# "*Dynamic*" *Osmotic Pressures.*

By the Earl of Berkeley, F.R.S., and E. G. J. Hartley, B.A. (Oxon).

(Received March 31,—Read April 22, 1909.)

1. The following paper is a preliminary account of what is apparently a new method of measuring osmotic pressures. The account is published now because during the course of the experiments we have unfortunately damaged the only two good semi-permeable membranes that we possess, and it will be some months before the damage can be repaired.

2. A word of explanation as to the use of "dynamic" to distinguish the osmotic phenomena we are about to describe seems necessary. In all discussions of osmotic pressures (except those involving diffusion) the locution "osmotic pressure" connotes some form of equilibrium between a solution and its solvent; in the experiments about to be recorded we have measured the rate at which the solvent flows into the solution, and the essence of the observations lies in the fact that there should be no approach to equilibrium. Thus the osmotic pressure here involved is substantially that assumed to act in Nernst's theory of diffusion.

3. The experiments described below will be seen to prove that the rate of flow is proportional to, and may be used to measure, the equilibrium osmotic pressures, at all events in dilute solutions. Moreover, the rate at which water passes through a semi-permeable membrane under a given hydrostatic pressure will be shown to be the same as the rate at which it would pass that membrane, when entering a dilute solution whose osmotic pressure has the same numerical value as the hydrostatic pressure formerly used. Thus in these experiments the osmotic pressures are directly correlated with hydrostatic pressure.

4. Briefly, the method is as follows: A porcelain tube, carrying a copper ferrocyanide membrane on the outside, is set up in the osmotic pressure apparatus,[*] with water on both sides of the membrane. The interior of the tube is in communication with a graduated capillary, while the outside water can be subjected to pressure; the first part of the experiment consists in noting the rate at which known hydrostatic pressures force water through the membrane. In the second part of the experiment the tube, with its capillary attached, is surrounded with the solution whose "dynamic osmotic pressure" is required, and a measurement is made of the initial rate at which the water is sucked through the membrane into the solution.

---

[*] See 'Phil. Trans.,' Series A, vol. 206 p 483.

5. It is of the utmost importance that the initial rates be measured; for very early in the research it was found that the rate at which the water is sucked into a solution varies enormously with the time the tube remains in that solution; in some cases the velocity of the water is reduced to less than half the initial rate, and in all cases the rates slow down to a minimum, as found by Vegard,* the minimum depending on the previous history of the tube. A great many experiments were made to elucidate the cause of this phenomenon, but they will not be detailed here as they do not seem to bear immediately on the main object of the research.

6. *The Experiments.*—The first method tried was devised so as to find whether the rates of passage of the water into various strengths of cane-sugar solutions was proportional to the osmotic pressure. A tube was set up in the osmotic pressure apparatus exactly as for a determination of the equilibrium osmotic pressure;† when equilibrium had been established between the water in the tube and the solution outside (by means of the mechanical pressure put upon the solution), the pressure was suddenly and completely released and the initial rate at which the water flowed into the solution was noted. The following are examples of the observations. The first column gives the concentration of the solutions in grammes per litre, and the second and third columns give the observed rates, in millimetres, of the capillary per second,‡ for the two tubes N and X. The last column gives the known osmotic pressures:—

| Concentration. | Tube N. | Tube X. | Equilibrium osmotic pressure. |
|---|---|---|---|
| grammes. | mm./sec. | mm./sec. | atmos. |
| 750 | 0·500 | Not determined | 134 |
| 660 | 0·365 | 0·369 | 101 |
| 540 | 0·276 | 0·275 | 67 |
| 420 | 0·185 | 0·190 | 44 |
| 300 | 0·126 | 0·124 | 27 |

It will be seen that there is good concordance between the rates for the two tubes, but they are not proportional to the osmotic pressures.

7. Thinking that this want of proportionality was due to the solution not being stirred, the experiments were repeated in the following manner:—Tube X, fitted with ring stirrers which could be moved up and down, was fixed in a vertical position, and the various solutions were brought up from underneath to submerge the membrane. The observed rates were practically the

---

* 'Proc. Camb. Phil. Soc.,' vol. 15, Part I, p. 17. † *Loc. cit.*

‡ One mm. of the capillary has a capacity of 0·0011 c.c.

same as in the previous case. It was noticed, however, that an increased speed of movement of the ring stirrers seemed to influence the rate slightly, so a more efficient stirring arrangement was devised.

8. In the new apparatus the tube is fixed vertically between two horizontal brass plates by means of dermatine rings and screw couplings, in such a manner that the area of exposed membrane is the same as in the osmotic pressure apparatus proper. Three four-bladed brass paddles are placed symmetrically round the tube with their axes vertical, and the edges of the blades, which are also vertical, pass within 1 mm. of the membrane when the paddles are rotated. The edges of the blades extend along the whole length of the membrane. In the experiments, the number of revolutions of the paddles was between six and three per second, and it was now found that the difference between practically no stirring and these rapid speeds was, in the case of the strongest solution, about 10 per cent. in the water rate.

