) This shows the effect of incomplete dissociation to be very considerable. Of course too, we have no a priori right to assume that the rate of migration of the ions is the same in KI as in water, or that it is the same in a weak as in a concentrated solution of KI .

Molecular condition of the dissolved iodine. Le

Blanc and Noyes concluded from freezing point experiments, that when iodine is added to a solution of KI it enters into combination to form a complex ion, probably I_3 . The fact that iodine thus added does not lower the freezing point of the KI solution is excellent evidence that the total number of molecules is not increased, but does not show whether the resulting

compound is KI_3 , KI_5 or some higher iodide. (22).

In 1877 Johnson actually obtained crystals having the definite composition KI_3 , by volatilization over concentrated sulphuric acid. This, while very strong evidence in favor of the KI_3 in solution theory, yet left room for question, for the existence of a solid compound does not necessarily prove that it exists in solution. (23).

The first really conclusive work was done by Max Roloff, who made use of the principle of partition coefficients between dissimilar solvents. (24). Roloff did not work with iodine in KI solution, but with bromine in KBr solution. The other solvent used was CS_2 . Roloff showed very conclusively that practically all of the bromine was present in KBr solution as KBr_3 , and not as any higher bromide. His method was to assume that the bromine formed a given bromide, KBr_3 , KBr_5 , or what ever seemed reasonable; and then from the known laws of partition between non-miscible solvents to deduce a function of concentration in each solvent that theoretically should remain constant with varying concentrations. Roloff then tested this hypothesis by actually determining the concentration over as large a range of ~~concentrations~~ as seemed practical. He thus showed that the bromine in a KBr solution is present as KBr_3 almost exclusively, and by analogy iodine in KI should be present as KI_3 . For a full discussion of the theory involved and for the data the reader

should consult the original article. (24)

Later (1896) Jakowkin, using the same methods as those used by Roloff, showed that the reaction was strictly analogous for other bases and for other halogens; in particular for iodine in KI solution. Jakowkin goes into much more detail than does Roloff. (25).

Two years later A.A.Noyes showed that the amount of free iodine (I_2) in solutions of KI far more dilute than any with which we worked is negligible. (26)

Still more recently Osaka showed that the freezing point of a solution of KI was actually raised by the addition of iodine. In fact there was a small rise in the freezing point as found by LeBlanc & Noyes, but they put this down as experimental error. However, Osaka showed that though small it was easily measurable, and further that it was greater for HI than for KI. From this he concludes that KI_3 and HI_3 must be somewhat less dissociated than KI and HI. He does not make quantitative computations because he feels that the data is not sufficiently accurate for this, though undoubtedly sufficient for a qualitative statement as made above. (27).

Work of the writer under the direction of Dr. Edgar.

In October 1912 the writer, under the guidance of Dr. Graham Edgar, began a series of experiments having as end in view to determine if possible the rate of diffusion of iodine in solutions of KI of various concentrations. In all cases it was decided to have the

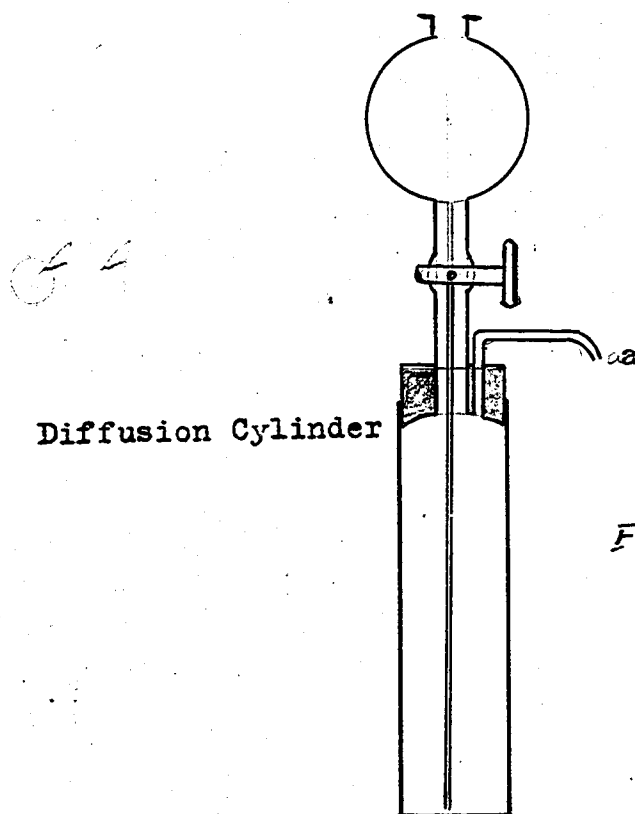
solutions of normal strength or some simple multiple thereof. The iodine was assumed to be present as KI_3 , and the calculated amount of KI was added extra to the solution containing the iodine. That is to say, the concentration of the KI exclusive of that forming triiodide was the same in both solutions (layers).

The apparatus used was modeled after that of Stefan, utilizing the four layer scheme and making use of Stefan's tables. (28, 29). As the values given in these tables required considerable interpolation, a set of curves was drawn on a suitable scale from which the values for x could at once be read.

The apparatus used by Edgar consisted of a flat-bottomed glass cylinder of about 100 c.c. capacity, carefully selected to have uniform diameter and an almost flat bottom. A mercury bottom could not be used because the mercury would be attacked by the iodine; nor was any liquid known suitable to use for this purpose. Three portions of KI solution of about 25 c.c. each were first run into the cylinder by means of a separatory funnel having a thin walled capillary tube for a stem. This capillary was set within the cut-off stem of the funnel by means of hard paraffine, great care being taken to prevent any paraffine getting on the inside of the capillary tube. This tube extended down to within 0.2 to 0.3 mm. of the bottom of the cylinder, thus causing the inflowing liquid to spread out into a thin sheet as it entered the cylinder. If

the layer containing the iodine was slowly and carefully run in there was no mixing of the layers so far as could be detected by the eye. When the last layer had been run in there was a space of about 0.5 cm between the top of the liquid and the ~~top~~^{bottom} of the cork. The cork was slightly hollowed on the under side, and covered with a thin coat of paraffine to protect it from the iodine. The delivery tube was so placed that it tapped the highest ~~the highest~~ point of the under side of the cork. (See fig. 2 .) When it was desired to remove the layers for titration, a very concentrated solution of KI (always having a higher specific gravity than that used in the experiment) was slowly run in through the funnel till the air space was exactly filled. Then the stopcock was turned and all excess of the displacing fluid was carefully removed from the funnel; first with a pipette, and then with a bit of rolled filter paper. Next there was introduced into the funnel, and slowly run into the cylinder the same amount of displacing fluid (strong KI solution) that was in each layer. This was measured in a pipette of the desired size. Thus, layer by layer the liquid was removed after diffusion had proceeded so far as seemed desirable. Experience showed that a period of from six to eight days was required to give a satisfactory quantity of iodine in the upper layers. All of these experiments were performed in a gas heated thermostat that kept constant temperature to within $\pm 0.1^{\circ}$ if

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Diffusion Cylinder

Fig. 1.

the gas pressure was constant.

The first experiments made by the writer were made with the apparatus just described; except that an electrically heated thermostat was substituted for the one heated by gas. This thermostat was very sensitive and would hold the temperature constant to within about 0.02° for a week if the temperature of the room did not vary more than 5° or 6° - and if the current was not cut off in the interval. As we had no cellar at our disposal, the temperature frequently did vary far more than this, and in consequence we frequently lost set after set of experiments. Also the current was frequently interrupted by various accidents to the city power plant, - repairing, rewiring, and so forth.

New apparatus used. It was decided to use a cylinder much shorter than before, and to have only two, instead of four, layers. That is, equal quantities of iodine solution and of pure KI solution were used. The cylinder was of the same general type as before, (see fig. 1.) but somewhat smaller in diameter and very much shorter. The length of the new cylinders actually used was about 7.5 cms, and the pipette used to measure each layer held about 15 c.c. The best results can be obtained with this apparatus when the time is from 3 to 4 days. The advantage of this shortening of the time is obvious and very great, but it is not attained without some disadvantage. The four layer system gives ~~the~~ theoretically three independent equations, from

which to evaluate the diffusion constant (K). It is true that in general some of the values are uncertain for mathematical reasons, i.e. the value of $\frac{h^2}{k.t}$ corresponding to a given titration figure changes very little for quite large changes in the titration figure. In spite of this the four layer system usually gives more than one independent value for "k" in a single experiment. In the two layer system, the only check is to run separate experiments, either at different times or with different cylinders. This ofcourse means more work, yet we found that the results were much more satisfactory than with the four layer system.

