S 80. *The Use of Radioactive Isotopes in the Study of the Diffusion of Ions in Solution.*

By J. S. ANDERSON and K. SADDINGTON.

A method is described by which the " self-diffusion " coefficient of an ion may be determined. It involves the preparation of two solutions which are identical except that in one of them the ion is " labelled " by means of a suitable radioactive tracer atom. A capillary cell is charged with the active solution and immersed in the inactive liquid for a known length of time so that normal diffusion can take place. The cell contents are then transferred to a suitable tray, evaporated to dryness, and the radioactive content measured in standard counting equipment. A reference tray is similarly prepared, a known volume of the active solution which has not undergone the diffusion process being used. The activity of this tray is measured immediately after that of the experimental tray, and from the values so obtained, that fraction of the original cell content which has passed out of it as a result of diffusion can be calculated. Knowing the length of the capillary cell and the time of diffusion, the self-diffusion coefficient of the ion may be calculated. Some results obtained on application of the method to the system of tungstic acids are described.

RATES of diffusion of particles in solution, as a means of determining molecular weights, have been investigated over a number of years, and have found extensive application in the study of high-molecular substances. Such measurements can also be of value in following changes of molecular complexity in inorganic systems, if the true diffusion coefficients of ions can be evaluated.

The methods generally employed in diffusion studies have been based on the analytical determination of the amount of solute which has passed by diffusion from a concentrated solution to a less concentrated solution or to the pure solvent; the use of two liquid layers, with a known concentration gradient between them, is necessary in order to determine the movement of the solute. Experimentally, measurements of this type can easily be vitiated through hydrodynamic mixing of the solutions, set up by convection, and, although the effect of convection may be avoided by interposing a permeable membrane or a porous diaphragm between the solutions, fresh uncertainties as to the true concentration gradient can be introduced thereby. A summary of experimental methods for the study of diffusion in solutions is given in Jellinek's " Lehrbuch der Physikalische Chemie," Vol. II, p. 836 (1928), and an account of membrane diffusion is to be found in " Physico-Chemical Methods," Vol. III, p. 133, by Reilly and Rae.

In applying diffusion measurements to the study of electrolyte solutions, the concentration gradient occasions a further difficulty. In the majority of cases, the cation and anion will diffuse at different rates. Although this would cause no difficulty in a chemically homogeneous system—that is, one in which the solute concentration was the same throughout—a diffusion potential will be set up when diffusion takes place across the interface between two solutions which differ in concentration. Owing to the mutual effect of the oppositely charged ions, the ion which diffuses at the faster rate will be retarded by the slower ion, and *vice versa.* The measured rate of diffusion, therefore, will not be that of either cation or anion independently, but will be an average rate of diffusion corresponding to the electrolyte molecule as a whole. To overcome this difficulty, Abegg and Bose (*Z. physikal. Chem.*, 1899, **30**, 545) recommended the addition of a ten-fold excess of a neutral electrolyte, distributed uniformly throughout the diffusion system. The diffusing ions are thus enabled to move in all parts of the system in a fairly uniform ionic atmosphere, so preserving electro-neutrality throughout the solutions. This device was adopted by Jander *et al.* (*ibid.*, 1930, *A*, **149**, 97 : *Kolloid-Beih.*, 1935, **41**, 9) in their work on the poly-acids.

The availability of radioactive isotopes now makes it possible to carry out an experiment hitherto theoretical in character only, namely, the investigation of self-diffusion in solutions, *i.e.*, diffusion under conditions involving no concentration gradient. The electro-striction effect is, therefore, automatically eliminated without the necessity of adding to the experimental solutions any foreign electrolyte. The use of such radioactive tracers has a further advantage from the theoretical standpoint : namely, the greater sensitivity which can be reached in the determination of materials by radioactive assay, which makes it possible to extend the investigations to solutions more dilute than could be used hitherto, and more nearly approaching, therefore, those ideal conditions for which Fick's diffusion equation (see below) is applicable in solutions of electrolytes.

The object of the present work was to explore the possibilities of using radioactive tracers in the study of diffusion processes. Solutions of sodium tungstate were used since the method is peculiarly suitable for the study of the reversible processes of aggregation in such solutions, where especial interest attaches to the nature of the polyacid anions (or, in other cases, polycations) formed as intermediates between the simple ions, such as the WO_4^{2-} ions, and the colloidal oxides precipitated at the isoelectric point.

EXPERIMENTAL.

