XIII. COUNTER DIFFUSION IN AQUEOUS SOLUTION.

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In the introduction to a description of some experiments published in this Journal W. A. Osborne and Miss L. C. Jackson [1914] have written: "If, for instance, there are two solutions one vertically placed above the other and in contact over a relatively small surface, and if both contain decinormal sodium chloride and one of them, necessarily the lower, contains ammonium sulphate of three molecular strength, then after some days' diffusion it is found that the sodium chloride concentration in the upper fluid is greater than decinormality whilst that in the lower fluid is correspondingly reduced."

In describing their analytical results the authors show that these conclusions were based solely on Cl and SO_4 determinations and that it was assumed that Cl represented NaCl and SO_4 represented $(NH_4)_2SO_4$.

Realising that incorrectness in this assumption might permit the establishment of these observations as interesting extensions of already recognised diffusion phenomena, I repeated this experiment, supplementing the Cl and SO_4 determinations by those of K and (NH_4). As a matter of convenience KCl was used instead of NaCl. The results, given below, confirm in every respect Osborne and Jackson's analytical determinations, but the additional data with regard to K and (NH_4) lead me to suggest the following alterations in the conclusions drawn: "...then after some days' diffusion it is found that the ammonia has diffused into the upper fluid faster than the equivalent quantity of sulphate, with the result that chloride has increased in concentration in the upper fluid while sodium (potassium) has increased in concentration in the lower fluid."

The experiments described in this note were chosen with the view of establishing the phenomenon as one resulting from the varying velocities of ionic diffusion.

EXPERIMENTAL.

To simplify explanation it is convenient to refer to the originally evenly distributed solute as the *test substance*, and the solute added to one solution only as the *diffusing substance*; also, in the case of simple inorganic electrolytes to speak of them as if they were completely dissociated.

The method of experiment devised by Osborne and Jackson was followed very closely. The volume of fluid above the tap was, as in their case, equal to that of the bore of the tap plus that below the tap. This was 15·75 cc. in some experiments and 17·5 cc. in others. Osborne used larger volumes in his experiments, an arrangement which demands longer diffusion periods for the same ionic differentiation of the test substance, but permits, because of the larger volumes of material provided, more accurate analytical determinations in the fluids after diffusion.

The bottom fluid is analysed before diffusion as a check on the analytical methods. After diffusion each was well mixed and analysed in the same manner.

Experiment 1.
Test substance 0·15 N KCl; *diffusing substance* 0·790 N HNO_3.

Volume of top fluid = volume of bottom fluid = 15·75 cc.

Before diffusion		K	Cl	H	NO_3
	Top fluid	0·1508 N	0·1508 N	—	—
	Bottom fluid	0·1508 N	0·1508 N	0·790 N	[0·790 N]
After diffusion for nine days					
	Top fluid	0·1388 N	0·1625 N	0·1250 N	[0·1013 N]
	Bottom fluid	0·1627 N	0·1398 N	0·6610 N	[0·6839 N]

The K was weighed as K_2SO_4; Cl weighed as AgCl; H by titration; NO_3 by difference, for the sum of the normalities of the anions and kations in any solution must be equal.

The figures above show that the H and NO_3 originally to be found only in the bottom fluid have diffused upwards into the top fluid but with unequal velocities. The H has moved faster than the NO_3. At the same time it is seen that the K and Cl originally both of them 0·1508 N throughout the whole system have diffused in such a fashion that K has increased in concentration in the lower fluid by 0·0119 N and Cl has increased in concentration in the upper fluid by almost exactly the same amount.

Experiment 2.

Test substance 0·15 N KCl; diffusing substance 0·25 N Ba(OH)$_2$.

Volume of top fluid = volume of bottom fluid = 15·75 cc.

Before diffusion		K	Cl	Ba	OH
	Top fluid	0·1508 N	0·1508 N	—	—
	Bottom fluid	0·1508 N	0·1508 N	0·2525 N	0·2525 N
After diffusion for 14 days					
	Top fluid	0·1603 N	0·1413 N	0·0238 N	0·0380 N
	Bottom fluid	0·1413 N	0·1591 N	0·2244 N	0·2060 N

Ba was weighed as BaSO$_4$ and K weighed as K$_2$SO$_4$ in filtrate. A correction was made for solubility of BaSO$_4$. Cl weighed as AgCl, OH by titration.

Here Ba and OH have diffused from the lower fluid which alone originally contained them into the upper fluid. The OH has moved the faster. With regard to the test substance KCl the K has increased in concentration by 0·0095 N in the top fluid and the Cl has increased by 0·0091 N, nearly the same amount, in the lower fluid.

Experiment 3.

Test substance 0·15 N KCl; diffusing substance 0·773 N NH$_4$OH.

Volume of top fluid = volume of bottom fluid = 17·5 cc.

Before diffusion		K	Cl	NH$_4$	OH
	Top fluid	0·1508 N	0·1508 N	0·7730 N	0·7730 N
	Bottom fluid	0·1508 N	0·1508 N	—	—
After diffusion for six days					
	Top fluid	0·1512 N	0·1500 N	0·7007 N	0·6971 N
	Bottom fluid	0·1521 N	0·1508 N	0·0723 N	0·0760 N

Here because of its lower specific gravity the solution containing the diffusing substance had to be placed on top. Although of three times the normality of the baryta used as diffusing substance the effect in upsetting the even distribution of K and Cl is so small as to be indistinguishable in the face of experimental error.

Experiment 4.

Test substance 0·15 N KCl; diffusing substance 3 N (NH$_4$)$_2$SO$_4$.