The method of procedure in this case was the same as for the four layer system, the iodine solution ofcourse forming the bottom layer. In general four cylinders were filled at the same time. After a period of from three to four days the top layer was removed as in the four layer case. As there is no check in the two layer system there was no advantage in removing the second layer. (Titration being very much more accurate than the other factors involved.) Some of the original iodine solution was always placed in the bath along with the cylinders, and a pipette full was removed at the same time that the samples were removed from the cylinders. A small porcelain ^{dish} was used to receive the iodine solution as it came drop by drop from the delivery tube. (a, fig. 1.) As soon as a sample was removed it was transferred to a small glass stoppered flask, a

pipette full of the original iodine solution being also put into a similar flask. When all four samples had been removed, the iodine in the flasks was titrated with sodium thiosulphate (approximately N/75). Starch paste was used as an indicator. Thiosulphate as weak as this will change strength from day to day; but this introduces no error as a fresh sample of the original iodine solution is titrated every time a determination is made. The equation used to determine k is:.

$$k = \frac{r^2}{t} \cdot \frac{2.30}{\pi} \cdot \log \frac{8}{\pi} \frac{V_0}{V_1 - 2V_2}$$

(The derivation of this formula will be given later)
 Here k is the diffusion constant, t the time in days, V_0 the total amount of iodine in the cylinder, V_1 the amount of iodine in the top layer after time t has elapsed, and r is the length of the total liquid column, i.e. both layers. It will be noted that the quantity V , occurs to the first power in both denominator and numerator of our fraction (and there only); hence, it does not matter in what unit V is measured. This is of great practical value, for it allows us to be indifferent to the exact strength of the thiosulphate used.

In a few cases, instead of placing the cylinder in the thermostat it was placed in a Dewar flask, being securely held in place by a well fitted cork. This was possible only in summer, and at such times as the temperature of the room was nearly 25° and fairly con-

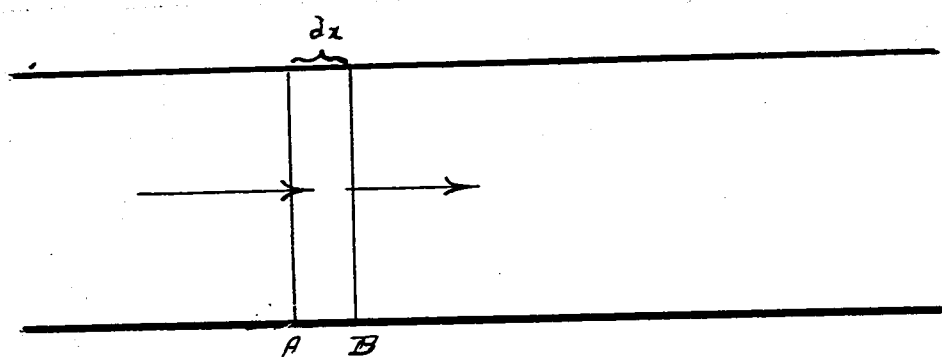


Figure 2.

stant. The flask was filled with water at as nearly room temperature as possible, the empty cylinder and thermometer inserted, and the whole left for about a day, so that the system might be in thermal equilibrium. Then the experiment was carried out as in the other cases. The temperature recorded for the experiment was the mean observed (4 times a day) during the run. Constants thus obtained were reduced to 25° by means of the formula given on a previous page. (16)

It was only rarely that conditions permitted of the use of this method, and as it offered no special advantages over the use of the thermostat, it was only used a few times. The one interesting thing learned from this method was that if the temperature change be slow and steady, no perceptible mixing is caused by a rise or fall of 0.5°, while experience showed that a temperature change of only 0.1° caused by the a break in the heating circuit of the thermostat was always fatal to results. Ofcourse, in the latter case the fall was comparatively rapid.

MATHEMATICS INVOLVED IN THE PROBLEM. Consider a substance diffusing in the direction indicated by the arrow in fig.2. Let u be the concentration at A, and $u - \frac{du}{dx}$ the concentration at B. If now we make the thickness of the layer very small $\frac{du}{dx}$ becomes $\frac{\partial u}{\partial x}$.

Hence we have the expression,

$$(u + \frac{\partial u}{\partial x} dx) - u$$

for the difference in concentration at A and B. Differentiating this expression we obtain for the change in concentration corresponding to dx , the thickness of the layer,

$$\frac{\partial u}{\partial x} + \frac{\partial}{\partial x} \left(\frac{\partial u}{\partial x} dx \right) = \frac{\partial^2 u}{\partial x^2} dx$$

The change in concentration with respect to time is, $\frac{\partial u}{\partial t}$, hence we can write,

$$(I) \quad \frac{\partial u}{\partial t} = k \frac{\partial^2 u}{\partial x^2}$$

Any solution of the equation (I) must be a function of x & t . Put,

$$u = f(x, t) = \cos nx \cdot e^{-\kappa n^2 t}$$

differentiate with respect to t and we have,

$$\frac{\partial u}{\partial t} = -\kappa n^2 \cos nx \cdot e^{-\kappa n^2 t}$$

and differentiating with respect to x we have,

$$\frac{\partial u}{\partial x} = -n \sin nx \cdot e^{-\kappa n^2 t}$$

differentiating again with respect to x we have,

$$\frac{\partial^2 u}{\partial x^2} = -n^2 \cos nx \cdot e^{-\kappa n^2 t}$$

Substituting in equation (I) we have an identity; hence, $u = \cos nx \cdot e^{-\kappa n^2 t}$, is a solution. In exactly the same way we can show that $u = \sin nx \cdot e^{-\kappa n^2 t}$ is a solution; and hence,

$$(II) \quad u = \sum_{n=0}^{\infty} (a_n \cos nx + b_n \sin nx) \cdot e^{-\kappa n^2 t}$$

is a solution. If this is to satisfy our conditions we must have for $t=0$, $u = f(x)$ known i.e. u_0 , and when $x=0$ or $x=r$

$$\frac{\partial u}{\partial x} = 0, \text{ at all times.}$$

(Here r is the total length of the column, i.e. both layers.)

Differentiating equation (II), and putting $x=0$, we have:

$$\frac{\partial u}{\partial x} = \sum_{n=0}^{\infty} -n(a_n \sin nx - b_n \cos nx) \cdot e^{-\kappa n^2 t} = 0$$

For this case $\sin nx = 0$; but as $e^{-\kappa n^2 t}$ can not be zero b_n must be zero for all values of n . If now we put $x=r$ the above equation becomes,

$$(III) \quad \frac{\partial u}{\partial x} = \sum -n \cdot a_n \sin nr = 0$$

Hence, nr must be some multiple of π , i.e. the values of nr must be,

$$0, \pi, 2\pi, 3\pi, 4\pi, \dots$$

Or n must be,

$$0, \pi/r, 2\pi/r, 3\pi/r, 4\pi/r, \dots$$

Equation (II) now becomes,

$$u = a_0 \cos 0 \cdot e^{\frac{-\pi^2 k t}{r^2}} + a_1 \cos \pi x/r \cdot e^{\frac{-\pi^2 k t}{r^2}} + a_2 \cos 2\pi x/r \cdot e^{\frac{-4\pi^2 k t}{r^2}} + \\ a_3 \cos 3\pi x/r \cdot e^{\frac{-9\pi^2 k t}{r^2}} + a_4 \cos 4\pi x/r \cdot e^{\frac{-16\pi^2 k t}{r^2}} \dots$$

It now remains to evaluate the coefficients a_0, a_1, a_2, \dots . Put $t = 0$, then will the above equation become,

$$u = f(x) = a_0 \cos 0 + a_1 \cos \pi x/r + a_2 \cos 2\pi x/r + \dots$$

Multiply both sides by $\cos n\pi x/r \cdot dx$, and integrate between the limits $x = 0$ and $x = r$.

