

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

**DIFFUSION OF ELECTROLYTES, NON-ELECTROLYTES AND COLLOIDAL ELECTROLYTES<sup>1</sup>**

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Diffusion is one of the simplest and most fundamental properties of substances in solution and yet its characteristics are seldom adduced even in discussing such closely allied phenomena as electrical conductivity or its dependence upon concentration. Surprise at this neglect largely disappears when the meager and somewhat conflicting data collected in "International Critical Tables" and in Landolt-Börnstein-Roth are scrutinized and when it is recalled that each number there recorded is the result of prolonged and laborious experiment dependent upon the most painstaking precautions, each result being independent and therefore of no assistance in obtaining further data. Hence, in some instances, the data are conflicting even as regards the sign of the effect of a single factor such as concentration.<sup>2</sup>

The first necessity is therefore to obtain a method by which data that are fully comparable with each other may be readily obtained. It will be shown that standardization of the method recently developed by Northrop<sup>3</sup> enables it to yield results in twenty-four hours that are readily reproducible to within a few tenths of a per cent. and that are thus favorably comparable with those of the laborious classical methods, while exhibiting the further advantage that they permit a ready study of the effect of such factors as viscosity, concentration or admixtures upon rate of diffusion of any one substance. It is shown that the diffusion of electrolytes diminishes to a significant extent with increase of concentration and that the reasoning employed in the discussion of electrical conductivity by Debye, Hückel and Onsager leads to the conclusion that this is in direct proportion to the ratio of the actual osmotic pressure to that at infinite dilution.

The Nernst equation, which applies only to the diffusion of electrolytes at extreme dilution, and the Einstein equation, which applies only to uncharged colloidal particles and large spherical molecules, are generalized and combined to a single equation which appears to hold good for all concentrations, even for such a complex case as solutions of soap, which are crystalloidal when dilute and contain two kinds of colloidal particles when more concentrated. The ready production of new data facilitates the

<sup>1</sup> Experiments by T. H. Liu.

<sup>2</sup> For example, taking from Landolt-Börnstein-Roth the data for potassium chloride, perhaps the most carefully studied electrolyte, Öholm at 18° finds for 0.01, 0.1 and 1.0 *N*, 1.46, 1.39 and 1.33, respectively, whereas, on the contrary, Thøvert at 17.5° obtains for 0.02, 0.1 and 0.9 *N*, 1.36, 1.38 and 1.52, respectively. Schulmeister obtained 1.10 for 1.3 *N* at 10°, but Graham-Stefan found 1.41 for 1.26 *N* at only 12.5°.

<sup>3</sup> J. H. Northrop and M. L. Anson, *J. Gen. Physiol.*, 12, 543 (1929).

examination of many interesting problems such as the dimensions and solvation of molecules and colloidal particles in solution, the great difference found between the gross viscosity of a system and that which determines its diffusion or conductance, and the effect of the simultaneous diffusion of various substances upon each other. For example, it is shown that different substances do not diffuse independently, but that one may construct a liquid diffusion pump whose action is analogous to that of the ordinary gaseous diffusion vacuum pump.

### Experimental Method

Northrop's method consists in separating two homogeneous bodies of solution by an indifferent membrane with pores of visible or microscopic size, confining the diffusion gradient to within this membrane. Membranes

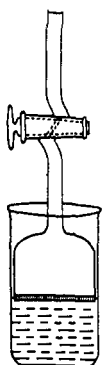


Fig. 1.—The diffusion cell.

of alundum and of sintered glass have been used. We have found it advantageous to buy cells direct from the Jena Glaszwerke<sup>4</sup> in order that the sintered glass may be fused directly to the remainder of the cell. The pore diameter which they designate as G-4 has proved most suitable, and for our purposes the cells required no alteration before use except to grind away the slightly projecting edge of the glass. The cell is shown in Fig. 1 dipping into a closely fitting beaker of water. We have found that the detailed procedure given in the following paragraph enabled us to obtain the results already indicated without any elaborate precautions for the avoidance of vibration or extreme constancy of temperature. The results are necessarily relative but are standardized, as in using a conductivity cell, by a measurement of a single standard solution such as 0.1 *N* potassium chloride, of which the absolute value is already established.

After testing for leaks, the volume of the diffusion cell up to the glass stopcock is determined by weighing. It is then suspended by a 5-mm. rubber tube about 15 cm. long and the suspension or stem adjusted until the diaphragm is accurately horizontal as tested against a large mercury surface. This is to minimize the possibility of streaming through the diaphragm. The cell is first cleaned by sucking cleaning solution through the porous disk, using a water pump at the upper end. The liquid is expelled again by applying a pressure of not more than one meter of water. After thorough rinsing, water freed from dissolved gas by boiling or shaking in vacuo is drawn through the diaphragm in order to dissolve any air therein. Bubbles are dislodged by sudden increase in suction, which may serve as a test for the removal of air. In removing the water the pressure is released just as the last layer is about to enter the diaphragm.

The solution to be investigated is freed from dissolved gas by boiling for a few minutes at room temperature in the vacuum of a good water pump. The cell is then rinsed and charged with the solution through the diaphragm and filled completely,

<sup>4</sup> Schott und Gen., Jena, Germany; American agent, J. E. Bieber, 1123 Broadway, New York City.

without bubbles, past the stopcock which is then closed. The cell is first immersed in a large beaker of pure, gas-free water, and before placing it in the surface of the beaker of gas-free water shown in Fig. 1, the last drop of adherent water is removed by slightly tilting the diaphragm and touching it with a glass rod.