Technique.—The technique employed is a modification of one used by Dr. H. London (private communication) for the measurement of the inter-diffusion coefficient of copper and zinc ions in solutions. In experiments under conditions such that a concentration gradient is present, there is also a gradient in specific gravity which can be used, as in Jander's work (*loc. cit.*), to suppress convection currents. When there is no density gradient, this stabilising effect is absent. This difficulty is overcome in the present work by using narrow capillaries as diffusion cells. A very small gradient in specific gravity is then sufficient to suppress convection, the small difference in concentrations necessary to obtain such a gradient being insufficient to have any appreciable effect on the results. That there is, in fact, no significant error due to convection is shown in that the measured diffusion coefficient does not drift with increase in the duration of the experiment, as the interface moves down the cell, and as end effects become less important.

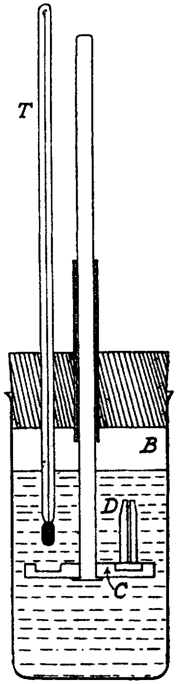
The apparatus is shown in Fig. 1. The diffusion cells, approximately 2 cm. long and of 0·8 mm. internal diameter, are made of glass capillary tubing of uniform bore. The ends are first ground perfectly flat; the diameter of each cell is then determined by a mercury thread, and the length measured with a micrometer. A ground-glass cover is then sealed on to the bottom end. The cells can be filled, emptied, washed out, etc., by using capillary pipettes operated either by hand or by means of a micro-manipulator. The cells, one of which is shown, *D*, are held in a Perspex carrier *C* supported in a rubber stopper which also carries a thermometer *T*. The stopper fits into the neck of a 150-ml. beaker *B* which is kept at a constant temperature of 20° ± 0·02° in a thermostat for the duration of the experiment.

In carrying out an experiment, *B* is charged with 100 ml. of inactive solution. The capillary cells are filled with a second solution—essentially the same as that in *B* as regards pH, concentration, etc., but differing in that in the preparation of this solution a radioactive isotope has been incorporated. The carrier *C* is fixed relative to the rubber stopper in such a way that the open ends of the cells are kept just above the level of the liquid in *B* for about an hour, in order that thermal equilibrium may be attained. The carrier is then gently lowered into the bath solution so as to immerse the cells completely.

Diffusion takes place for a known length of time—usually about 3 days. The contents of each cell are then transferred to a suitable tray, the cells washed out, and the washings added to the same tray. The liquid portion of the tray contents is gently evaporated off, and the radioactive content of the tray measured in standard α- or β-counting equipment.

A reference tray is prepared in the same way, a known volume of the capillary solution being used in which radioactive decay has also occurred, but which has not been subjected to the diffusion process. The activity of this tray is measured in the same equipment, under the same conditions and immediately after the experimental tray. From the values obtained for the experimental and reference samples it is possible to calculate what fraction of the amount of radioactive isotope originally present has been transferred out of the cell as a result of the diffusion process. The decrease in radioactivity due to natural decay only is automatically corrected for by determining the activity of the reference tray immediately after that of the experimental tray.

FIG. 1.



The usual assumption in this type of experiment is made, *viz.*, that, despite the slight difference in mass, the tracer atoms behave in precisely the same way as the inactive atoms.

If, therefore, it is found that a fraction $(1 - \gamma)$ of the active isotope originally present in the cell diffuses out of it in a given time, this value also represents that fraction of the total concentration, active plus inactive, of the element under investigation which passes by diffusion out of the cell under the same conditions.

Fick's law states that

$$\partial c/\partial t = D.\partial^2 c/\partial x^2 \quad . \ . \ . \ . \ . \ . \ . \quad \text{(i)}$$

The expression (i) can be integrated so as to obtain the expression (ii) which is applicable to the conditions as outlined above :

$$\gamma = \frac{8}{\pi^2}\left[e^{-\theta} + \frac{e^{-9\theta}}{9} + \frac{e^{-25\theta}}{25} + \ldots\right] \quad . \ . \ . \ . \ . \quad \text{(ii)}$$

where γ is that fraction of the original amount of radioactive isotope which is left in the capillary cell at the end of the diffusion, and $\theta = \pi^2 Dt/4l^2$, where D = diffusion coefficient at 20°, t = time of diffusion, and l = length of capillary cell. By use of equation (ii), the value of D can be calculated from a knowledge of t, l, and γ.