$$\int_{x=0}^{x=r} f(x) \cdot \cos n\pi x/r \cdot dx = \int_{x=0}^{x=r} a_0 \cos 0 \cdot \cos n\pi x/r \cdot dx + \\ \int_{x=0}^{x=r} a_1 \cos \pi x/r \cdot \cos n\pi x/r \cdot dx + \int_{x=0}^{x=r} a_2 \cos 2\pi x/r \cdot \cos n\pi x/r \cdot dx \\ \dots \dots \dots \int_{x=0}^{x=r} a_n \cos^2 n\pi x/r \cdot dx + \dots \dots \dots$$

Make use of the relation that,

$$2 \cos A \cdot \cos B = \cos(A + B) + \cos(A - B)$$

The first term may be written,

$$\int_{x=0}^{x=r} a_1 \cos \pi x/r \cdot \cos n\pi x/r \cdot dx = \frac{1}{2} a_1 \left\{ \int_{x=0}^{x=r} \cos \frac{(n+1)\pi x}{r} \cdot dx + \int_{x=0}^{x=r} \cos \frac{(n-1)\pi x}{r} \cdot dx \right\}$$

Evaluating the above integral between the assigned limits we obtain zero. In the same way all terms except the n.th fall out.

Making use of the relations,

$$\sin^2 A = \frac{1}{2}(1 - \cos 2A) \quad \text{and} \quad \cos^2 A = 1 - \sin^2 A, \text{ and hence,}$$

$$\cos^2 A = \frac{1}{2}(\cos 2A + 1), \quad \text{and putting } \frac{n\pi x}{r} = A,$$

and substituting in the n.th term we have,

$$ar/n\pi \int_{x=0}^{x=r} \cos A \cdot dA = ar/2n\pi \int_{x=0}^{x=r} \cos 2A \cdot dA + ar \cdot A/2n\pi = \\ ar/4n\pi \cdot \sin A + ar \cdot A/2n\pi.$$

Within the assigned limits the sine of A is always zero (being a multiple of π):- Hence, replacing A by its value $n\pi x/r$, and solving for a_n we have,

$$a_n = 2/r \cdot \int_{x=0}^{x=r} f(x) \cdot \cos n\pi x/r \cdot dx$$

For this special case, when $t = 0$, $u = u$, from $x = 0$

to $x = r/2$; $u = 0$ from $x = r/2$ to $x = r$, hence:

$$a_n = 2u/r \int_{x=0}^{x=\pi/2} \cos n\pi x/r \cdot dx = 2u/n\pi \cdot \sin n\pi/2$$

Hence: $a_1 = 2u$, $a_2 = 0$, $a_3 = 2u/3$, $a_4 = 0$, $a_5 = 2u/5$,

(Note that we can not obtain a_0 from the above formula because it takes the indeterminate form $0/0$.) To determine a_0 take our equation before integrating and put $t = \infty$, $f(x)$ or u now clearly becomes $\frac{1}{2}u_0$, and all other terms on the right except the first or "zero" term vanish; hence, $a_0 = \frac{1}{2}u_0$.

We can now write the complete solution for our case, which is;-

$$(IV) \int_{x=0}^{x=\frac{\pi}{2}} f(x) \cdot dx = \int_{x=0}^{x=\frac{\pi}{2}} u \cdot dx = ru/4 + 2u/\pi \cdot r/\pi \cdot \sin \pi/2 \cdot e^{-\frac{\pi^2 x^2}{r^2}} + 0 + 2u/3\pi \cdot r/3\pi \cdot \sin 3\pi/2 \cdot e^{-\frac{9\pi^2 x^2}{r^2}} + 0 - \dots\dots\dots$$

Note that all the even terms fall out (because they contain the ~~the~~ expression $\sin \underline{m}$, where \underline{m} is an integral. Also as the series stands we see that the sines are alternately $+1$ and -1 , hence we can write,

$$(V) \int_{x=0}^{x=\frac{\pi}{2}} f(x) \cdot dx = 2u_0 \cdot r \left\{ 1/8 + 1/\pi^2 \cdot e^{-\frac{\pi^2 x^2}{r^2}} - 1/9\pi^2 \cdot e^{-\frac{9\pi^2 x^2}{r^2}} + 1/25\pi^2 \cdot e^{-\frac{25\pi^2 x^2}{r^2}} - 1/49\pi^2 \cdot e^{-\frac{49\pi^2 x^2}{r^2}} \dots\dots\dots \right\}$$

Numerical Considerations. For our case,

$r = 50$ approximately

$k = 1.2$ "

$t = 3$ "

The third term in (V) becomes therefore:

$$X = 1/89 \cdot e^{-\frac{9\pi^2 \cdot 1.5 \times 3}{50}} = 1/89 \cdot e^{-8}$$

Put $e^{-8} = N$, then will $\ln_e N = 8$; and hence

$$\log_{10} N = .4343 \times 8 = 3.47 \text{ (approximately)}$$

Finding the number corresponding to this logarithm from tables, we have;

$$N = 3000 \text{ (approximately)}$$

$$\text{Hence, } X = \frac{1}{89 \times 3000} = 3.75 \times 10^{-6} = .00000375$$

This value is obviously too small to have any significance; and as all succeeding terms are very much smaller and alternating in sign, we can with perfect safety discard all after the first two.

Computing the amount of diffusing substance in either layer after lapse of time t . Let V_0 be the amount of iodine(say) originally put in the cylinder, V_1 the amount left in the lower layer after time t , V_2 that found in the upper layer after time t . Obviously,

$$V_2 = \sigma \int_{x=0}^{x=r} u \cdot dx = 2\sigma \cdot u_0 \cdot r \left\{ 1/8 + 1/H^2 \cdot e^{-\frac{\pi^2 k t}{r^2}} \right\}$$

(Where σ is the cross section.) Also,

$$V_0 = \frac{1}{2} \sigma \cdot u_0 \cdot r$$

Therefore,

$$V_2 = 4 V_0 \left\{ 1/8 + 1/H^2 \cdot e^{-\frac{\pi^2 k t}{r^2}} \right\}$$

Or,

$$e^{-\frac{\pi^2 k t}{r^2}} = \left\{ \frac{V_2}{4V_0} - \frac{1}{8} \right\} H^2$$

Put $V_2 = V_0 - V_1$, and solve for k ,

$$\begin{aligned} k &= -\frac{r^2}{H^2 t} \cdot \ln_e \left\{ \frac{V_0 - 2V_1}{V_0} \cdot \frac{H^2}{8} \right\} = \frac{r^2}{H^2 t} \ln_e \left\{ \frac{V_0}{V_0 - 2V_1} \cdot \frac{8}{H^2} \right\} \\ &= \frac{r^2}{H^2 t} 2.30 \cdot \log_{10} \left\{ \frac{8}{H^2} \cdot \frac{V_0}{V_0 - 2V_1} \right\} \\ &= \frac{r^2}{H^2 t} 0.233 \cdot \log_{10} \left\{ 0.8106 \frac{V_0}{V_0 - 2V_1} \right\} \end{aligned}$$

This last is the formula used in all cases for computing k by the two layer method.

I wish here ~~to~~ specially to acknowledge my indebtedness to Dr. C.M. Sparrow for time and assistance freely given in aiding me to an understanding of the mathematics involved in this problem.

PRELIMINARY TABLE.

Diffusion of Iodine in Potassium Iodide.

Values obtained by Dr. Graham Edgar alone previous to the author's first work. This work was done with apparatus involving the four layer system, and each value given is the mean of the most concordant values for two, three, or four layers.

100 gms. KI per litre K = 1.093

200 gms. KI per litre K = 1.191

400 gms. KI per litre K = 1.278

Translated into terms of normal solutions the above becomes:

0.60 normal K = 1.093

1.20 normal K = 1.191

2.40 normal K = 1.278

These values are made use of in future tables, due note being made of the fact in each case.

TABLE I.

Diffusion of Iodine in Potassium Iodide .