The preliminary diffusion proceeds for a few hours or whatever time is necessary to establish a steady diffusion column within the disk. This can be calculated from the time required for that part of the solution which is within the diaphragm to diffuse out entirely; for hydrochloric acid about two hours is required. Finally, the cell is transferred, after removal of adherent liquid as before, to a clean beaker containing a quantity of gas-free water equal to the volume of the cell. The space between cell and beaker is closed with a ring of rubber dam to minimize evaporation. The measurement now begins. The preliminary diffusion not only creates the uniform diffusion gradient within the diaphragm but enables the solutions to attain the temperature of the thermostat in which the apparatus is placed.

After sufficient diffusion has occurred to permit of an accurate analysis of the dilute solution formed in the beaker, the cell is removed and wiped with filter paper, including the inside of the tubing above the stopcock. The solution is extruded through the diaphragm, the first 10 cc. or so being discarded and a sample of the remainder being taken for analysis.

We have made use of cells whose diaphragms had the following characteristics:<sup>5</sup>

Material	Trade designation	Approximate pore radius, Å.	Diameter and thickness, cm.
Glass	G-3	$(15-20) \times 10^4$	$5 \times 0.2$
Glass	G-4	$(2-5) \times 10^4$	$5 \times .2$
Alundum <sup>6</sup>	RA225	$(8-10) \times 10^4$	$5 \times .2$
Alundum	RA98	$(10-15) \times 10^4$	$5 \times .2$

The glass diaphragms allow faster diffusion than those of alundum. Diffusion in the finer glass diaphragm is as fast as in the coarser one, while the possibility of streaming is eliminated. It will be noted that the pores have about ten thousand times the diameter of such large molecules as sucrose and one or two thousand times the diameter of hemoglobin or the smaller particles of blue gold.

**Method of Calculation.**—From Fick's equation for the amount  $ds$  diffusing per interval of time  $dt$

$$ds = DA \frac{dc}{dx} dt$$

where  $D$  is the diffusion coefficient and  $A$  the effective area of all the pores. The diffusion gradient,  $dc/dx$ , being linear within the disk, may be set equal to  $\Delta c/\Delta x$ , where  $\Delta x$  is the thickness of the disk, whence  $ds/dt = DA \cdot \Delta c/\Delta x$  and since the volume  $V$  of water in the beaker is equal to that in the cell,  $ds/dt = D(A/\Delta x)(c_0 - 2c)$ , where  $c_0$  is the initial concentration and  $c$  is the concentration to which the solution in the beaker has attained and

<sup>5</sup> The pressure required to force air bubbles freely through the diaphragms under water confirmed the radii ascribed to the alundum disks but indicated slightly smaller values than those here given for the glass diaphragms.

<sup>6</sup> Norton Co., Worcester, Massachusetts.

where  $c = s/V$ . Hence,  $dc/dt = Dk'V(c_0 - 2c) = Dk''(c_0 - 2c)$  where  $k'$  and  $k''$  are constants. Therefore,  $\ln(c_0 - 2c) = -2Dk''t + \text{const.}$  Therefore

$$KD = \frac{\log_{10} c_0 - \log_{10} (c_0 - 2c)}{t_E}$$

where  $K$  may be entitled the cell constant,  $t_E$  is the elapsed time, and  $c$  is 0 at the beginning of the experiment if the diffusion is taking place into water. By measuring the diffusion of a standard substance such as 0.1  $N$  potassium chloride, whose diffusion coefficient is known<sup>7</sup> to be 1.448 at 20°, the cell constant  $K$  is determined and all diffusion constants  $D$  measured with that cell are expressed in absolute values.

**Critical Tests of the Experimental Method.**—Northrop<sup>8</sup> states that "hydrochloric acid, lactose and several salts were used" and that "the same cell constant was obtained." He applied his cell to the determination of the molecular weight of carbon monoxide hemoglobin, which he found to be  $68,500 \pm 1000$ . At first sight this appears highly satisfactory, but actually there is a glaring and unexplained discrepancy with the diffusion observed by Svedberg and Nichols<sup>9</sup> in the ultracentrifuge, which yielded a value of 113,000,<sup>10</sup> from which it was deduced that hemoglobin particles could not be spherical. Hence it is necessary to scrutinize the method more closely.

**A. Homogeneity of the Solutions in Cell and Beaker.**—Mechanical stirring introduces much more error than it obviates. Mixing is largely automatic since the heavier portion of the solution overlies the lighter portion in both cell and beaker. Imperfect mixing would be revealed in a change of the value of  $KD$  with longer elapsed time and might be greatest for fast diffusing substances such as hydrochloric acid. However, the following is the consistent series of data obtained at 20.5° for 0.5  $N$  hydrochloric acid after the experimental procedure described above was adopted. Cell F used in these six experiments had a capacity of 91 cc., and the hydrochloric acid was determined by titration. The second and third columns are the number of cubic centimeters required to titrate the whole of the diffused hydrochloric acid and the number of cubic centimeters to titrate 25 cc. of the solution recovered from the cell, respectively. It is the ratio of these numbers rather than their absolute values which appears in the calculation.

Similarly, values of  $KD$  equal to 274 and 272 were obtained in cell B for 0.4  $N$  acetic acid when the times were sixty-three and forty-one hours, re-

<sup>7</sup> E. Cohen and H. R. Bruins, *Z. physik. Chem.*, 103, 404 (1923); 113, 157 (1924).

<sup>8</sup> J. H. Northrop and M. L. Anson, *J. Gen. Physiol.*, 12, 549 (1929).

<sup>9</sup> J. B. Nichols, "Colloid Symposium Monograph," The Chemical Catalog Co., Inc., New York, 1928, Vol. VI, p. 296.

