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XXIII. *On the Coefficient of Diffusion of Certain Saturated Solutions.* By BASIL W. CLACK, M.Sc. (Lond.), Lecturer in Physics at Birkbeck College.

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ABSTRACT.

This Paper gives an account of experiments on the Diffusivity of saturated solutions of KCl, NaCl and KNO₃ at constant temperatures near 18°C., when the steady state of diffusion has been attained, employing a method similar to that previously used by the author (Proc. Phys. Soc., Vol. XXI., p. 863, 1908; Vol. XXIV., p. 40, 1911; Vol. XXVII., p. 56, 1914; Vol. XXIX., p. 49, 1916).

The solution under investigation is maintained at complete saturation by the presence of salt crystals in the diffusion vessel. The theory takes into account the change in volume of this salt as it dissolves, and an expression is obtained for the coefficient of diffusion at complete saturation, which depends on the rate of change in weight of the diffusion vessel with time. The experimental results are found to agree very closely with the values obtained by extrapolation from the results previously found for less concentrated solutions. By the present Paper the author has thus extended the range of concentration over which he has studied diffusion from very dilute solutions right up to complete saturation.

I. *Introduction.*

In the study of the diffusion of salts through water, not only have investigators very rarely employed steady conditions, in which the concentration of the solution remains constant at each point of the diffusion tube all the time the experimental readings are being taken, but in the majority of instances the solutions under investigation have been comparatively dilute, and very few experiments have been undertaken in which relatively concentrated solutions are employed.

The author has already insisted on the importance of adopting the steady state in these researches (see Proc. Phys. Soc., Vol. XXI., p. 863, 1908; Vol. XXIV., p. 40, 1911; Vol. XXVII., p. 56, 1914; Vol. XXIX., p. 49, 1916), and in the present Paper a method is described in which this condition is employed in the study of saturated solutions.

II. *Apparatus.*

The apparatus contains a diffusion tube, *A*, which has been made rectangular in cross-section in order to make the same apparatus applicable to another investigation which the author hopes to carry out in the future. The tube, which has a width of about 4 cm. and a breadth of 1 cm., and is

5 cm. high, is made of glass plates cemented together with zinc oxide and water glass cement, and is fitted at its lower end into a shallow glass box, *B*, about 4 cm. square and 1 cm. high, as shown diagrammatically in the figure.

The whole of this apparatus is filled with air-free saturated

solution, and the concentration of the solution at the lower end of the rectangular diffusion tube is maintained constantly at complete saturation by filling the shallow box with crystals of the salt under investigation. The diffusion cell thus filled

is suspended from one arm of a delicate balance by a fine platinum wire, gauge No. 33, and hangs a few centimetres below the surface in a large tank containing about 30 litres of distilled water maintained at a constant temperature of about 18°C. in a thermostat room.

After diffusion has been proceeding for a sufficient time, the concentration of the solution at the upper end of the diffusion tube may be taken as zero on account of the very large volume of water present in the tank. Thus the concentration of the solution in the diffusion tube varies from saturation at its lower end to zero at its upper end, and at every point remains constant with time—*i.e.*, the steady state has been established. When this condition has been obtained, the rate at which salt diffuses out of the cell has become constant, and observations of the weight of the cell every day enables this rate of diffusion to be determined. As the weight changes in these experiments by about 1 mg. in eight or nine minutes, it is only necessary to adjust the mass in the other pan of the balance to the nearest milligramme less than that of the cell, and wait until the pointer is seen to move to the zero of the micrometer scale fitted in the eyepiece of the observing microscope. The usual precautions already described are taken to avoid disturbance of the solution during these weighings.

As the diffusion cell has so small a volume, any variation of the density of the water in the bath, caused by slight variations in temperature, or by the addition of diffused salt to it, only produces a negligible effect on the weight observed, and hence it is not necessary in these experiments to employ a compensating cell suspended from the other arm of the balance.

III. *Theory.*

The theory of the method outlined above is slightly complicated by the change in volume of the salt crystals as they dissolve. It is known that on solution a decrease in volume usually occurs, so that water must enter the cell from the tank to make up for this change in volume, and the diffusion of the salt out of the cell takes place simultaneously with the entrance of water into it.