Normality of KI_3 , 1/20 --- o --- of KI , 1/1 .

$$K = \frac{l}{t} 0.233 \cdot \log \left\{ 0.8106 \frac{V_o}{V_o - 2V_i} \right\}$$

date 1913.	*	L	L'	t days	V _o	V _i	Temp.	K	K@25°
July 15-19.	a	7.54	56.9	3.72	26.20	8.18	25°	1.20	1.20 ₀
"	b	7.56	57.2	3.73	"	8.18	25°	1.19	1.19 ₀
"	c	7.60	58.0	3.74	"	7.90	25°	(1.12)	
"	d [#]	7.57	57.3	3.75	"	7.95	22½°	1.12	1.19 ₀
"	e [#]	7.57	57.3	3.74	"	8.40	25°	(1.26)	
July 21-25	a	7.54	56.9	4.01	26.50	8.51	24.8°	1.175	1.18 ₀
"	b	7.56	57.2	4.02	"	8.54	24.8°	1.183	1.19 ₀
"	c	7.60	58.0	4.02	"	8.52	24.8°	1.194	1.20 ₀
"	d [#]	7.57	57.3	4.01	"	8.25	23°	1.167	1.207
"	e [#]	7.57	57.3	4.02	"	8.25	23°	1.165	1.205
MEAN -									1.204

* Letters in this column were distinguishing marks on cylinders, scratched with a diamond.

These cylinders were not in thermostat, but in a vacuum flask filled with water at room temperature.

Bracketed values for K are not counted in mean.

(Work of author under guidance and direction
of Dr. Graham Edgar)

TABLE II.

Diffusion of Iodine in Potassium Iodide.

Normality of KI_3 , 1/20 --- o --- of KI , 1/2.All cylinders in thermostat at 25° .

Date 1913.	*	ϕ	ϕ'	t	V_o	V_i	K
September 27 - 30	a'	7.48	56.2	3.02	38.50	11.08	(1.21 <u>o</u>)
"	c	7.60	58.0	3.02	"	11.20	(1.28)
"	d	7.57	57.3	3.02	"	12.30	(1.49)
"	e	7.57	57.3	3.02	"	11.50	(1.46)
Sep. & Oct 30 - 4	a'	7.48	56.2	3.68	39.00	11.80	1.10 <u>o</u>
"	c	7.60	58.0	3.68	"	13.20
"	e	7.57	57.3	3.69	"	11.50	1.09 <u>o</u>
"	d	7.57	57.3	3.69	"	13.0
October. 4 - 8	a'	7.47	56.2	3.75	39.40	12.20	(1.14)
"	c	7.60	58.0	3.75	"	11.88	(1.12)
"	d	7.57	57.3	3.75	"	11.70	1.07 <u>o</u>
"	e	7.57	57.3	3.75	"	11.70	1.07 <u>o</u>
October. 16 - 21	a'	7.48	56.2	3.73	42.00	16.40	(1.135)
"	c	7.60	58.0	3.73	"	12.40	1.07 <u>2</u>
"	d	7.57	57.3	3.73	"	12.50	1.07 <u>2</u>
"	e	7.57	57.3	3.75	"	12.50	1.07 <u>2</u>
						MEAN	1.08 <u>o</u>

Bracketed values, or uncomputed values of K not counted in mean.

(Work of the author under guidance and direction of Dr. Edgar)

TABLE III.

Normality of KI_3 , 1/20 --- o --- of KI , 1/4

Diffusion of Iodine in Potassium Iodide.

All cylinders in thermostat at 25° .

Date 1913.	*	l	l'	t	V_o	V_i	$K @ 25^{\circ}$
October 25 - 29	a'	7.48	56.2	3.70	49.05	14.5	(1.055)
"	c	7.60	58.0	3.70	"	14.40	1.083
"	d	7.57	57.3	3.70	"	14.50	1.080
"	e	7.57	57.3	3.70	"	14.50	1.080
						MEAN	1.080

(Work of the author under the guidance and direction
of Dr. Graham Edgar)

TABLE IV.

Diffusion of Iodine in Potassium Iodide.

Normality of KI_3 , 1/20 --- o --- of KI , 2.All cylinders in thermostat at 25° .

Date 1913.	*	t_1	t_2	t	V_0	V_1	K @ 25°
September	a'	7.48	56.2		35.32	10.20	1.25
"	e	7.50	58.6		"	10.15	1.26
"	d	7.57	57.3		"	10.26	1.27
"	e	7.57	57.3		"	11.10	(1.65)
						MEAN	1.26

Solely the work of Dr. Edgar, done early in September,
the author being sick at that time.

TABLE V.

Diffusion of Iodine in Potassium Iodide.

Normality of KI_3 , 1/20 --- o --- of KI , 3.All cylinders in thermostat at 25° .

(Work of the author under the direction of Dr. Edgar)

Date 1913.	*	l	l^2	t	V_o	V_i	$K @ 25^\circ$
Oct. - Nov 30 - 1	a'	7.48	56.2	3.10	41.30	12.54	(1.283)
"	c	7.60	58.0	3.10	"	14.45
"	d	7.57	57.3	3.10	"	14.70
"	e	7.57	57.3	3.10	"	20.20
November 4 - 7	a'	7.48	56.2	3.20	48.30	14.30	(1.220)
"	c	7.60	58.0	3.21	"	14.30	1.255
"	d	7.57	57.3	3.21	"	14.20	(1.223)
"	e	7.57	57.3	3.22	"	16.0
November 8 - 12	a'	7.48	56.2	3.74	48.6	15.85	1.285
"	c	7.60	58.0	3.74	"	15.75	1.300
"	d	7.57	57.3	3.74	"	15.50	1.250
"	e	7.57	57.3	3.74	"	18.
November 14 - 17	a'	7.48	56.2	3.06	48.90	14.45	1.275
"	c	7.60	58.0	3.06	"	14.30	1.285
"	d	7.57	57.3	3.06	"	14.30	1.275
"	e	7.57	57.3	3.06	"	14.30	1.275
November 24 - 27	a'	7.48	56.2	2.92	51.00	14.95	1.305
"	c	7.60	58.0	2.92	"	14.50	1.268
"	d	7.57	57.3	2.92	"	cracked	
						MEAN	1.277

TABLE VI.

Diffusion of Iodine in Potassium Iodide.

Normality of KI_3 , $1/20$ --- o --- of KI , $4\frac{1}{2}$.All cylinders in thermostat at 25° .

Date 1913.	*	l	l^2	t	V_o	V_i	$K @ 25^\circ$
December 5 - 8	a'	7.48	56.2	3.73	33.50	13.60
"	c	7.60	58.0	3.73	"	10.6
"	d	7.57	57.3	3.73	"	12.4
December 10 - 13	a'	7.48	56.2	3.145	44.75	13.50 [#]	(1.291) 1.280
"	c	7.60	58.0	"	"	13.20	1.271
"	d	7.57	57.3	"	"	13.30	1.276
						MEAN	1.278

(Work of the author under the guidance and direction
of Dr. Graham Sugar.)

In this case 2 drops too much were drawn off with
the layer titrated. Making an approximate correction
one obtains the unbracketed figures for K.

This and the last ##### table were especially
difficult to obtain owing to the exceedingly small
difference between the specific gravity of the KI solu-
tion and that containing the iodine.

Determination of Viscosity and Density of KI Solutions.

The apparatus used in determining the density consisted of a very accurate set of hydrometers, graduated to three decimal places and readily estimated to the fourth place. The viscosity determinations were made with the usual Ostwald-Poiseuille apparatus. The one used for the first nine values was a commercial viscosity meter having a very short period of delivery (about 45 seconds at 25°). The last four determinations were made with an apparatus made by Dr. Edgar for the purpose, and having a period of delivery of about 100 seconds. For our purposes the results found by using either apparatus are sufficiently accurate.


The formula used to obtain the relative viscosity is: $\eta/\eta_0 = t_0/t$, (30, 31). In table VII η at 25° for water is taken to be unity, the viscosity at 25° is taken to be 0.50 of that at zero, and the viscosity of water at zero is taken to be 0.018086 C.G.S. units. (32, 33). For our immediate purpose the unit chosen is of no importance, yet in view of the fact that ~~that~~ no satisfactory table of viscosities for potassium iodide solutions is known, it seemed worth while to give these values in terms of all commonly used units. The best data that could be found on this subject was that of Taylor & Rankin (1903). Their results, so far as comparable, agree fairly well with ours; but as he worked with only three concentrations his data was not sufficient for our purposes. Getman (1906 - 1908) also de-

terminated the viscosity of KI solutions of different concentrations, but his work was done at 18°.