<sup>10</sup> Nichols made the obvious error of inverting the ratio in his arithmetic and writes 41,000 instead of 113,000.

TABLE I  
DIFFUSION OF 0.5 *N* HYDROCHLORIC ACID AT 20.5°

$t_E$ , hours	$c$	$c'$	$KD$
19.90	20.22	35.52	688
21.04	20.70	34.42	687
20.97	20.75	34.56	689
40.07	44.85	40.18	686
16.43	16.70	35.50	687
9.20	9.86	37.30	687

spectively. Likewise, for 0.1 *N* potassium chloride with two different methods of analysis  $KD$  was equal to 407 and 409 in cell F when the times were forty-two and twenty-five hours, respectively. Finally, the ratio between the diffusion coefficients for 0.1 *N* potassium chloride at 20° and 1.0 *N* sucrose at 25° was 3.79 by this method as compared with 3.82 from Öholm's data.

**B. Temperature Expansion.**—A fortuitous alteration of temperature by 0.2° would cause an expansion of only 0.006% and cause an absolute error of 0.038% in such an experiment as the first in the table just cited.

**C. Streaming through the Diaphragm.**—With a fine glass diaphragm such as that employed in cell F it requires seventeen minutes to force through 91 cc. of 0.1 *N* potassium chloride using a pressure of 85 cm. of water. From this it follows that if there is an inaccuracy of 0.2 mm. in leveling the diaphragm, the flow in twenty-four hours will be about 0.006 cc., causing an error of 0.06% in the result. A sugar solution would be heavier but much more viscous. Another effect of gravity might be sedimentation; this is quite negligible for molecules but for gold particles of 50 Å. radius it might be 4.6% as great as diffusion.

**D. The Nature of the Diaphragm.**—The most important question that arises with regard to this method of measuring diffusion is whether or not the neighborhood of the extensive surfaces within the diaphragm affects the nature or extent of the diffusion. In the first place, the high mobility of substances upon a solid or liquid surface exposed to a gaseous phase must here be lacking where the solid is immersed in a liquid and the whole space is close-packed with matter. The second conceivable possibility is in the opposite direction and has to be considered more seriously. It is that the surfaces may tend to suppress diffusion through the orientation and immobilization of the adjacent solvent molecules. Even if this does occur, and even if it extends to a thickness of many molecular diameters, it might be largely obscured by the fact that the average pore diameter is of the order of 10,000 molecular diameters, and it would completely disappear from the results if the effect were the same upon different solutes. The only way of testing the effectiveness of this or any other specific action of the various diaphragms is by seeing if they give the same numerical result independent of whether glass or alundum is used and of whether the pores

are coarse or fine, and by comparing such results with those of the classical methods. For this purpose the following results are adduced.

Cells B, F and G were of fine alundum, glass (G-4), and coarse alundum, respectively, and their cell constants were 294.3, 282.0 and 185.0, respectively. Hydrochloric acid was determined by titration, whereas potassium chloride and sucrose were measured by the Zeiss interferometer, having first prepared a (straight line) graph of interferometer reading against concentration with known solutions. More concentrated solutions were diluted before using the interferometer.

TABLE II  
DIFFUSION WITH DIFFERENT DIAPHRAGMS

Solution	Temp., °C.	Cell	$t_E$ , hours	$c$	$c'$	$KD$
0.05 <i>N</i> sucrose	25	F	24.87	139	178	129.6
.05 <i>N</i> sucrose	25	F	30.60	157	177	129.8
.4 <i>N</i> HCl	21	F	19.03	21.63	39.35	696
.4 <i>N</i> HCl	21	F	19.38	22.05	39.25	696
.1 <i>N</i> KCl	20	F	41.97	248	177	406
.1 <i>N</i> KCl	20	F	25.27	18.85	43.63	409
.1 <i>N</i> KCl	20	F	27.60	20.23	43.07	408
.05 <i>N</i> sucrose	25	B	24.52	137	177	135.5
.4 <i>N</i> HCl	21	B	19.18	21.05	39.20	729
.4 <i>N</i> HCl	21	B	18.80	20.87	39.30	728
.1 <i>N</i> KCl	20	B	29.00	203	179	425
.1 <i>N</i> KCl	20	B	25.42	18.32	43.40	427
.05 <i>N</i> sucrose	25	G	25.25	111	181	85.2
.05 <i>N</i> sucrose	25	G	30.85	123	181	85.4
.4 <i>N</i> HCl	21	G	19.23	14.63	41.65	457
.4 <i>N</i> HCl	21	G	19.57	14.90	41.70	457

When the above data are compared in various ways, it is seen that the results appear to be independent not merely of the diaphragm but of the method. For example

$$\frac{KD \text{ for } 0.4 \text{ } N \text{ HCl in "F"}}{KD \text{ for } 0.4 \text{ } N \text{ HCl in "G"}} = 1.524 \text{ and } \frac{KD \text{ for } 0.05 \text{ } N \text{ sucrose in "F"}}{KD \text{ for } 0.05 \text{ } N \text{ sucrose in "G"}} = 1.520$$

$$\frac{KD \text{ for } 0.4 \text{ } N \text{ HCl in "B"}}{KD \text{ for } 0.4 \text{ } N \text{ HCl in "G"}} = 1.593 \text{ and } \frac{KD \text{ for } 0.05 \text{ } N \text{ in sucrose "B"}}{KD \text{ for } 0.05 \text{ } N \text{ in sucrose "G"}} = 1.588$$

$$\frac{KD \text{ for } 0.4 \text{ } N \text{ HCl in "F"}}{KD \text{ for } 0.1 \text{ } N \text{ KCl in "F"}} = 1.709 \text{ and } \frac{KD \text{ for } 0.4 \text{ } N \text{ HCl in "B"}}{KD \text{ for } 0.1 \text{ } N \text{ KCl in "B"}} = 1.708$$