If v_0 = velocity downwards with which the water enters the top of the diffusion tube, and if

L = total length of the diffusion tube in centimetres,

A = its area of cross-section in square centimetres,

N = concentration of saturated salt solution in gms./c.c.

D = density of saturated salt solution in gms./c.c.

c = mass of salt diffusing out of the cell/sec. when the steady state has been reached,

i = change in weight of cell/sec. when the steady state has been reached,

then it has been shown by the author (Proc. Phys. Soc., Vol. XXIX., pp. 51, 52, 1916) that

$$K = Li / \left\{ AN \left[1 - \frac{v_0 N}{2c} + \frac{v_0(v_0 - bc)N^2}{3c^2} \right] (1 - \delta) \right\},$$

where it has been assumed that the relationship between the density and the concentration of the solution, which is approximately a linear one, may be expressed with sufficient accuracy as $d = 1 + an$. Thus a is a constant whose value may be taken as equal to the mean slope of the true curve connecting d and n and b is written for $(1 - a)$.

In previous work it was found unnecessary to include the third term in the square bracket, since $(v_0 - bc)$ was so small that this term was negligible, but in the present case rather different conditions result from the solution of the salt crystals in the reservoir, and this has the effect of slightly increasing the value of the term under discussion.

We have seen that as salt leaves the cell by diffusion, water enters it. Let δ = the ratio of the mass of water entering the cell to the mass of salt leaving it in a given time when the steady state has been attained.

Then δ can be calculated as follows :—

Let N = concentration of saturated salt solution in gms/c.c.

D = density of saturated salt solution in gms/c.c.

Z = density of the salt crystals.

V_1 = volume of solution in the cell of any given instant.

v_1 = volume of salt in the cell of any given instant.

V_2, v_2 corresponding quantities at a later instant.

Then loss of salt in this time interval

$$= V_1 N + v_1 Z - V_2 N - v_2 Z$$

$$= (v_1 - v_2) Z - (V_2 - V_1) N.$$

Again, gain of water in the interval

$$= (V_2 - V_1)(D - N)$$

Now

$$\delta = \frac{\text{gain of water}}{\text{loss of salt}} = \frac{(V_2 - V_1)(D - N)}{(v_1 - v_2)Z - (V_2 - V_1)N}.$$

But $V_1 + v_1 = V_2 + v_2$ = total volume of cell,

i.e., $V_2 - V_1 = v_1 - v_2$,

i.e., $\delta = (D - N)/(Z - N).$

From published tables of densities the value of δ can thus

be determined. For the salts investigated in this Paper its value is in the neighbourhood of 0.5.

Again it is clear that in the steady state the mass of water entering the cell per second = (mass of salt leaving it per second) δ ; that is

$$v_0 = c\delta.$$

Hence we have

$$K = Li / \{ AN[1 - \frac{1}{2}N\delta + \frac{1}{3}N^2\delta(\delta - b)](1 - \delta) \}.$$

The difference between δ and b is, even in the present work, so small that the omission of the third term in the square bracket only produces an error in K which amounts in all cases to a fraction of 1 per cent.

IV. Results.

The results obtained by this method, using saturated solutions of the salts mentioned, are collected and tabulated below :—

Salt.	KCl.	NaCl.	KNO ₃ .
Temperature °C. ...	17.3	17.1	18.1
Normality ...	4.03	5.44	2.575
N.gms/cc. ...	0.300	0.318	0.260
D.gms/cc. ...	1.178	1.202	1.154
Z.gms/cc. ...	1.977	2.150	2.092
δ ...	0.5236	0.4827	0.4878
b ...	0.4059	0.3640	0.4080
L cms. ...	5.04	5.04	5.04
A sq. cms. ...	4.22	4.22	4.155
i gm/day ...	0.1687	0.1486	0.1115
$K \times 10^6$ C.G.S. ...	1.767	1.349	1.253

These results are indicated by circles in the graphs given below in which the curves already published in 1916 (*loc. cit.*) are extended so as to include the saturated solutions studied in the present research.

