

of osmotic pressures in plants and animals, chemotaxis, the theory of ionisation and its application to the germicidal action of disinfectants, the permeability of membranes and the influence of this on secretion, the velocity of reactions, catalysis, colloidal solutions, and the bearing of physical chemistry on serum therapy, in which connection the work of Ehrlich, Arrhenius, and Madsen is briefly reviewed. Altogether this book supplies a decided want, and can be thoroughly recommended.

LETTERS TO THE EDITOR.

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Osmotic Pressure.

IN the issue of NATURE for May 3 (p. 19) appeared an abstract of a recent paper by Prof. Kahlenberg on "Osmosis and Osmotic Pressure." In Prof. Kahlenberg's paper, and also in the abstract, it is claimed that his experiments invalidate van 't Hoff's theory of osmotic pressure, by which the concordance between the pressure of gases and the osmotic pressure of dilute solutions was established. As the basis of that theory seems sometimes to be misunderstood, may I be allowed to recall the principles on which it is founded?

In a paper published in the *Zeitschrift für physikalische Chemie* for 1887, van 't Hoff showed that, from the well-known experimental relation between the solubility of a gas and the pressure, it followed by a simple application of the second law of thermodynamics that the osmotic pressure of a dilute solution must possess the same value as the ordinary pressure of a gas at the same concentration. The solution must be so dilute that the dissolved systems, each made up of a particle of solute as nucleus, and the portion of solvent which it influences, are beyond each others' spheres of action. The proof has been put in a modified form by Lord Rayleigh (*NATURE*, 1897), and Prof. Larmor has obtained the same result by using the fundamental conceptions of the molecular theory as a basis, instead of the experimental solubility relations of a gas (*Phil. Trans.*, A, 1897). In all these proofs no assumption is made as to the nature of osmotic pressure. It may be due to molecular impacts or to chemical affinity, or to some other undiscovered cause. The strength (and weakness) of a thermodynamic proof lies in this very independence of assumptions as to the mechanism by which the effects are produced. Prof. Kahlenberg and his followers seem to consider that the thermodynamic theory of solutions stands or falls with the hypothesis that the pressure is due to molecular bombardment.

If the conditions assumed in the proofs are realised, the whole authority of thermodynamics goes to support the result. The importance of experiments on osmotic pressure, such as those of Prof. Pfeffer, Lord Berkeley and Mr. Hartley, and Prof. Kahlenberg, lies in the question how far the assumptions made in the thermodynamic proofs can be realised experimentally. This is a much humbler rôle than that assigned to the experiments by Prof. Kahlenberg, who claims that the application of gas laws to solutions is based on the few observations of Pfeffer and others by which those laws have been verified directly. Nevertheless, the experiments are of great interest. The gas value for the osmotic pressures measured by Pfeffer shows that the conditions laid down in the thermodynamic theory are realised in practice: (1) that for sugar solutions in water an approximately perfect semi-permeable membrane has been obtained; (2) that no selective action such as could be produced by a Maxwellian daemon is in operation; (3) that the molecules of cane sugar in solution are the simple molecules indicated by the chemical formula, though they may or may not be combined with solvent molecules; (4) that a solution which is dilute in the thermodynamic sense can

be realised at possible concentrations; (5) that a theory deduced for volatile solutes may be extended to other cases. When other solutions and different membranes are employed, one or more of these conditions may fail, and the theoretical value be beyond the reach of experimental attainment. Prof. Kahlenberg remarks that because a semi-permeable membrane does not exist, a theory which postulates one cannot be maintained. We might construct a parallel statement by saying that because a frictionless piston is not practically obtainable, in Carnot's engine and the science of reversible thermodynamics physicists and engineers have imagined a vain thing.

But I may point out that at least two perfect semi-permeable surfaces are probably known: (1) when a solution freezes to give the solid of the pure solvent, the solid is compressed into a smaller volume of liquid solution; the surface of the growing crystals is semi-permeable. (2) When a volatile solvent evaporates from the solution of a non-volatile solute, the free surface of the liquid is again a semi-permeable membrane. From these two facts follows the validity of the thermodynamic relations between the osmotic pressure on the one side and the freezing point and vapour pressure on the other. This is important, for it enables us to use measurements of freezing points or vapour pressures when it is not possible to realise the experimental conditions necessary for a satisfactory determination of the true osmotic pressure.

Osmotic pressure is a thermodynamic conception. The pressures observed in practice may or may not represent the same thing. We may define osmotic pressure as the excess of hydrostatic pressure it is necessary to exert on a solution in order that it may be in equilibrium with the solvent through a perfect semi-permeable membrane. With this definition we may use the conception of osmotic pressure as a basis for a Carnot's cycle and a thermodynamic theory of solutions. Prof. Kahlenberg writes that opponents of van 't Hoff's idea have generally held that the so-called osmotic pressure is an ordinary hydrostatic pressure, brought about by the entrance of liquid into the osmotic cell. It is delightful to find one point at least in which the supporters of van 't Hoff, and van 't Hoff himself, are in complete agreement with his opponents.

In the abstract of Prof. Kahlenberg's paper which appeared in NATURE we are warned that, among the general ruin of physical theories which is to follow his experiments, the hypothesis of ionic dissociation is involved. I confess that the warning leaves me unmoved. The idea that the ions of electrolytic solutions are dissociated from each other during their movement (though possibly or probably combined with the solvent) is required by the electrical phenomena. The abnormally great osmotic pressures of certain electrolytes dissolved in water indicate some kind of dissociation, but cannot tell us whether or not that dissociation takes place so as to give rise to electrified systems. In simple salts such as potassium chloride, which we know by their electrical properties to be electrically dissociated, it is difficult to see how a second kind of simultaneous dissociation could occur. But that non-electrical separation is sometimes found is indicated by some older experiments of Prof. Kahlenberg himself, who found that solutions of diphenylamine in methyl cyanide show abnormally low molecular weights, but are non-conductors of electricity. The theory of ionic dissociation rests upon electrical evidence, and by such evidence it must be tried.

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CONSIDERABLE importance seems to be attached to a recent paper by Prof. Kahlenberg on "Osmosis and Osmotic Pressures" (*Jour. Phys. Chem.*, vol. x.), as is evidenced by a separate summary published in NATURE (May 3, p. 19). In these circumstances it may not be out of place to point out that the conclusions Prof. Kahlenberg deduces are not warranted.

On p. 142 he says "indirect measurements of osmotic pressures . . . from vapour tensions . . . involves the assumption that the gas laws hold for solutions." This is contrary to fact. We have shown experimentally (see vol. lxxvii. *Proc. Roy. Soc.*) that aqueous solutions of cane sugar give the same osmotic pressure whether observed