The diffusion coefficients of 0.05 *N* sucrose at 25° in cells B, F and G are 0.461, 0.460 and 0.461, respectively; whereas Öholm's values corrected for temperature and viscosity by Einstein's equation would be 0.457. Similarly, for 0.4 *N* hydrochloric acid at 21° they are 2.476, 2.473 and 2.470, respectively, as compared with Öholm's corrected value, 2.43. Again, the ratio of the diffusion constant here found for the hydrochloric acid to that found for the sucrose is 5.37, whereas from Öholm's corrected data 5.31 would be predicted.

**Theoretical Formulation of Diffusion Data.**—Nernst,<sup>11</sup> on the basis of the close connection between the forces giving rise to diffusion and osmotic pressure, derived the well-known equation for electrolytes in extreme dilution

$$D = \frac{2RT}{\frac{1}{U} + \frac{1}{V}}$$

where  $U$  and  $V$  are the ionic mobilities at infinite dilution as measured by electrical conductivity. Thus for an electrolyte whose ions have the same mobility at 18°,  $D = 0.02243U$ . This last expression is applicable to neutral molecules or colloidal particles of the same size as an ion of mobility  $U$  or  $V$ . In this way Nernst could estimate the approximate diffusion coefficients of neutral molecules or un-ionized electrolytes. Haskell's<sup>12</sup> formula is an expansion of that of Nernst for the diffusion of electrolytes which dissociate into ions of unequal valency.

The other theoretical contribution is that of Einstein<sup>13</sup> for uncharged spherical particles or molecules very large in comparison with those of water

$$D = \frac{RT}{N6\pi\eta r}$$

where  $r$  is the radius of the particle,  $\eta$  the viscosity of the medium and the denominator is the sum total of the resistance to movement of each of the particles calculated by Stokes' law.

It is evident that the numerators of the Nernst and Einstein equations are alike in containing the osmotic term  $RT$  for each molecular species. Likewise, their denominators contain the sum total of the resistances to movement experienced by the different ions, molecules and particles present. We may therefore generalize the reasoning which Nernst and Einstein have applied to these two particular cases and write in the numerator the actual osmotic term  $iRT$  and in the denominator the sum of all the resistances to motion of the ions, molecules and particles evaluated by whatever methods are available in each case. Hence

$$D = \frac{iRT}{\text{sum of resistances}} = \frac{iRT}{\Sigma(1/U_m)}$$

where  $1/U_m$  is the resistance to movement of a particular species and is also equal to  $RT/D_m$  where  $D_m$  is the diffusion coefficient of that molecular species.

For example, for an incompletely dissociated uni-univalent electrolyte, such as potassium chloride may be at higher concentrations, the diffusion coefficient at any concentration is given by the formula

<sup>11</sup> W. Nernst, *Z. physik. Chem.*, 2, 613 (1888); "Theoretische Chemie," 10th ed. 1921, pp. 425-431.

<sup>12</sup> R. Haskell, *Phys. Rev.*, [1] 27, 145 (1908).

<sup>13</sup> A. Einstein, *Z. Elektrochem.*, 14, 235 (1908).

$$D = \frac{iRT}{\alpha \frac{1}{\bar{v}} + \alpha \frac{1}{\bar{v}} + (1 - \alpha) \frac{1}{U_{KCl}}}$$

**The Diffusion of Electrolytes.**—The Debye-Hückel-Onsager<sup>14</sup> theory is an analysis of the chief forces acting upon free ions in aqueous solution. They enumerate three whose sum should determine the electrical conductivity of the solution. The first is that due directly to the electrical charge overcoming ordinary friction and is represented by the mobility at infinite dilution. The second, which diminishes the conductivity, is unfortunately termed the electrophoretic force and represents the opposing effects of the viscous drags of the two clouds of ions moving through the same solution in opposite directions. The third likewise tends to lower the conductivity and is called the electrical force of relaxation and is due to the fact that any movement of an ion must be followed by a slight alteration in the distribution and arrangement of all surrounding ions. The result of the last two terms is that the conductivity  $\Lambda$  at any concentration is given by the expression  $\Lambda = \Lambda_{\infty} - \Lambda_I - \Lambda_{II}$  so that the conductivity diminishes with increase in concentration if ionization remains 100% complete.

Now diffusion is simpler than electrical conduction. The prime force acting upon an ion is that represented by the osmotic term  $RT$  as driving force and by  $1/U_{\infty}$  as resistance. The second influence enumerated by Debye and Hückel, namely, the opposing viscous drags of the ions when moving past each other in opposite directions, is here essentially eliminated because all ions are moving in the same direction. The negligibility of this effect is most obvious for a case such as potassium chloride where both ions are equally fast but it is likewise true of all other simple electrolytes because after the first few moments in which the Nernst diffusion potential is set up, equal amounts of both ions are diffusing together. Onsager<sup>15</sup> has expressed a similar opinion for such electrolytes as potassium chloride. Cataphoretic forces then will not intervene to lessen the movement of ions with increase of concentration.

The third force envisaged by Debye and Hückel is due to the relaxation or alteration in the distribution of the ionic atmosphere whenever an ion is displaced. It may not be entirely eliminated in diffusion but it is certainly minimized when, as here, we have a linear diffusion gradient and all the ions are traveling in the same direction. What is happening is a uniform dilution of the ionic atmosphere and this is minimized when, as in some of our experiments, the diffusion takes place, not into pure solvent, but only into a slightly less concentrated solution.

