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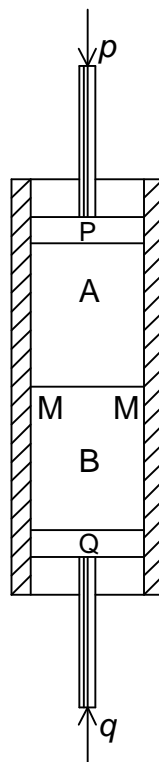
ON OSMOTIC PRESSURE AGAINST AN IDEAL SEMI-PERMEABLE MEMBRANE.¹

To approach the subject of osmotic pressure against an ideal impermeable membrane by the easiest way, consider first a vessel filled with any particular fluid divided into two parts, A and B, by an ideal surface, MM. Let a certain number of individual molecules of the fluid in A, any one of which we shall call D (the dissolved substance), be endowed with the property that they cannot cross the surface MM (the semi-permeable membrane); but let them to be in other respects exactly similar to every other molecule of the fluid in A, and to all the molecules of the fluid in B, any one of which we shall call S (the solvent), each of which can freely cross the membrane. Suppose now the containing vessel and the dividing membrane all perfectly rigid.² Let the apparatus be left to itself for so long time that no further change is perceptible in the progress towards final equilibrium of temperature and pressure. The pressure in A and B will exactly the same as they would be with the same densities of the fluid if MM were perfectly impermeable, and all the molecules of the fluid were homogenous in all qualities; and MM will be present on one side only, the side next A, with a force equal to the excess of the pressure in A above the pressure in B, and due solely to the impacts of D molecules striking it and rebounding from it.

If now, for a moment, we suppose the fluid to be "perfect gas," we should find the pressure on MM to be equal to that which would be produced by the D molecules if they were alone in the space A; and this is, in fact, very approximately what the osmotic pressure would be with two ordinary gases at moderate pressures, one of which is confined to the space A by a membrane freely permeable by the other. On this supposition the number of the S molecules per unit bulk would be the same on the two sides of the membrane. And if, for example, there are 1000 S molecules to one D molecule in the space A, the pressure on the piston P would be 1001

times the osmotic pressure, and on Q 1000 times the osmotic pressure. But if the fluid be "liquid" on both sides of the membrane, we may annul the pressure on Q and reduce the pressure on P to equality with the osmotic pressure, by placing the apparatus under the receiver of an air-pump, or by pulling Q outwards with a force equal and opposite to the atmospheric pressure on it. When we do this, the annulment of the integral pressure of the liquid on the piston Q is effected through balancing by attraction, of pressure due to impacts between the molecules of the liquid S and the molecules of the solid piston Q. We are left absolutely without theoretical guide as to the resultant force due to the impacts of S molecules and D molecules striking the other piston, P, and rebounding from it, and their attractions upon its molecules; and as to the numbers per unit volume of the S molecules on the two sides of MM, except that they are not generally equal.

No molecular theory can, for sugar or common salt or alcohol, dissolved in water, tell us what is the true osmotic pressure against a membrane permeable to water only, without taking into account laws quite unknown to us at present regarding the three sets of mutual attractions or repulsions: (1) between the molecules of the dissolved substance; (2) between the molecules of water; (3) between the molecules of the dissolved substance and the molecules of water. Hence the well-known statement, applying to solutions, Avogadro's law for gases, has manifestly no theoretical foundation at present; even though for some solutions other than mineral salts dissolved in water, it may be found somewhat approximately true, while for mineral salts dissolved in water it widely far from the truth. The subject is full of interest, which is increased, not diminished, by eliminating from it fallacious theoretical views. Careful consideration of how much we can really learn with certainty from theory (of which one example is the relation between osmotic pressure and vapour pressure at any one temperature) is exceedingly valuable in guiding and assisting experimental efforts for the increase of knowledge. All chemists and physicists who occupy themselves with the "theory of solutions," may well take to heart warnings, and leading views, and principles, admirably put before them by Fitzgerald in his Helmholtz Memorial Lecture (*Transactions* of the chemical society, 1896) of January 1896 (pages 808-99).
KELVIN.



1. Communicated to the royal society of Edinburgh, January 18, by Lord Kelvin.

2. In the drawing, the vessel is represented by a cylinder closed at each end by a piston to facilitate the consideration of what will happen if, instead of supposing it rigid, any arbitrary condition as to the pressures on the two sides of the membrane is imposed.