In drawing the curves for Fluidity, Density, and Diffusion, the axes were so shifted as to give a set of curves that could all be drawn on the same sheet for the sake of comparison. A full discussion of these curves will be found in ~~the~~ proper place.

TABLE VII.

Diffusion of Iodine in comparison with Viscosity
and Density of the KI solution. @ 25°.

Normal- ity.	Time of flow.	Z Rel. 25°	Z' Rel. 0°	η Absol't	F Fluidity	ρ Density	K Diff.
0.125	44.4	0.992	0.496	00897	1.01	1.0125	
0.25	43.8	.997	.499	00898	1.01	1.0275	1.08
0.50	41.8	.976	.488	00883	1.02½	1.058	1.08
0.60	* 1.09
0.75	40.2	.967	.483	00874	1.03½	1.089	
1.00	38.6	.952	.476	00861	1.05	1.118	1.20
1.20	* 1.194
1.50	36.2	.940	.470	00849	1.06	1.176	
2.00	34.2	.933	.467	00843	1.07	1.236	1.26
2.40	* 1.278
2.50	32.6	.932	.466	00842	1.07	1.295	
3.00	31.4	.937	.469	00847	1.07-	1.352	1.277
3.50		.943	.472	00852	1.06	1.4105	
4.00	*	.960	.480	00858	1.04½	1.468	
4.50	*	.978	.489	00884	1.02	1.526	1.278
5.00	*	1.015	.508	00918	0.996	1.583	

Z Viscosity relative to water @ 25°.

Z' Viscosity relative to water @ 0°.

η Absolute viscosity, C.G.S. units.

F Fluidity, reciprocal of Z.

* Obtained by Dr. Graham Edgar alone.

(Except as noted, work of Dr. Graham Edgar and the author.)

TABLE VIII.

Ordinates for the curves on the next page
and

The Diffusion Constant computed from these curves.

Normal- ity	$(F-1)100$	$(\rho-1)20$	y'' ($K-102$)50	y'' From Curve	K' Curve	K Exper.	value of value of $K'E$
0.125	1.	0.25					#
0.25	1.	0.55	$\frac{3.0}{(2.4)}$	1.8	1.056	$\frac{1.08}{(1.055)}$	$\frac{2.2}{1.0} \%$
0.50	2.5	1.2	3.0	3.7	1.094	1.08	1.3 %
0.60	3.6	4.4	1.108	1.09	1.6 %
0.75	3.5	1.8		5.3	1.126		
1.00	5.	2.4	9.0	7.3	1.166	1.20	2.8 %
1.20	9.0	8.4	1.188	1.194	.5 %
1.50	6.4	3.5		9.9	1.220		
2.00	7.	4.7	12.0	11.7	1.254	1.26	.5 %
2.40	12.9	12.6	1.272	1.278	.5 %
2.50	7.	5.9		12.8	1.276		
3.00	6.7	7.0	12.9	13.7	1.294	1.277	1.3 %
3.50	6.	8.2		14.2	1.304		
4.00	4.2	9.4		13.7	1.294		
4.50	2.	10.5	12.9	12.5	1.270	1.278	.6 %
5.00	-0.4	11.7		11.3	1.246		

? y'' is ordinate for the dotted curve, made by adding the density and fluidity curves.

* The bracketed values are obtained from an actually found experimental value (Table III) that was not averaged in obtaining the mean.

Long before this curve method of obtaining probable values for K , had been thought of, an error of 2% was estimated.

PLATE I .

Feb. 1914. S.H. Diggs.

SCALE: EACH DIVISION 1, 2, 5, 10, 100, 1000, ETC.
OR 0.5, 0.2, 0.1, 0.01, 0.001, ETC.

THIS EDGE MUST BE EITHER TOP OR LEFT - HAND SIDE OF SHEET

RESERVE THIS MARGIN FOR BINDING

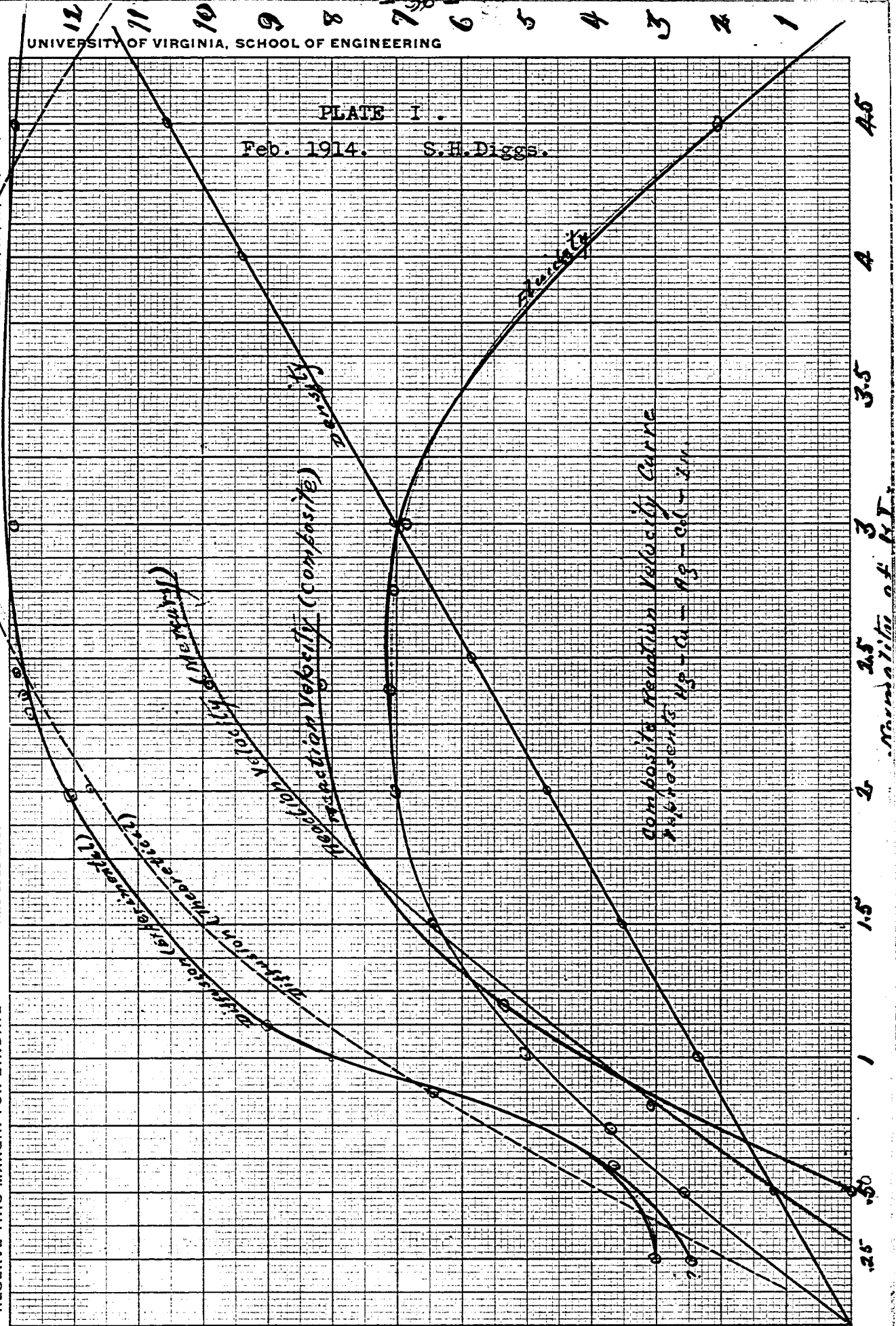


TABLE IX.

A comparison of Reaction Velocity Constants
with
Diffusion, Fluidity, and Density.

Also Ordinates for Reaction Velocity Curve.