The net result is that in diffusion the denominator of our generalized

<sup>14</sup> P. Debye and E. Hückel, *Physik. Z.*, **24**, 305 (1923); L. Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).

<sup>15</sup> L. Onsager, *Trans. Faraday Soc.*, **23**, 356 (1927).



equation, representing the forces opposing movement, remains appreciably constant as long as the ions are not changed or replaced. This leaves the observed decrease with concentration to be explained primarily by the change in the effective osmotic pressure as given in the numerator.

The diffusion data that we have obtained for potassium chloride are given in Table III. The cell constants were obtained from measurements of 0.1 *N* potassium chloride at 20°, giving values of *KD* for cell G-3 of 503, 501 and 504, and for cell G-4 of 481, 480 and 484; whence the cell constants are 348.0 and 332.7, respectively.

TABLE III  
DIFFUSION COEFFICIENTS OF POTASSIUM CHLORIDE AT 25°

Concn., <i>N</i>	Cell	<i>t</i> <sub>E</sub> , hours	<i>c</i>	<i>c</i> '	<i>KD</i>	<i>D</i>
0.02	B	20.47	119.6	122.4	500	1.698
.02	F	21.67	120.0	123.2	477	1.672
.02	G-3	22.75	134.3	121.0	588	1.691
.1	G-3	25.82	27.40	41.70	568	1.631
.5	F	30.30	21.25	39.14	445	1.580
.5	B	28.68	20.15	39.10	466	1.567
.5	G-4	23.46	22.75	39.25	524	1.572

It is possible to account for these data as a first approximation within less than 2% by using the simplified formula  $D = iRT/(1/U + 1/V)$ , in which it is assumed that only the numerator changes while the denominator remains constant. This assumption will be referred to briefly again. In this way, taking values for *i* from a table in Taylor's "Treatise on Physical Chemistry" (where *i* is van't Hoff's empirical ratio between osmotic effect observed and that expected for an ideal non-electrolyte), we derive Table IV for 25°. The same formula would predict at 20° a value of 1.428 for 0.1 *N* potassium chloride, which is 1.38% less than that of the standard value of Cohen and Bruins.

TABLE IV  
COMPARISON OF OBSERVED WITH PREDICTED EFFECT OF CONCENTRATION FOR THE DIFFUSION OF POTASSIUM CHLORIDE AT 25°

Concn., <i>N</i>	0	0.02	0.1	0.5
<i>D</i> (obs.)	...	1.685	1.631	1.573
<i>D</i> (calc.)	1.721	1.664	1.605	1.544

Other electrolytes likewise exhibit diffusion coefficients at moderate concentrations which are significantly less than those predicted for complete ionization at infinite dilution, *D*<sub>∞</sub>. Some examples of our data at 25° and of Öholm's at 18° are given in Table V.

Inspection of the data in "International Critical Tables" or Landolt-Börnstein-Roth confirms this deficiency in the diffusion constants for moderate concentrations as compared with those predicted by the Nernst equation for infinite dilution, and the greatly increased magnitude of the

TABLE V  
COMPARISON OF DATA WITH THOSE OF ÖHOLM

Solution	$D$ at 25°	$D_{\infty}$ at 25°	$D$ at 18°	$D_{\infty}$ at 18°
0.1 <i>N</i> HCl	2.674	2.841	2.23	2.43
.5 <i>N</i> HCl	2.663	2.841	2.22	2.43
.1 <i>N</i> LiCl	0.985	1.046	0.951	0.994

effect for ternary electrolytes such as potassium sulfate or for solutions where complexes are known to form would appear to substantiate our contention that the chief factor in diminishing the coefficient of diffusion as the concentration is increased is the falling off in the numerator  $iRT$ .

There are three current views as to the reason for the decrease in  $i$  with increase in concentration. The first holds to 100% dissociation with the attempt to explain all the data by a combination of interionic attraction with other effects. Both the others retain the principles of interionic attraction but one, in the terminology suggested by Bjerrum, assumes 100% ionization but with a larger and larger proportion of the ions "associated" to form neutral pairs as concentration increases. The third view, now widely held, is that dissociation is not complete. McBain and Van Rysselberge<sup>16</sup> decided that mere "association" or clustering is insufficient to explain the fact that anionic clusters or complex anions are commonly formed and complex cations are not, whereas the symmetrical operation of electrical forces would produce comparable numbers of both.

The denominator of our general diffusion equation will, of course, seldom remain quite constant with diminishing dissociation on account of the conflicting effects of molecular volume and of hydration or polarization of the solvent by an ion as compared with a neutral molecule. The magnitudes involved cannot be obtained from a direct comparison between the Nernst prediction for acetic acid 1.37 as against the observed value 0.9 on account of the abnormal mobility of the hydrogen ion. It is more pertinent to recall that, as Nernst suggested, for large organic ions the mobility is equal to that of a neutral molecule of the same size.<sup>17</sup>

The Northrop method can equally well be used with non-aqueous solutions. For example, a saturated solution of potassium chloride in 95% ethyl alcohol gave a value for  $D$  of 0.817 at 25°. The Arrhenius conductivity ratio indicates 25% dissociation of the potassium chloride, whence by proportion and taking into account the viscosity ratio between alcohol and water, the diffusion coefficient of undissociated chloride in water would be 0.824 if the molecules were identical in the two solvents. The only interest of this approximation is that the resistance to movement of the potassium chloride molecule so indicated is only 4% greater than the sum of those of the potassium and chlorine ions, which is a rough justification of the

<sup>16</sup> J. W. McBain and P. J. Van Rysselberge, *THIS JOURNAL*, **52**, 2336 (1930).