The series within the square brackets in equation (ii) is rapidly convergent, and calculation shows that for cells of length about 2 cm. and diameter 0·8 mm., and diffusion times of the order indicated, the error introduced in the value of γ by taking the first term only of the series is less than 0·5%.

The modified expression $\gamma = 8e^{-\theta}/\pi^2$ has therefore been used in the calculation of the diffusion coefficients.

Study of the Polytungstic Acids.—The technique described above has been used to study the process of aggregation of the anions, as the hydrogen-ion concentration of a sodium tungstate solution is increased. The constitution of the isopolytungstates formed thereby must be regarded as still uncertain. Whereas normal sodium tungstate, Na_2WO_4, crystallises from alkaline solutions, sodium paratungstate, $3Na_2O,7WO_3$,aq. or $5Na_2O,12WO_3$,aq., is obtained from solutions of pH 4—6. Between the alternative formulations $[W_7O_{24}]^{6-}$ and $[W_6O_{21}]^{6-}$ for the paratungstate anion, the published analytical data do not distinguish. By analogy with the constitution of the paramolybdate anion $[Mo_7O_{24}]^{6-}$ (Sturtevant, *J. Amer. Chem. Soc.*, 1937, **59**, 630), and with the 6-molybdo- and 6-tungsto-tellurate and -periodate anions, $[TeMo_6O_{24}]^{6-}$, $[TeW_6O_{24}]^{6-}$, $[IMo_6O_{24}]^{5-}$, $[IW_6O_{24}]^{5-}$ (cf. Abegg, "Handbuch der Anorganischen Chemie," 1921, Vol. 4, Part 1, ii, 977—1065), the first formulation would appear likely, but Jander (*Kolloid-Beih.*, 1935, **41**, 18 *et seq.*) and Souchay (*Ann. Chim.*, 1943, **18**, 61) consider that the analogy is not valid, and that the paratungstates are derived from an acid $H_6W_6O_{21}$. It was hoped that by precise diffusion measurements the complexity of the anions existing in acid tungstate solutions could be established.

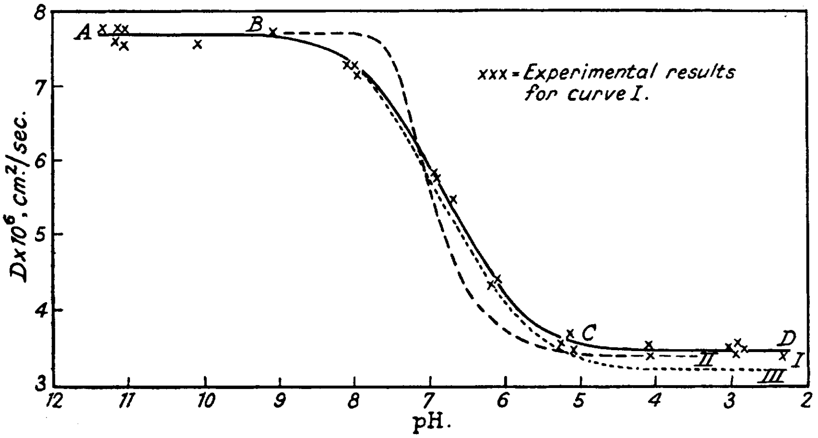
Procedure.—A known weight of tungsten trioxide is irradiated in the atomic pile for about 4 days, as a result of which it becomes radioactive owing mainly to the presence of the ^{187}W isotope of half-life 24·1 hours. This active tungsten trioxide is dissolved in a slight excess of N-sodium hydroxide and diluted so as to afford a 0·5N-solution of sodium tungstate of pH approximately 11. From this stock solution suitable dilutions are made, with simultaneous adjustment of the pH, so as to obtain a range of solutions of a given concentration and of varying, known pH values. These solutions are used for filling the capillary diffusion cells. Bath solutions of corresponding pH values and of concentrations 0·98—0·99 of those of the capillary solutions are similarly prepared with inactive material. The remainder of the experiment is then carried out as already described.

Results and Discussion.

Measurements were made with sodium tungstate solutions of concentrations varying from 0·0025 to 0·05M. A typical set of results for the 0·05M-solutions is shown in Fig. 2, curve I, in which the values of the diffusion coefficient D at 20° are plotted against pH.