Normal- ity	Fluidi- ty	Density	Diff.	A <i>average</i>	B Mercury	y_{Zn}	y'_{Hg}
0.125	1.01	1.0125					
0.25	1.01	1.0275	1.08				
0.50	1.02½	1.058	1.08				
0.60	1.09	8.71	8.81	1.05	1.55
0.75	1.03½	1.089					
1.00	1.05	1.118	1.20				
1.20	1.194	9.38	9.55	5.40	5.25
1.50	1.06	1.176					
2.00	1.07	1.236	1.26				
2.40	1.278	10.13	10.48	8.15	9.90
2.50	1.07	1.295					
3.00	1.07	1.352	1.272				
3.50	1.06	1.4105					
4.00	1.05½	1.468					
4.50	1.02	1.526	1.278				
5.00	0.996	1.583					

Reaction Velocities taken from the work of Van Name
and Edgar; see page 24.

$H_2 - Cu - Ag - Cd$ - averaged
A is reaction velocity for zinc, B for mercury.

$y = (A - 8.50)5$ (ordinate of "velocity constant" curve for Zn.)

$y' = (B - 8.50)5$ (" " " " " " Hg.)

TABLE X . (See plate II)

Densities and Viscosities of Solutions
of Lithium & Sodium Chloride.

(For comparison with potassium iodide)

Normal	Densit NaCl-15°	Visc. 25°	Density LiCl	Visc. LiCl	Density <i>ZnSO₄</i>	Visc.
0.125	1.0057	1.0126	1.0018	1.0116	1.008	1.0358
0.25	1.0112	1.0239	1.0047	1.0314	1.184	1.0824
0.50	1.0210	1.0471	1.0109	1.0665		1.1726
1.00	1.0426	1.0973	1.0231	1.1423	1.184	1.3671
1.50	1.0643		1.0355			
2.00	1.0862		1.0481		1.421	
2.50	1.1082		1.0597			
3.00	1.1313		1.0715			
3.50	1.1552		1.0836			
4.00	1.1781		1.0912			
4.50	1.2040		1.1100			
5.00			1.1222			
	*	#	##	* #*	*	#

* Van Nostrand's Chemical Annual (1913)

Landolt & Börnstein (4 Auflage)

" " " Page 273

Wagner, Zeit. für Phys. Chemie V, 31.

(Transformed from per cent to normal data by the writer)

PLATE II.

March 1914.

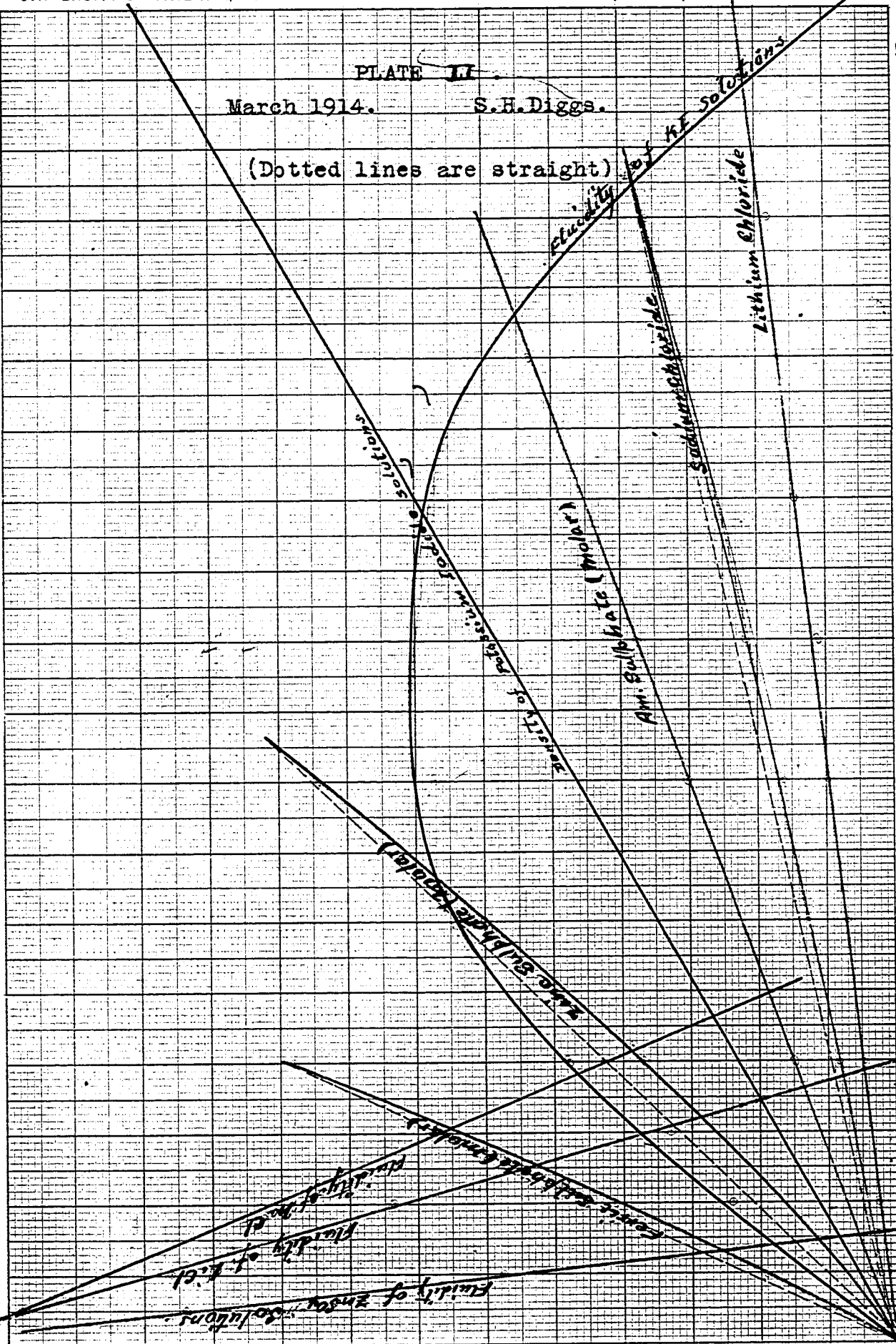
S.H. Diggs.

(Dotted lines are straight)

OR 0.6, 0.2, 0.1, 0.01, 0.001, ETC.

THIS EDGE MUST BE EITHER TOP OR LEFT - HAND SIDE OF SHEET

RESERVE THIS MARGIN FOR BINDING



Normality or Mols/Litre

Ordinates for Density Curves.

Discussion of Results. General Confirmation of the Work of
Van Name & Edgar, and others.

If we examine table IX, we see that there is no apparent discrepancy between the relative increase in the rate of reaction velocity with increasing concentration of KI and that of diffusion under the same circumstances. This becomes clearer if we examine the curves of these quantities. In fact we may say that within experimental error the curves for diffusion and for reaction velocity are parallel. (It is to be noted that the scale on which these curves are drawn magnifies the errors.) It is to be regretted that the work so done by Van Name and Edgar, and by Van Name and Bosworth do not give us any points on our curve beyond a concentration of 2.5 N, and hence we can only guess as to the probable form of the curve at higher concentrations. It would be very interesting and instructive to obtain a curve for reaction velocities covering all concentrations covered by the diffusion or viscosity data. As it is, there is no way to know if the reaction velocity curve continues to rise or like the diffusion curve falls or becomes flat at higher concentrations. In the absence of evidence the latter seems the more probable, for two reasons; (a) the velocity curve though still rising, is rising much more slowly near the end, (b) the reaction velocity curve has approximately the same form as the diffusion curve so far as it is known, and hence it seems reasonable to assume that it will, probably continue to have the same form.

General Theory of Diffusion. The phenomenon of diffusion may be defined in three ways according to the point of view,

Viz.:

1. As an empirical fact.
2. As a consequence of the kinetic theory.
3. As a result of the second law of thermodynamics, i.e. from the view point of energy relations.

1. Diffusion may be defined as the mixing which takes place when two dissimilar but miscible liquids are left in contact for some time under conditions precluding mechanical motion or convection. Or diffusion may be defined as the mixing taking place in a system that is isolated, thermally and mechanically.