<sup>17</sup> For example, T. Svedberg, *Z. physik. Chem.*, **76**, 146 (1911).

assumption of the constancy of the denominator in the equation used for Table IV. A completely non-polar molecule might be expected to have a higher mobility.

**Diffusion of Soap as a Colloidal Electrolyte.**—The surprising range of applicability of our diffusion equation is illustrated by the information yielded for soap solutions, such as potassium laurate at 25°. The proportions of the various constituents for the different concentrations of potassium laurate have been deduced by McBain and Jenkins<sup>18</sup> from conductivity and osmotic data. It will be seen that the diffusion results are in reasonable agreement with the detailed information already available with regard to each of these constituents.

The experimental data are collected in Table VI. To avoid hydrolysis 0.0015 equivalent of potassium hydroxide was added per liter to the more dilute solutions, and the same addition was made to the water in the beaker.

TABLE VI  
DIFFUSION OF POTASSIUM LAURATE INTO WATER (0.0015 *N* KOH) AND INTO LESS CONCENTRATED SOLUTIONS OF POTASSIUM LAURATE AT 25°

Soln., <i>N</i>	In beaker	Cell	<i>t</i> , hours	<i>c</i>	<i>c'</i>	<i>KD</i>	<i>D</i>
0.025	Water	G-3	23.10	87.0	511	241.4	0.695
.025	Water	G-4	26.65	90.2	509	233.0	.700
.025	Water	G-3	30.07	95.5	504	244.1	.702
.15	Water	G-3	24.00	187	2912	163.7	.470
.15	Water	G-4	23.92	180	2907	155.4	.467
.50	Water	G-4	20.45	377	2373.	146.8	.441
.025	Water						.699
.125	0.05 <i>N</i>	G-4	23.00	115	1421	158.0	.475
.3	.2 <i>N</i>	G-4	19.70	119	1920	149.0	.447
.5	.4 <i>N</i>	G-3	23.41	132	1929	146.8	.421
.5	.35 <i>N</i>	G-3	22.12	164	2925	145.1	.417

The experimental values in Table VI are plotted in Fig. 2 together with the point for zero concentration taken from the Nernst equation assuming mobilities of potassium ion as 74.5 and simple laurate ion as 23.2, which gives the value 0.813 at 25°. It will be noted that the diffusion coefficients as measured against water are only slightly higher than those which are confined to a narrower range of soap solution.

Instead of trying to predict independently the diffusion coefficients for representative concentrations, we may examine those found to see if they agree with reasonable expectation. For example, taking first the 0.025 *N* solution in which potassium laurate is supposed to be a simple electrolyte with no colloid and about 66% dissociated, the diffusion due to the ions should be  $0.66 \times 0.813 = 0.532$ . The difference between this and the observed value, 0.699, leaves 0.163 ascribable to potassium laurate molecules. Hence, the diffusion coefficient of the latter is  $0.163/0.34 =$

<sup>18</sup> J. W. McBain and W. J. Jenkins, *Trans. Chem. Soc.*, 121, 2328 (1922).

0.480, and from the Nernst formula for a molecule  $D_m = 0.02243 U_m T / 291$  the value of  $U_m$  expressed in electrical units gives a mobility of 20.9 for the potassium laurate molecule. This appears quite plausible when compared with the value of 23.2 for the laurate ion. (The temperature correction 291/298 is the osmotic correction, not that of the mobility.)

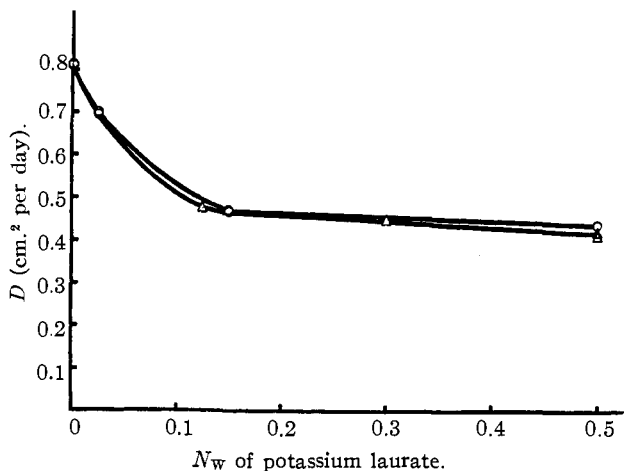


Fig. 2.—Diffusion of potassium laurate at 25°: (a) O, into water (0.0015 *N* KOH); (b) Δ, into less concentrated solutions of potassium laurate.