Volume of top fluid = volume of bottom fluid = 17·5 cc.

Before diffusion		K	Cl	NH$_4$	SO$_4$
	Top fluid	0·1508 N	0·1508 N	—	—
	Bottom fluid	0·1508 N	0·1508 N	2·91 N	2·91 N
After diffusion for 15 days					
	Top fluid	0·1391 N	0·1581 N	0·3365 N	0·2609 N
	Bottom fluid	0·1577 N	0·1434 N	2·6100 N	2·5933 N

NH$_4$ by Kjeldahl; SO$_4$ weighed as BaSO$_4$; Cl weighed as AgCl. The determination of such small quantities of K in the presence of so much ammonium sulphate could not be performed with accuracy; in driving off the (NH$_4$)$_2$SO$_4$ so that the K$_2$SO$_4$ remaining might be weighed a loss of two or three per cent. seemed unavoidable. This fact is reflected in the inconsistencies in the analytical figures for the fluids after diffusion.

The analytical figures of these four experiments, together with those of Osborne and Jackson, suggest the following generalisation with regard to diffusion experiments conducted in this fashion.

The ion of the test substance having the opposite sign to the faster ion of the diffusing substance accumulates in the direction of the diffusion; the other ion of the test substance accumulates in the other direction. When the diffusing substance is feebly ionised such change in the distribution in the ions of the test substance does not occur.

Further remarks in this note will, for this reason, refer only to Experiments 1, 2 and 4 above.

THEORETICAL.

In all solutions it is a necessary condition that at any part of the volume positive and negative ions must be present in amounts electrically compensating. Those solutions in which some process of natural diffusion is occurring or has occurred are, in view of the fact that they manifest no external electrical phenomena, no exception to this rule. When, therefore, an electrolyte diffuses into an unionisable solvent its two ions must diffuse in company whether they are dissociated or free. If they differ in intrinsic mobility the faster ion will tend to diffuse ahead of the other, but because of the intense electrical field so established will succeed in doing so only to an inappreciable degree. By breaking down this field, however, the process may be allowed to proceed. If this is done by the direct application of an electric field from external sources the process is *electrolysis*. If it is the result of a differential migration of the ions of another electrolyte introduced into the system whereby all potential gradients are neutralised it is *counter diffusion*.

At this point it will be well to distinguish between what may be deduced from first principles with regard to these experiments and what facts are learnt from the analytical results.

In experiments arranged in this manner, with the top and bottom fluids exactly equal in volume, the test substance equally distributed throughout, and the diffusing substance originally in the bottom fluid only, fundamental space relationships and the principle of electrical compensation demand:

(*a*) The sum of the normalities of the anions is equal to the sum of the normalities of the kations in each fluid both before and after the experiment. [This is true, of course, of every solution.]

(*b*) The change of normality of either ion of the test substance in the

top fluid, owing to diffusion, is equal and opposite in sign to the change of normality of the same ion in the bottom fluid.

(c)   The sum of the changes of normality of the ions of the test substance in either fluid is equal but opposite in sign to the sum of the changes of normality of the ions of the diffusing substance in that fluid, if normalities of negatively charged ions are treated as negative quantities and the summation performed algebraically.

These three generalisations, deduced directly from first principles, provide an excellent check on analytical results.   They may be represented in the general case by a set of simple simultaneous equations insufficient in number to determine absolutely the values of the unknown quantities.

The *experiments* made provide *further* information:

(a)   That ion of the diffusing substance which is usually regarded as having the greater intrinsic velocity diffuses upwards to an extent greater than does the other; at least it does so in the three experiments above where the ions of the test substance, KCl, have approximately equal intrinsic velocities.

(β)   The ratio of the nett migrations of the two ions of the diffusing substance is much less than the ratio of their accepted intrinsic velocities.

(γ)   The migrations of K and Cl past the plane of the original boundary separating the two fluids are approximately equal; presumably because of their nearly equal migration velocities.   These ions therefore share equally in the task of compensating for the unequal migrations of the ions of the diffusing substance.

It may be noted that it follows from the generalisations (c) and (β) above, that the nett migrations of the ions of the test substance past the plane of the original boundary must be smaller than the nett migrations of the ions of the diffusing substance.

Examples of all these generalisations may be seen by referring to the figures of Experiment 1 and those deduced therefrom given below:

	Test substance		Diffusing substance	
	K +	Cl −	H +	NO_3 −
Change of normality of top fluid, i.e. nett migration past the plane of the original boundary	− 0·0120	+ 0·0114	+ 0·1250	+ 0·1013
	(sum = − 0·0234)		(sum = + 0·0237)	

It follows, too, that when a binary electrolyte diffuses into water it becomes, to a minute extent, acid or alkaline according as the anion or kation of the diffusing substance is the faster.   By adding litmus to

the water ahead of the diffusion front Durrant [1906] has observed the development of alkali in this manner by the diffusion of nitric acid.

Beyond those of Osborne and Jackson, who originated this method, I have not been able to find any descriptions of experiments where *differential* diffusion has been followed analytically. Durrant's observations [1906], although quantitative, were made rather on the distance migrated by different ions in the same time, and not upon the differences in quantity of the different ions passing a certain point.

The main interest in these results, however, lies in their relation to the theory of boundary potentials, for they represent a summation of the diffusions between the two liquids and, therefore, an integration of a function of the contact potential. The recognised complexity of these calculations will be reflected in any further attempt to predict from accepted data the results obtained above by analysis.

REFERENCES.

Durrant (1906). *Proc. Roy. Soc.*, **78**, 342.
Osborne and Jackson (1914). *Biochem. J.*, **8**, 246.