2. Diffusion may be defined as mixing due to the random motion of molecular particles, in distinction from mixing due to directed motion of masses of the substance, e.g. mechanical mixing or convection.

3. Diffusion may be defined as mixing due to the decrease of the free energy of the system (increase of the entropy) in accordance with the second law of thermodynamics.

It should be noted that just as diffusion may be defined from the view point of the kinetic theory, so by a reciprocal process we may say that the facts of diffusion furnish the most striking, and to many minds the most convincing, proof of the kinetic theory.

In general it would follow as a consequence of the kinetic theory that the rate of diffusion should be a function of the temperature, of the size and nature

of the molecule, and of the medium through which diffusion takes place. (The mathematical treatment of diffusion when the temperature, kind of molecule, and medium are constant, has been taken up in detail for our particular case on a previous page.) Nernst has developed a very complete theory of diffusion for electrolytes which has already been mentioned in this article. In so far as an electrolyte is dissociated the separate ions will have independent motions within a certain narrow range, this range is very sharply limited by the large electrostatic forces that must come into play as soon as an accumulation of one kind of charge is perceptible in any part of the solution. (34)

On the above theory as a basis Nernst deduces the expression already given for the velocity of diffusion of an electrolyte; viz.:

$$K = \frac{2 uv}{u + v} \cdot g \cdot RT \cdot 10^{-9}$$

where u and v represent the ionic mobilities of the cation and anion respectively, and g is a constant depending on the unit in which K is given. It is assumed that conditions during diffusion are the same as when u and v are measured. This is not the case for us, and there is no way in which we can do more than guess the ionic mobilities under conditions of varying concentrations of KI.

Theory of the "Reststrom". If a very low potential difference be maintained between two electrodes immersed in a conducting solution it is found that a weak cur-

rent flows, even when this potential difference is far below the "decomposition potential" for the solution. Further, this current (Reststrom) does not obey Ohm's law, even approximately, for it remains almost constant through changes in the e.m.f. of several hundred per cent, say from 0.1 to 0.3 volt. Nernst and Merriam have shown that with rapid stirring at a given rate the Reststrom is practically constant over a very large range of potential differences, and is closely proportional to the rate of diffusion of the depolarizer. They make the assumption that this "Reststrom" is due to the diffusion of the ion or depolarizer (as the case may be) through the thin unstirred layer which they assume to cover the electrodes. (35)

Work of Harry Heymann. In 1912 Heymann made use of the "Reststrom" as a means of further establishing the "diffusion theory of reaction velocity in heterogeneous media". He worked with platinum catalysis of hydrogen peroxide, iodine in KI, and the solution of copper in $I_2 + KI$. In the preface to his article he calls attention to the fact that Van Name & Edgar had covered much the same ground, using various metals in $I_2 + KI$ solutions. Using a solution of N/1 KI in which was dissolved iodine Heymann determined the "Reststrom" using potentials varying from 0.1 to 0.45 volt. The "Reststrom" within these limits was practically constant as it was for Nernst & Merriam.

Heymann found that the thickness of the "unstirred

layer" decreased with more rapid stirring as did Van Name and Edgar. Heymann made a single determination of the diffusion constant for iodine in normal KI, directly, by a method practically similar to that used in this work. Using his value and extrapolating by Nernst's formula we obtain for the diffusion constant at 25° 1.19 . This is in close agreement with our observed data. Extrapolation is hardly fair however over so large a range of temperatures, as Heymann worked at about 8° . In the second part of his article Heymann discusses the work of Van Name & Edgar at length, and quotes much of their data to show that it is in line with the deductions made by Nernst, Merriam, and himself from experiments with the "Reststrom". He closes by saying,

"Aus an grossen Anzahl von Reststrombestimmungen fand ich, dass der Diffusionskoeffizient des Jods mit steigender KI-Konzentration stark wächst, und zwar ziemlich analog den von Van Name und Edgar gemessenen Auflösungsgeschwindigkeiten von Metallen in gleich konzentrierten Jodkaliumjodidlösungen." (36)

This, of course, is in accord with the results of the present writer also.

Discussion of some of the probable factors involved.

For our case as the temperature was held constant, and the iodine content (free) was also constant, the only independent variable was the concentration of the

KI. It is not so easy however to be sure that we have under consideration all of the dependent variables, and even if so it is in some cases difficult to determine what function such variables are of the concentration. The following factors will be discussed.

1. Density.
2. Fluidity (or reciprocal viscosity).
3. Dissociation of the KI_3 molecule into ions.
4. Effect of the common ion (K).

These factors will be taken up and discussed separately, and so far as possible the relation existing between them and the concentration of the KI will be determined.

Density & Concentration. A glance at the density curve for KI solutions (plates I & II) will show how exactly density and concentration go together for this salt. A careful scrutiny of table VII will show the same. Density curves for some other solutions will be found on plate II. While these curves are approximately straight lines, all have some perceptible curve except that for KI solutions, which is a straight line exactly, at least so far as our measurements show.

All curves on plate II are drawn on the same scale as those on plate I, and therefore are fairly comparable. The data was obtained from Van Nostrand's Chemical Annual (1909), Biedermann's Chemiker-Kalender (1913), Landolt-Börnstein-Roth's Tabellen (4th Auflage), or from original sources. In most cases laborious compu-

tations had to be made to transform by interpolation values given in per cent, into values for normal or molar solutions. This suggests the need for a set of tables giving the various physical properties of solutions for normal and molar concentrations instead of the usual per cent concentrations. Such tables should cover the fullest possible range, and not merely values below and up to normal as is the case for those few tables that use normality as the concentration unit.

The previously noted fact, that the density of KI solutions is directly and strictly proportional to the concentration of the KI prevents density from having any value as a variable. That is, we can not distinguish between the effects of density, as such, and of concentration, as such.

Fluidity & Concentration. By fluidity is meant the reciprocal of viscosity. For our purposes it matters little what units be used, but for convenience I have always taken the viscosity of pure water at 25° as unity, except when specifically stated otherwise. As in the case of density, viscosity is usually given in terms of per cent concentrations, and has to be changed to normal or molar terms before it is of real use for comparison. The only data of interest for us that could be found when this work was being done was that of Taylor & Rankin, who measured the viscosity of KI solutions at the following concentrations, 1.0 N, 2.0 N, and 3.0 N, at several temperatures. (37).

In view of the meagerness of the available data we determined the viscosity of various KI solutions (see table VII), and from this data the curves on plates I and II are drawn. If we examine plate II, we see that for most salts (ZnSO_4 , LiCl , & NaCl are shown.) the fluidity rapidly falls as the concentration increases, that both density curves and fluidity curves are almost straight lines; and hence the one varies inversely as the other. For KI the fluidity curve is very peculiar, it first rises and then falls, being fairly symmetrical and having a maximum at about 2.5 normal concentration.

If we examine the diffusion curve (plate I) in comparison with the fluidity curve we see that it rises, as was to be expected, with the fluidity curve; but much more rapidly. Further, at about the concentration at which the fluidity curve shows a maximum, the diffusion curve becomes almost flat. Thus we see that diffusion can not depend on viscosity alone for our case, as was thought probable when the work was begun. It is interesting to note that so long as the fluidity curve rises, the diffusion curve rises more rapidly than either the fluidity curve or the density curve; and that as these two curves begin to go apart the diffusion curve ceases to rise and becomes flat. This seems to indicate some relation between the density and the rate of diffusion similar to that between the fluidity and the rate of diffusion. (Ofcourse here density and concentration of KI go hand in hand.)

Degree of Dissociation of KI_3 . Osaka has shown that KI_3 is probably less dissociated than KI (27). Hence, its dissociation would be very much driven back in strong KI solution. This would mean a far larger proportion of undissociated KI_3 molecules in such solutions. If now we assume that the effects of increasing viscosity is less on KI_3 than on the ions of the same salt, we have a possible explanation of the observed facts. This explanation is, ofcourse, very far from satisfactory, for we do not know that the effect of increasing viscosity on the KI_3 and its ions is as indicated. (Argumentum ad ignorantium) Yet in the absence of something better it may serve as a hint of a possible explanation.