For 0.5 *N* potassium laurate there is a wholly different picture in that the soap is now almost entirely in the form of colloid, ionic micelle and neutral micelle. The former is supposed to carry about ten charges and possess a mobility of about 74.5 which is equal to that of the potassium ion. From Haskell's equation we may calculate the diffusion coefficient for a decavalent electrolyte with ten potassium ions to one anion at 25°.

$$D = 0.02243 \times \frac{298}{291} \times \frac{(74.5)^2}{2 \times 74.5} \left( \frac{1}{10} + \frac{1}{1} \right) = 0.941$$

Since only 37% of the solution is in this form, the diffusion contributed by it will be  $0.37 \times 0.941 = 0.348$ . That contributed by the 1% of simple ions will be  $0.01 \times 0.813 = 0.008$  and that contributed by the 2% of simple potassium laurate molecules  $0.02 \times 0.480 = 0.0096$ . The sum, still omitting that due to the 60% of neutral micelle  $(KL)_x$ , is 0.366, whereas the total observed is 0.419. This leaves 0.053 for the neutral micelle, whose diffusion coefficient is therefore  $0.053/0.60 = 0.088$ . The significance of this low diffusion constant may be developed by evaluating from it the radius of the neutral micelle according to Einstein's equation for a spherical particle which yields the value 24 Å., or an effective diameter of 48 Å. It is probable that the neutral micelle is not spherical and that its thickness is twice the length of lauric acid, namely, 30 Å. On the other hand, McBain

and Jenkins<sup>19</sup> showed by ultrafiltration that its maximum diameter was much less than 150 Å. A real test of this deduction will be possible when we have carried out similar measurements with sodium oleate in which according to ultrafiltration the neutral micelle is very large.

Returning for a moment to the consideration of the ionic micelle with its ten charges,  $D = RTU = (0.0230 \times 74.5)/10 = 0.171$  and the diameter of the ionic micelle equals  $0.0883/0.171 \times 48 = 25$  Å. If the ionic micelle has a radial arrangement, as seems probable, this is less than twice the length of a laurate radical extended to its maximum length, 15 Å., but it is only to be expected that here the chains would coil to a shorter length.

**Deductions from the Diffusion Coefficient of Sucrose.**—Using cells B, F and G, 0.05 *N* sucrose at 25° gave diffusion constants equal to 0.461, 0.462, 0.461, 0.462, 0.462; mean, 0.462, as compared with Öholm's 0.457. For 1.0 *N* sucrose the values 0.381 and 0.376 are obtained with cell G as compared with Öholm's 0.384. This is a remarkable result. The viscosity of these two solutions as determined in a capillary flow viscometer is, namely, 1.047 and 3.080, respectively, times that of water, whereas the diffusion coefficients differ only by 18% in spite of the fact that Einstein's equation predicates that diffusion is inversely proportional to the viscosity.

Evidently, when the increase in viscosity is caused by the diffusing substance, the viscosity correction is definitely not that demanded by Einstein's equation using the viscosity of the solution, but is much less. An explanation may be ventured by picturing that while the increase of the viscosity is due to indiscriminately increased collisions of the large molecules,<sup>20</sup> in diffusion when one diffusing molecule of sucrose is hit by another, the retardation of one is often compensated by the acceleration of the other. The situation is reminiscent of that of the closely allied subject of conductivity where it is notorious that the attempt to set it proportional to the first power of the viscosity is an overcorrection. In soap solutions the "viscosity" may vary 1000-fold without affecting the conductivity.

Ulich<sup>21</sup> considered that the reason that many ions have an electrical mobility much greater than corresponds to their supposed size and the viscosity of water, like the small effect which sugar or gelatin or jellies exert upon the electrical mobility of ions, is due to their being very small in comparison with the large molecules such as (H<sub>2</sub>O)<sub>6</sub> or similarly (H<sub>2</sub>O)<sub>8</sub>, etc. This, however, does not hold in our case where the large molecules of sucrose are unaffected by the high viscosity which they themselves impart.

Calculating the size of the sucrose molecule from its diffusion coefficient in 0.05 *N* solution, assuming it to be a spherical particle with the density

<sup>19</sup> J. W. McBain and W. J. Jenkins, *Trans. Chem. Soc.*, 121, 2340 (1922).

<sup>20</sup> A. Einstein, *Ann. Physik*, [4] 19, 289 (1906).

<sup>21</sup> H. Ulich, *Z. Elektrochem.*, 36, 504 (1930).

of solid sucrose, its molecular weight is 388 as compared with its formula weight 342. The difference would be equivalent to a hydration of about two molecules of water.<sup>22</sup>

**The Mutual Effect of Diffusing Substances upon Each Other.**—It is commonly assumed that substances diffuse quite independently and that they do not influence each other's rate unless they react with each other. Our experiments show that this is by no means true.

Experiments were carried out at 20° with cells B and C, the latter having an alundum diaphragm "RA 228," using 0.5 *N* hydrochloric acid. First, it was diffused into water, giving values of diffusion constants  $D = 2.452$  and 2.448. Next 10% of dextrose was dissolved in the 0.5 *N* hydrochloric acid and it was diffused into water, giving the values 2.386 and 2.391. Next, 0.5 *N* hydrochloric acid was allowed to diffuse into 10% dextrose in water, giving values of  $D$  of only 1.716 and 1.730. Finally, when 10% dextrose was present, both in the hydrochloric acid and in the water into which it was diffusing, the values of  $D$  were 2.049 and 2.044. Using an Ostwald capillary viscometer, the viscosity of 10% aqueous dextrose at 20° was found to be 0.01291 as compared with that of water 0.01005, the ratio being 1.283.

Now the ratio of the values of  $D$  when dextrose was entirely absent to that when the 10% dextrose was present on both sides of the diaphragm is only 1.196 as compared with the viscosity ratio 1.283. As in the case of sucrose, the viscosity of the solution does not bear a linear proportionality to the effect upon rate of diffusion.

When the dextrose was diffusing with the hydrochloric acid into water, the value of  $D$  for the hydrochloric acid was 1.386 times greater than when the dextrose was diffusing in the opposite direction, although the average viscosity and concentration of dextrose must have been nearly the same within the diaphragm in both cases. Hydrochloric acid diffusing alone into water is only 1.025 times faster than when 10% dextrose is diffusing with it. Our explanation is that the molecules in the two diffusing columns bombard each other and thus retard or accelerate each other's motion according as they are opposed or in the same direction.