The flat portion AB of the curve shows that for solutions of pH greater than 9, the value of D is approximately constant, having a mean value of $7 \cdot 7 \times 10^{-6}$ cm.^{2} sec.$^{-1}$. The value of D then decreases gradually as the pH is decreased from pH 9 to 5, after which D again shows little change over the range of pH 5—2·3 (the lowest value studied so far). This is indicated by the horizontal part *CD* of the curve which corresponds to a mean value for *D* of $3{\cdot}47 \times 10^{-6}$ cm.^{2} sec.$^{-1}$. Each region of constant diffusion coefficient corresponds to a series of solutions in which, despite differences in pH, there is roughly the same ionic complexity. In solutions of pH greater than 9 the only type of ion present in significant amount is the simple, uncondensed ion, whilst over the pH range 2·3—5 a second ion is essentially predominant. Over the pH range 5—9 the curve indicates a transition from one ion to the other with no one species predominating.

FIG. 2.



The evaluation of the diffusion data involves a knowledge of the relation between the ionic or molecular weight and the diffusion coefficient in liquid systems, and for this a full theoretical treatment is at present lacking. Riecke's discussion (*Z. physikal. Chem.*, 1890, **6**, 564) leads to a relation which is formally analogous to Graham's law, namely, $D_1\sqrt{M_1} = D_2\sqrt{M_2}$, where D_1, M_1 are the diffusion coefficient and (unknown) molecular weight of the substance being investigated, and D_2, M_2 are the corresponding values for some reference substance, of known molecular weight and as similar as possible in character (*i.e.*, in size and charge, if an ion) to the substance being investigated. Although this simple relation is valid for the limiting cases of molecules diffusing in a gas, and the diffusion of colloidal particles in a solution, it is certainly a crude approximation for the diffusion of ions in an electrolyte solution; the ionic radius and ionic charge undoubtedly enter both directly, into factors modifying the Riecke–Graham law relation, and indirectly, by controlling the solvation and the effective diffusing mass of the ion.

Jander and Brintzinger have used the Riecke–Graham relation, with some reference ion of supposedly known ionic weight, in discussing their diffusion measurements. That this involves considerable ambiguity is shown by the present work, and by measurements we have made upon the diffusion of the $[Co(CN)_6]^{3-}$ and the $[Co(en)_3]^{3+}$ ions. In the instance under discussion, the ion present in alkaline solution is undoubtedly the uncondensed tungstate ion. If this is effectively present as the WO_4^{2-} ion (ionic weight 248), the ionic weight of the condensed ion predominating in acid solutions is calculated from the Graham–Rieke relation as *ca.* 1220, a value too low to be compatible with either of the formulæ advanced for the paratungstate ion. If the (not unplausible) assumption be made that, in solution, the simple tungstate ion diffuses as $[WO_4,2H_2O]^{2-}$, of ionic weight 284, the ionic weight of the condensed ion is found to be 1400, which corresponds most nearly to a hexatungstate ion. However, as stated above, neither the validity of this calculation nor the degree of hydration of the simple tungstate ion is certain, and our results do not exclude the possibility that the paratungstate ion is, in fact, that of a heptatungstic acid.

Although this question remains unsettled, it is nevertheless possible to derive from our measurements some information concerning the aggregation process. The paratungstate ion must be formed by one or more reversible condensation reactions of the general type

$$nWO_4^{2-} + 2mH^+ \rightleftharpoons [W_nO_{4n-m}]^{(2n-2m)-} + mH_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If, following Jander and Souchay, we assume $n = 2m = 6$, we have

$$6WO_4^{2-} + 6H^+ \rightleftharpoons [W_6O_{21}]^{6-} + 3H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

FIG. 3.

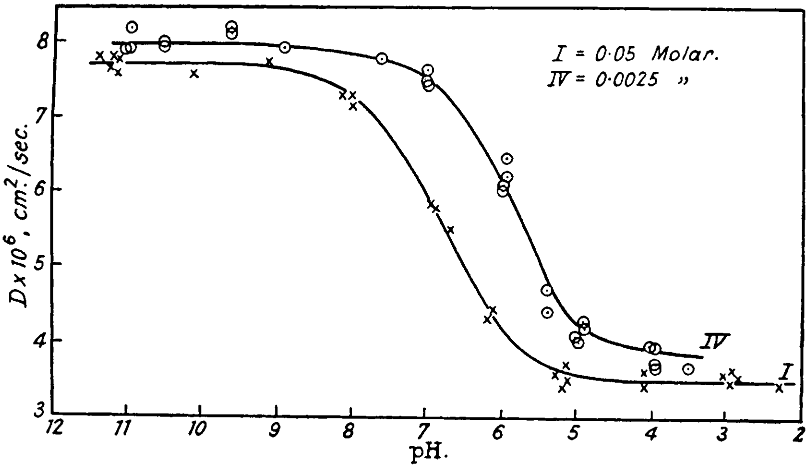


FIG. 4.