9. Before giving the results of the experiments with the new apparatus, we will record the measurements of the flow of water through the membrane under different hydrostatic pressures. These were obtained with tube X in the osmotic pressure apparatus, using a Schaeffer and Budenberg standard dead weight pressure gauge to give the pressures. In the table, the first column gives the pressure on the water, and the corresponding rate of flow is noted in the second column.

| Pressure. | Rate. | Ratio of rates. | Ratio of pressures. |
|---|---|---|---|
| atmos. | mm./sec. | | |
| 20·41 | 0·1075 | 1 | 1 |
| 40·82 | 0·2203 | 2·05 | 2 |
| 61·24 | 0·3240 | 3·01 | 3 |
| 81·65 | 0·4303 | 4·00 | 4 |
| 102·06 | 0·5319 | 4·95 | 5 |
| 122·47 | 0·6378 | 5·93 | 6 |

The average rate per atmosphere pressure is 0·00528 mm. per second. It is evident from these figures that the rates may be taken as proportional to the pressure, a conclusion which has some interest of its own; but we will reserve the discussion of this for another opportunity, when a more detailed account of the whole work can be given.

10. On setting up tube X in the new stirring apparatus and proceeding in the manner already outlined, we obtained the results tabulated below. The first column gives the concentration (grammes per litre), the second the observed rate, the third gives this rate divided by 0·00528 (the average rate per atmosphere hydrostatic pressure found in the last experiment). The

numbers in this column are taken as the "dynamic" osmotic pressures of the solutions. The fourth column gives the equilibrium pressures for the solutions—determined experimentally[*] for the stronger solutions, and calculated from Boyle's Law for those that are weaker.

Tube X.

| Concentration. | Rates. | Rates/0·00528 = dynamic osmotic pressure. | Equilibrium osmotic pressure. |
|---|---|---|---|
| grammes. | mm./sec. | atmos. | atmos. |
| 750 | 0·571 | 108·2 | 134·7 |
| 660 | 0·472 | 89·5 | 100·8 |
| 540 | 0·315 | 59·7 | 67·5 |
| 300 | 0·134 | 25·4 | 26·8 |
| 96·2 | 0·0341 | 6·46 | 6·36 |
| 45 | 0·0155 | 2·94 | 2·97 |

It will be seen that the agreement between the last two columns is very good for the lower numbers, but that the larger values diverge considerably. We are not ready as yet to offer a satisfactory explanation of this discrepancy.

11. A similar set of experiments was made with tube N, but unfortunately the membrane was damaged before the rate of flow under hydrostatic pressure could be determined. The results are tabulated as in the last table,

Tube N.

| Concentration. | Rates. | Rates/0·00528 = dynamic osmotic pressure. | Equilibrium osmotic pressure. |
|---|---|---|---|
| grammes. | mm./sec. | atmos. | atmos. |
| 750 | 0·552 | 104·6 | 134·7 |
| 558·5 | 0 324 | 61·3 | 71·8 |
| 300 | 0·1272 | 24·2 | 26·8 |
| 150·8 | 0·0552 | 10·5 | 11·8 |
| 93·75 | 0·03285 | 6·23 | 6·18 |
| 45 | 0·01537 | 2·91 | 2·97 |
| 20 | 0·006680 | 1·27 | 1·32 |
| 10 | 0·003443 | 0·65 | 0·66 |
| 2·02 | 0·000747 | 0·141 | 0·134 |

and we have felt justified in dividing the observed water rates by the same factor as in the case of tube X, because the two tubes have behaved throughout all our researches in an exactly similar manner,[†] and, moreover,

---

[*] *Loc. cit.*

[†] This is apparent in the table in paragraph (6).

a measurement of the hydrostatic pressure rate, when the tube was known to be slightly damaged, gave a value of 0·00540 mm./sec. per atmosphere pressure, a value which is not greatly different from that used in the table.

Here, again, the agreement between the last two columns is good for the lower values, and attention may be drawn to the fact that the rates for the two tubes are very similar.

12. All the experiments here recorded were carried out at 0° C., or as near as possible to that temperature, but it may be mentioned that some somewhat imperfect experiments show that the temperature coefficient is quite large—in fact, a difference of 1° (near 0° C.) may cause a difference in the rates of 10 per cent.

13. There are two further points that seem worth mentioning. One is that we have reason for believing that fairly accurate experiments can be made on more dilute solutions than 2·02 grammes per litre. This may be of importance as giving an easier way of measuring very small osmotic pressures than that employed in the direct equilibrium method.

The other point is that the determination of the rate of flow under a hydrostatic pressure is a more delicate test of the semi-permeability of the membrane than is the actual measurement of the amount of sugar which comes through during a direct equilibrium pressure experiment.*

14. In conclusion, it may be emphasised that these preliminary results show that osmotic phenomena can be measured kinetically (we do not mean that the kinetic theory of osmotics is thereby inferred), and that the results are, for dilute solutions, the same as when measured statically. The method puts directly in evidence the driving forces or partial pressures which have to be considered in the dynamical theory of diffusion of solutions.

---

* *Cf. loc. cit.*, Appendix A.