When the strong acid, hydrochloric, was replaced by the weak acid, acetic, similar effects were produced by the addition of dextrose. 0.5 *N* acetic acid diffusing alone into water gave  $D = 0.929$  and 0.924. When diffusing with 5% dextrose into water the diffusion was, if anything, rather faster,  $D$  being 0.929 and 0.927, in spite of the enhanced viscosity. But when the acetic acid alone diffused into 5% aqueous dextrose, the rate was 29% less,  $D$  being 0.657 and 0.651.

Dextrose had been used because of its chemical indifference to hydrochloric and acetic acids. Urea is known to combine with acids, its equi-

<sup>22</sup> Compare J. W. McBain and S. S. Kistler, *J. Phys. Chem.*, 33, 1806 (1929).

librium constant having been measured, and when 0.5 *N* hydrochloric acid alone was allowed to diffuse into 5% aqueous urea, *D* actually increased from the value 2.450 for water to 2.501 and 2.490. When the 5% urea was diffusing with the hydrochloric acid into water, *D* fell to the much lower values 1.974 and 1.972. The effects are therefore exactly opposite to those where no chemical combination occurs.

Bombardment by the molecules of an indifferent diffusing column may produce an effect which may be called a liquid diffusion pump since it is analogous to that in a gaseous diffusion vacuum pump. To demonstrate this, the cell was charged with 0.5 *N* acetic acid and the beaker with 0.5 *N* acetic acid containing 10% dextrose. After twenty-three hours the concentration of the acetic acid in the cell had increased and that in the beaker had decreased by about  $-0.6$  and  $+1.0\%$ , respectively. In a similar experiment after forty-seven hours the changes were  $-1.6$  and  $+1.8\%$ , respectively. When hydrochloric acid was used instead of acetic acid, in twenty-four hours the changes were  $-0.4$  and  $+0.7\%$ . On the other hand, when 5% urea was with 0.5 *N* hydrochloric acid in the cell and 0.5 *N* hydrochloric acid alone in the beaker, the changes were in the opposite direction; hydrochloric acid passed from the beaker to join the urea in the cell, the changes being in twenty-four hours  $+0.8$  and  $-0.6\%$ .

Other results with ethyl and methyl alcohols suggest that the bombarding effect of a diffusing column may be approximately proportional to the square of its concentration and to the cross-sectional area of its molecules. It is evident that diffusions of more than one substance are not independent of each other. For example, it is not safe to employ buffer solutions without considering the effects here recorded.

### Summary

A procedure is given for the use of the Northrop diffusion cell with diaphragm of sintered glass by which very rapid determinations of diffusion may be made reproducible to within a few tenths of a per cent. It is shown that such results are independent of the nature and porosity of the diaphragm and are equal to the best obtained by the laborious classical methods.

The Nernst equation for electrolytes at infinite dilution and the Einstein equation for uncharged spherical particles are generalized to include all cases of diffusion. It is shown that for simple electrolytes the predominant influence is the value of the van't Hoff *i* factor.

As an instance of the method of summation of the effects due to different constituents in predicting total diffusion, the data for a typical soap solution are analyzed and found to be in agreement with previous information as to their properties. The data for sugar solutions show that the viscosity contributed by the dissolved substance is not that which determines rate of diffusion.

The diffusion column of one substance may, by the bombardment of its molecules, accelerate, retard or even reverse the diffusion of another substance.

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## THE PHOTOELECTRIC PROPERTIES OF AMMONIA CATALYSTS

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An extended series of experiments carried out at this Laboratory has shown that reduced  $\text{Fe}_3\text{O}_4$  is an excellent catalyst for the synthesis of ammonia<sup>1</sup> and that the activity is materially influenced by the presence of small amounts of impurities or promoters. A general investigation of the physical properties of these catalysts has been undertaken to determine, if possible, the function of the promoter, as well as add to our knowledge of surface catalysts.

An investigation of the thermionic properties *in vacuo* of a large number of possible catalysts carried out by Dr. C. H. Kunsman<sup>2</sup> has resulted in the discovery that these substances, for the most part, are excellent emitters of positive ions. A comparison of the positive ion emissivities and the catalytic properties<sup>3</sup> showed that no direct relationship existed between different catalysts, although for a given catalyst it is possible that some such correlation does exist.

The present paper deals with the photoelectric properties of several of these catalysts both *in vacuo* and in the presence of nitrogen, hydrogen and traces of oxygen.

The catalysts chosen for this research were described by Almquist and Crittenden<sup>4</sup> and are those which have received the greatest amount of study. The composition and activities of these catalysts are given in Table I.

TABLE I  
DATA ON CATALYSTS

No.	Total Fe, %	$\text{Al}_2\text{O}_3$	$\text{K}_2\text{O}$	% $\text{NH}_3$ at 450°	
				30 Atm.	100 Atm.
918	72.86	..	..	3.30	5.49
920	72.58	..	0.20	1.57	3.43
921	71.99	1.31	..	5.35	9.35
922	71.99	1.05	0.26	5.80	13.85

The composition percentages are for the unreduced material.

<sup>1</sup> Larson and Brooks, *Ind. Eng. Chem.*, **18**, 1305 (1926).

<sup>2</sup> Kunsman, *J. Franklin Inst.*, **204**, 635 (1927).

<sup>3</sup> Kunsman, *THIS JOURNAL*, **51**, 688 (1929).

<sup>4</sup> Almquist and Crittenden, *Ind. Eng. Chem.*, **18**, 1307 (1926).