XXXI. COUNTER DIFFUSION IN AQUEOUS SOLUTION.

By WILLIAM ALEXANDER OSBORNE AND
LILIAS CHARLOTTE JACKSON.

From the Physiological Laboratory, University of Melbourne.

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Although we cannot put forward a satisfactory theory for the results of our experiments yet we think that they are of sufficient interest to merit publication—they may at least direct attention to a peculiar feature of diffusion so far undescribed. The following experiments are based upon the discovery of one of us (W. A. O.) that if a strong concentration of solute is allowed to diffuse into some solvent, and if both solution and solvent contain, in addition, another substance in weak concentration, in this case sodium chloride, there is an increase in concentration of the latter dilute substance in the path of the advancing diffusion. 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.

METHODS.

Vertical glass cylinders were employed each of 23 millimetres internal diameter and with a tap near the middle which had a bore exactly the same diameter as that of the cylinder. The volume from the bottom of the cylinder to the top of the bore of the tap was estimated and a corresponding volume measured off above the closed tap. In the earlier experiments the volume of fluid employed was 100 cm.³ below and 100 cm.³ above, but we found later that quicker results could be obtained by taking 30 cm.³ instead of 100. The lower diffusion fluid was poured into the cylinder until it

rose above the tap. The tap was closed and the upper part of the cylinder cleaned out with distilled water and dried. The upper diffusion fluid was then placed in the cylinder above the tap and a glass stopper inserted. The cylinder, still kept vertical, was then set up in a sheltered part of the laboratory, the tap was turned on, and diffusion allowed to take place at room temperature. When a sufficient interval of time had elapsed the tap was turned, the upper fluid well mixed and poured out. The upper part of the cylinder was then washed with distilled water and dried. The tap was then opened and the lower portion of fluid poured into a separate beaker and well mixed. Sodium chloride, or rather the chloride present, was estimated by the Volhardt procedure. Sulphate was determined gravimetrically as barium sulphate in the usual way and the concentration of ammonium sulphate calculated from the results. Glucose was estimated polarimetrically care being taken as regards mutarotation. The hypobromite method was considered sufficiently accurate for urea. By percentages are meant grams of solute in 100 cm.³ of solution.

The following experiments are typical of many others which we performed showing results of strong ammonium sulphate solution in affecting the increase of concentration of chloride.

Experiment I.

Before diffusion—

Above tap, 30 cm.³ NaCl 0.58 %.

Below tap, 30 cm.³ NaCl 0.57 %, (NH₄)₂SO₄ 39.6 %.

After diffusion for seven days—

Above tap, 30 cm.³ NaCl 0.63 %, (NH₄)₂SO₄ 5.6 %.

Below tap, 30 cm.³ NaCl 0.53 %, (NH₄)₂SO₄ (by difference) 34.0 %.

Experiment II.

Before diffusion—

Above tap, 30 cm.³ NaCl 0.58 %.

Below tap, 30 cm.³ NaCl 0.57 %, (NH₄)₂SO₄ 39.6 %.

After diffusion for 21 days—

Above tap, 30 cm.³ NaCl 0.66 %, (NH₄)₂SO₄ 6.0 %.

Below tap, 30 cm.³ NaCl 0.46 %, (NH₄)₂SO₄ (by difference) 33.6 %.

The differences in the chloride concentration are certainly striking and well outside the limits of error. We next tried the effect of two ammonium sulphate solutions of different concentrations in separate cylinders placed together under similar conditions of temperature and for the same time.

Experiment III.

A. Before diffusion—

Above tap, 30 cm.³ NaCl 0.56 %.Below tap, 30 cm.³ NaCl 0.56 %, (NH₄)₂SO₄ 26.4 %.

After diffusion for 7 days—

Above tap, 30 cm.³ NaCl 0.62 %, (NH₄)₂SO₄ 4.1 %.Below tap, 30 cm.³ NaCl 0.49 %, (NH₄)₂SO₄ (by difference) 22.3 %.

B. Before diffusion—

Above tap, 30 cm.³ NaCl 0.56 %.Below tap, 30 cm.³ NaCl 0.56 %, (NH₄)₂SO₄ 52.8 %.

After diffusion for one week.

Above tap, 30 cm.³ NaCl 0.64 %, (NH₄)₂SO₄ 7.3 %.Below tap, 30 cm.³ NaCl 0.46 %, (NH₄)₂SO₄ (by difference) 45.5 %.

The stronger solution of ammonium sulphate effected therefore a greater heaping up of the chloride. In order to avoid the difficulties associated with an ionisable salt we tried diffusion with cane sugar and also with glucose.

Experiment IV.

Before diffusion—

Above tap, 100 cm.³ NaCl 0.58 %.Below tap, 100 cm.³ NaCl 0.58 %, Cane sugar 34.2 %.

After diffusion for seven days—

Above tap, 100 cm.³ 0.60 % NaCl.Below tap, 100 cm.³ 0.56 % NaCl.*Experiment V.*

Before diffusion—

Above tap, 30 cm.³ NaCl 0.58 %.Below tap, 30 cm.³ NaCl 0.57 %, Glucose 36 %.

After diffusion for seven days—

Above tap, 30 cm.³ NaCl 0.60 %, Glucose 5.6 %.Below tap, 30 cm.³ NaCl 0.54 %, Glucose (by difference) 30.4 %.

Organic non-electrolytes have therefore the same property. On the assumption of a simple kinetic explanation based upon molecular volumes we tried equimolecular mixtures of glucose, C₆H₁₂O₆, and urea, CON₂H₄.

Experiment VI.

Before diffusion—

Above tap, 100 cm.³ NaCl 0.56 %, Urea 12 %.Below tap, 100 cm.³ NaCl 0.54 %, Glucose 36 %.

After diffusion for seven days—

Above tap, 100 cm.³ NaCl 0.56 %.Below tap, 100 cm.³ NaCl 0.54 %.

Experiment VII.

Before diffusion—

Above tap, 100 cm.³ NaCl 0.57 %, Urea 12 %.

Below tap, 100 cm.³ NaCl 0.58 %, Glucose 36 %.

After diffusion for 14 days—

Above tap, 100 cm.³ NaCl 0.58 %.

Below tap, 100 cm.³ NaCl 0.56 %.

Experiment VIII.

Before diffusion—

Above tap, 100 cm.³ NaCl 1.16 %, Urea 12 %.

Below tap, 100 cm.³ NaCl 1.16 %, Glucose 37.2 %.

After diffusion for 14 days—

Above tap, 100 cm.³ NaCl 1.17 %, Glucose 2.8 %.

Below tap, 100 cm.³ NaCl 1.15 %, Glucose (by difference) 13.4 %.

Experiment IX.

Before diffusion—

Above tap, 30 cm.³ NaCl 0.58 %, Urea 12 %.

Below tap, 30 cm.³ NaCl 0.55 %, Glucose 35 %.

After diffusion for seven days—

Above tap, 30 cm.³ NaCl 0.59 %, Urea (by difference) 10.9 %, Glucose 3.3 %.

Below tap, 30 cm.³ NaCl 0.55 %, Urea 1.1 %, Glucose (by difference) 31.7 %.

The results of this last group are not quite so definite. We tried the same solution as in Experiment IX allowing diffusion to continue for seven weeks but got no greater effect. It will be seen, however, that the differences obtained, though they may extend but little beyond the limits of error, all point in the same direction. We leave the investigation at this stage trusting that some light may be thrown on the subject from the theoretical side.