In general it is supposed that ions migrate faster than the corresponding undissociated salt. This would seem probable a priori as the undissociated molecule must be larger, unless the ion is hydrated to a greater extent than the molecule. Ohlm has made a special study of the rate of diffusion of electrolytes, comparing the diffusion constant calculated from Nernst's formula with experimental values. In most cases the observed rate of diffusion was less than that calculated, and the discrepancy was far greater for weak than for strong electrolytes. This is easiest explained by assuming that the undissociated molecule migrates more slowly than the ions, hence, the diffusion constant calculated for complete dissociation will always be too great unless the dissociation be complete.

These observations are not in accord with the experimental facts for our case, and they apparently contradict the possible explanation suggested on a previous page; however, the theory of Nernst and the experiments of Öholm have value for water solution only and need not hold for KI solution.

Influence of an added electrolyte having a Common Ion.

It has been shown by Abegg & Bose (38) that the effect of an added electrolyte having an ion common with the diffusing electrolyte is to make the rate of diffusion approach that of the ion that is not common. The following scheme, taken from the article by Abegg & Bose, will make clear why this should be so, and as a matter of experimental fact it is so.

Let us consider two diffusion systems. In the first let there be two layers of the same electrolyte A.B having in one layer the concentration c and in the other layer the concentration $c + dc$. In the second system let there be the same electrolyte having the same concentration, and also the added electrolyte A.X having the same concentration C in both layers - C being very great in comparison with c . Then will the scheme given below represent the concentration of all kinds, supposing the dissociation to be complete. we see that in system two, the common ^{ion} A has practically the same concentration in both layers, and hence it diffuses very slowly. This leaves the uncommon ion as the only factor of importance in the rate of diffusion.

Ofcourse in practice these conditions are not realized, but the rate ~~de~~^{of} diffusion approaches that of the uncommon ion as the concentration of the added electrolyte increases in comparison with that of the original diffusing electrolyte.

Scheme copied from Abegg & Bose. (38)

I		II	
A (c)	A (c + dc)	A (c+C)	A (c + C+dc)
B (c)	B (c + dc)	B (c)	B (c + dc)
		X (C)	X (C)

For our case this would mean that the rate of diffusion would approach nearer and nearer to that of the I_3 ion as the concentration of the KI increased. As the migration velocity for I_3 is certainly less than for K we should expect the rate of diffusion to fall off with increasing concentration of KI. This it does not do. (According to Bredig the migration number for I_3 is 44.2, according to Crotogino it is 60, that for K is well known to be about 65.3 (39,40,41)). The above forces us to conclude that other and more potent factors are working in the opposite direction.

Discussion of Plate I. A careful review of the factors just discussed leads us to the consideration of the only two independent variables (or variables not known to be simply related) having important and traceable effect on the diffusion. These are the fluidity and the density of the solution. The effect of the fluidity is as one would theoretically expect it to be, at least

up to about 2 N; but it is not clear why the rate of diffusion should increase with density, though it certainly does as is shown by the curves on plate I.

The simplest assumption that can be made as to the effects of viscosity, and density, respectively, is that the rate of diffusion varies directly as the density and inversely as the viscosity; or that the rate of diffusion varies as the product of density and fluidity. This assumption however can not be even approximately true, for it would necessitate a very much more rapid increase in the rate of diffusion than is shown by experiment. However, the writer has deduced an empirical expression, by means of the three curves in question, which gives a very satisfactory numerical relation between the diffusion constant and the fluidity and density. It is,

$$50(K - 1.02) = 100(F - 1) - 20(\rho - 1)$$

or

$$K = 2F + 0.4\rho - 1.42$$

K calculated according to this equation gives the dotted curve for diffusion on plate I. The difference between the diffusion constant thus calculated and that actually found by experiment is given in the last column of table VIII. The maximum variation is 2.8 %. This is hardly greater than the probable maximum error, and the average variation is certainly within the probable error of experimentation. While it is not to be expected that this equation expresses the exact relation, it is probable that it is a fairly close approximation.

It is of interest to note that the curve thus calculated shows a maximum at a concentration of about 3.5 N, a point at which we have no experimental data, and falls to very nearly the observed value at 4.5 N, the next point at which we have an experimental value for the diffusion. The writer hopes at some time in the near future to find by experiment whether or not such a maximum really exists at about this concentration. Also it would be interesting to see if the diffusion curve falls, as does the ~~experimental~~^{theoretical} curve, at concentrations higher than 4.5 normal. All that we can say at present is that the empirical equation given above in all probability gives a fair approximation to the truth.

The following empirical formula also gives a fair approximation^o to the experimental value for diffusion constants,

$$K = F\sqrt{P} + A$$

where A is a constant (about 6). This formula seems to have a somewhat more rational basis than the one previously given, but it does not agree quite so well with the experimental facts. Table XI gives the values so calculated, and also those obtained by the former method, in comparison with the experimental data. In any case it is necessary to assume that the density is an important and direct factor in the rate of diffusion. (Ofcourse we can not distinguish between density and concentration.)

TABLE XI.

A comparison of diffusion as calculated from the formula

$$(I) \quad K = 2F + 0.4 \rho - 1.42$$

and the formula,

$$(II) \quad K = F \sqrt{\rho} + A \quad (\text{Where } A = \underline{6})$$

and the experimental values.

Normality	Diffusion I	Diffusion II	Diffusion Experimental
0.125
0.25	1.06	1.08	1.08 (1.065)
0.50	1.09	1.09	1.08
0.60	1.09
0.75	1.13	1.14
1.00	1.17	1.17	1.20
1.20	1.194
1.50	1.22	1.21
2.00	1.25	1.25	1.26
2.40	1.28
2.50	1.28	1.28
3.00	1.29½	1.30	1.28
3.50	1.30	1.32
4.00	1.29½	1.34
4.50	1.27	1.32	1.28
5.00	1.25	1.31

Summary.

1. It has been shown that the rate of diffusion of iodine in KI solution increases with the concentration of the potassium iodide, as was anticipated from the results of reaction velocity experiments performed by Van Name and Edgar.
2. Determinations of the density and viscosity of KI solutions were made for the following concentrations, 0.125 N, 0.25 N, 0.50 N, 1.00 N, 1.50 N, and so on up to 5.00 N.
3. Curves have been drawn showing the relation of fluidity (viscosity), density, and diffusion, to concentration of potassium iodide, and to each other.
4. A comparison has been made with some other well known salts, and curves to illustrate this have been drawn. Also an empirical expression has been found to express approximately the relation between the fluidity, density and diffusion, for our particular case, i.e. iodine in KI solution.
5. The diffusion theory of reaction velocity in general, and the work of Van Name and Edgar in particular, has been completely confirmed, in so far as the disturbing effect of increased concentration of KI is concerned.

For aid, assistance, encouragement, and guidance, always freely given, the writer wishes particularly to thank Professor Graham Edgar, under whose direction and with whose assistance the work was done. He also wishes to thank Professor L.G. Hoxton and Professor C.M. Sparrow for many hints and for encouragement in performing the work.

University of Virginia.
March 18, 1914.

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1909.

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1909.

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1905.

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Van NAME & EDGAR

1910.

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DIFFUSION OF IODINE IN POTASSIUM IODIDE.

The work of ^{Edgar} Van Name and ~~#####~~ and of Van Name and Bosworth discussed above showed plainly that "An increase in the concentration of the potassium iodide produces a marked acceleration of the reaction." As no data were available bearing upon the rate of iodine in potassium iodide solutions varying in concentration to anything like the amount involved in the experiments of Van Name and his coworkers ~~#####~~ a few rough determinations were made by Van Name and Edgar. These, however, owing to the experimental difficulties encountered and to the lack of time to push further a side investigation, only gave a rough and unsatisfactory confirmation of the hypothesis. During the winter of 1911 - 12 Dr. Graham Edgar ~~and~~ ~~#####~~ made a few determinations of the same kind at the University of Virginia.

The results of these preliminary investigations showed that it was very probable that the original hypothesis was ~~#####~~ correct as to iodine diffusing more rapidly in strong than in weak potassium iodide solutions, also that the value of the diffusion constant was somewhere about 1.1 . It also developed that experimental difficulties were much greater than had been anticipated.