V. Definite Concentration.

The value of the Diffusivity obtained above is that for the solution in the diffusion tube, which varies in concentration from saturation to zero. This coefficient the author has called the "Mean Diffusivity" and has shown that the coefficient of Diffusion, K_n , for a solution of a definite concentration can be calculated theoretically from the value of the Mean Diffusivity by a formula (No. 6) given on p. 56 in

the Paper referred to. In applying this calculation to the present case it is advisable as before to include the term containing n^2 , and we obtain

$$\begin{aligned} K + \{1 - \frac{1}{2}n\delta + \frac{1}{3}n^2\delta(\delta - b)\} / \{1 - n\delta + n^2\delta(\delta - b)\} ndK/dn \\ = c / \{1 - n\delta + n^2\delta(\delta - b)\} dl/dn \\ = K_n. \end{aligned}$$

The following results are obtained by this method for the coefficient of Diffusion of saturated solutions of the salts mentioned at the temperature indicated :—

Salt.	Temperature.	$K_n \times 10^5$.
KCl	17.3°C.	2.107 C.G.S.
NaCl	17.1	1.522
KNO ₃	18.1	1.171

These results are also included in the graphs and are indicated by crosses. The curves associated with them show the value of the coefficient of diffusion at other definite concentrations calculated in the same way. It will be observed that both the Mean Diffusivity and the Diffusion Coefficient for the saturated solutions employed agree to within 1 per cent. with the corresponding values obtained by extrapolation from the results previously found for less concentrated solutions, and an inspection of the curves shows that the range of concentration over which the author has studied diffusion by this method has been approximately doubled by the work included in this Paper.

The research has been carried out at Birkbeck College, and I should like to record my continued indebtedness to Dr. A. Griffiths, in whose department the work was done, for his kind interest and assistance.

DISCUSSION.

Dr. A. GRIFFITHS dealt with the fundamental expression for diffusion. He explained the theoretical foundation of the diffusion-equation used by Mr. Clack and himself, and stated that this equation was an extension of Fick's Equation, or that Fick's Equation could be considered to be a limiting case of their equation. He said that Fick's Equation implicitly assumes that the liquid is at rest during a diffusion operation, whereas in fact the changes in concentration in all experiments known to himself inevitably produce movement of the liquid. An extension of Fick's hypothesis is, therefore, inevitable. He explained that the equation used by Mr. Clack and himself assumed that in addition to the diffusion as expressed by Fick, there is a movement of the diffusing salt equal in value to that of the water-component of the salt solution. He stated that the quantity defined by δ in earlier Papers by Mr. Clack and himself should have been defined as the ratio of the mass of water entering the diffusing cell to the

mass of salt leaving the cell. The modification of the definition makes no change whatever when a linear relation may be assumed between density and concentration; and, in any case, makes a change smaller than errors of experiment. The change becomes smaller with the concentration, and is zero at infinite dilution.

The coefficients of diffusion for the weakest solutions of potassium and of sodium chloride were each 16 per cent. less than the theoretical values given by the Nernst equation for infinitely dilute solutions. The value of the coefficient for potassium nitrate was 11 per cent. less than the theoretical. These differences could not be considered very remarkable if it were remembered that Perrin's value (based on work with liquids) for the electronic charge was 11 per cent. less than the generally accepted value. The fundamental hypotheses for liquids probably require a close examination. One of his students had interpreted Mr. Clack's results by the equation $K = K_1r + K_2(1-r)$, where K is the coefficient obtained by Mr. Clack, K_1 is the coefficient of diffusion of the completely ionised salt, K_2 is the coefficient of diffusion of the non-ionised salt, and r is the ionisation-ratio. In the case of potassium nitrate this equation represents the results obtained by Mr. Clack wonderfully well over the whole range of concentration, and it represents the results well in the case of potassium chloride and of sodium chloride when the concentrations are not great.

Capt. C. W. HUME did not think the concentration at the top of the diffusion tube would be zero. The effect of this error would be equivalent to a constant increase in the length of the tube.

Mr. F. E. SMITH asked if experiments could not be made by measuring differences in electrical conductivity. Such methods, it appeared to him, would enable results to be obtained much more rapidly.

Mr. CLACK, in reply, said that earlier in his researches he had investigated the end-correction suggested by Mr. Hume and concluded that it was negligible. As regards the conductivity method, this had been tried, but he was at present experimenting with an optical method with which it should be possible to obtain results for all concentrations in one experiment.