

GENERAL DISCUSSION ON OSMOTIC PRESSURE.

At the Meeting of the Society held on Tuesday, January 29, 1907, a General Discussion on **Osmotic Pressure** took place. Professor H. E. Armstrong, F.R.S., was in the chair.

The discussion was opened by the **Earl of Berkeley**, who exhibited and described his Apparatus for the Direct Measurement of Osmotic Pressure.

The ordinary direct method of measuring osmotic pressures is to obtain equilibrium on the two sides of the semi-permeable membrane by means of the pressure of a head of liquid. The method devised by the author and Mr. E. G. J. Hartley substitutes mechanical pressure, which is put straight on to the solution, and equilibrium thus obtained. Reversing the usual arrangement, the solution is put outside the semi-permeable tube, in an outer containing tube of gun-metal, and the solvent inside, suitable mechanical arrangements being provided for rendering the joints leak-tight. The pressure is obtained from a plunger worked with a pile of weights and delivered through a mercury U-tube to the solution outside the septum. Equilibrium is obtained or calculated by watching through a telescope the motion of the solvent in a gauge. The measurements may be made at any desired temperature. Corrections are applied for the imperfect semi-permeability of the membrane by analysing the solvent to see if any solution has passed into it.*

A vapour pressure method for measuring osmotic pressure was also described.† This is a modification of the Ostwald and Walker dynamical method. Air is sucked through a train of glass vessels containing first sulphuric acid, to dry it, then the solution from which it gets saturated up to the vapour pressure of the latter, then the solvent, of which it here takes up more, and finally sulphuric acid again. There are two trains of vessels arranged to oscillate about a central axis, so that the air does not actually bubble *through* the liquids, which is unsatisfactory, but merely passes *over* them, small platinum tubes being placed in the tubes to increase the wetted surface. The whole apparatus can be placed in a bath and worked at any desired temperature. Arrhenius' relation modified for concentrated solutions was used for calculating the osmotic pressures from the lowered vapour pressures, and very concordant results were shown to have been obtained between measurements made by the direct-pressure and the vapour-pressure methods. The author is of opinion that the latter method will chiefly have to be relied upon to furnish accurate data for the further study of osmotics.

Both of these methods are described in full in the Papers referred to below.

Mr. W. C. Dampier Whetham, F.R.S., spoke on "Indirect Methods of Measuring Osmotic Pressure."

I should like, first of all, to express my admiration of the apparatus which Lord Berkeley has shown to us, and to say that although we have seen the

* See also *Trans. Roy. Soc.*, vol. 106, 1906, p. 481.

† See also *Proc. Roy. Soc.*, vol. 77, 1906, p. 156.

apparatus which has led to such extremely interesting results, we have not seen all the many forms of apparatus which failed, but led, by slow development, to this great success. The work has really been going on for years, and only one who has followed, as I have, the different vicissitudes of it can appreciate fully the enormous amount of labour and skill which has been shown by Lord Berkeley and Mr. Hartley.

I have been asked to say something to-night about indirect methods of measuring osmotic pressure. One of them has been described to us already, this extraordinarily accurate vapour pressure method; and I believe, with Lord Berkeley, that it is the only way to which we can look for a really thorough investigation of osmotic phenomena. Therefore, it becomes of extreme interest to consider the theory of it as fully as we are able. The formula which Lord Berkeley has developed to connect osmotic and vapour pressures is—

$$\log \frac{p}{p^s} = \frac{P\sigma_0}{A} v$$

where p and p^s are the vapour pressures of the solvent and solution respectively, P the osmotic pressure, σ_0 the density of the vapour reckoned at the standard atmospheric pressure A , and v the volume of unit mass of the solvent. This expression is not quite the same as that obtained by the consideration of a thermo-dynamic cycle of operations, and the cause of the discrepancy has been worked out by Mr. Spens. The thermo-dynamic formula which is reached by the ordinary van't Hoff cycle may be written in the same form, but the quantity v , instead of denoting the volume of unit mass of the solvent, now signifies the change of the volume of the solution when unit mass of the solvent enters through a semi-permeable wall. The two results become identical, in cases where there is no change in volume of the solvent as it enters the solution. In solutions of sugar, any change in volume is small, and experiments on such solutions cannot decide between the two formulæ. Consequently, it becomes of great interest to develop further such observations as the one which Lord Berkeley has described with calcium ferrocyanide, to see whether with solutions in which a volume change does occur, the thermo-dynamic result is verified. If in reality we are measuring the ordinary thermo-dynamic osmotic pressure, that is to say, the pressure at which a solution is in equilibrium with its solvent through an ideal semi-permeable wall, the thermo-dynamic cycle must, I think, lead to the right result; but, from an experimental point of view, it is most important to carry the observations further, and see which of the two formulæ agrees with the facts.

Now that Lord Berkeley and Mr. Hartley have developed the vapour pressure method to such a state of perfection, we may claim to possess the means of determining indirectly the osmotic pressures of concentrated solutions. Turning to the other end of the scale, we are still dependent on Mr. Griffiths' partly published results on freezing-points for a knowledge of the osmotic pressures of very dilute solutions. Mr. Bedford has been continuing the experiments, and his results are awaited with interest.