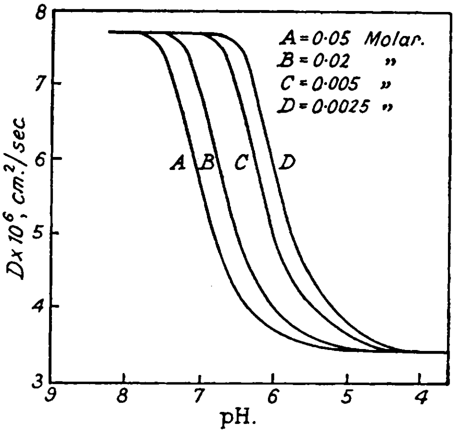
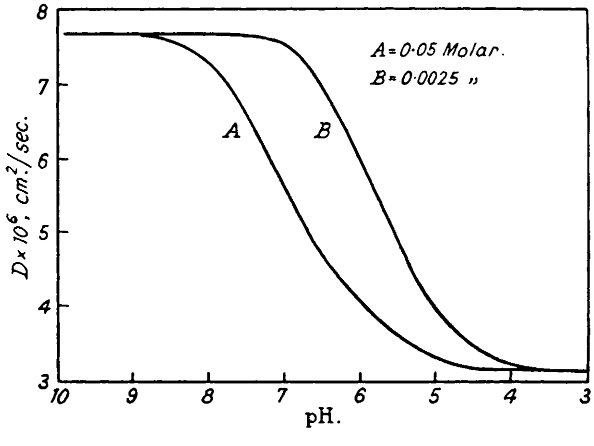


FIG. 5.



This condensation may, alternatively, take place in successive stages : for example

$$3WO_4^{2-} + 2H^+ \rightleftharpoons [W_3O_{11}]^{4-} + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$2[W_3O_{11}]^{4-} + 2H^+ \rightleftharpoons [W_6O_{21}]^{6-} + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Evidence for the occurrence of an intermediate stage in the condensation process is provided by a comparison of the experimental data (Fig. 2, I) with diffusion coefficient–pH curves calculated on the alternative assumptions. This may be carried out as follows.

By applying the law of mass action to equation (2) and using the experimental curve to obtain that value of the pH corresponding to the state in which one-half of the total tungsten is still present as the simple ion, we can evaluate the equilibrium constant for the single equilibrium (2). This value can then be used to calculate pH values corresponding to other degrees of aggregation, so that an ideal curve may be drawn on the basis of this single equilibrium. The curve II was calculated in this way for a 0·05M-solution, and shows a sharp drop between the two regions of constant diffusion coefficients. If a similar treatment is applied to equations (3) and (4), again using the experimental curve I to obtain data from which to calculate the appropriate equilibrium constants, a second ideal curve III for a 0·05M-solution may be plotted on the assumption that the equilibria (3) and (4) represent the mechanism of the aggregation process. This curve III is seen to fit the experimental curve I much more nearly than does curve II. Nevertheless, the fact that no definite step occurs between pH's 9 and 5 in curve I indicates that the intermediate ion does not predominate in a solution of any pH value.

The effect of a change in total concentration of the solute is seen on comparing curve I with the curve IV (Fig. 3). The latter is the experimental curve for a 0·0025M-solution, and the comparison shows that increasing dilution causes an increase in the value of D for a given pH, corresponding to a decrease in the degree of aggregation. The same effect is shown in the series of ideal curves of Fig. 4 calculated as for curve II, and in the series of ideal curves of Fig. 5 calculated as for curve III.

The experimental curve I may be compared with that obtained by Jander (*Kolloid-Beih.*, 1935, **41**, 21) for 0·1N-tungstate solutions. Because of the method used, Jander found it necessary to plot, not D, but Dz against pH, where z is the specific viscosity of the solution. Nevertheless, the curve so obtained also shows a region in which the value of Dz is constant, which extends in this case down to pH 8, followed by a gradual fall until pH 6 is reached, when a second constant value for Dz is obtained.

Finally, in the solutions here examined, down to the lowest pH employed, *viz.*, 2·3, the diffusion curves show no indication of the presence of a dodecatungstate ion corresponding to the crystalline metatungstates.

We thank the Director, Atomic Energy Research Establishment, for permission to publish this paper.

ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, DIDCOT, BERKS.

[*Read, April* 1*st*, **1949.**]