an amount of osmotic work P(t⅛-Z'ι). If the heat of solution be measured in a calorimeter, no work is done, so that, if we call this calorimetric heat of solution L, the two quantities are connected by the relation L = λ-∣-P(ι⅛-th). If L is zero or negligible, λ-— P(r2-Vi) and we have dij∕dT=-P/T or dP∕P≈—dT/T, which, on integration gives log P = log T÷C, or P≈⅛T, *i.e.* the osmotic pressure is proportional to the absolute temperature. This result must hold good for any solution, but if the solution be dilute when saturated, that is, if the solubility be small, the equation shows that if there be no heat effect when solid dissolves to form a saturated solution, the solubility is independent of temperature, for, in accordance with the gas laws, the osmotic pressure of a dilute solution of constant concentration is proportional to the absolute temperature. It follows that if the thermodynamic heat of solution be positive, that is, if heat be absorbed to keep the system at constant temperature, the solubility will increase with rising temperature, while if heat be evolved on dissolution, the solubility falls when the system is heated.

In all this investigation it should be noted that the heat of solu­tion with which we are concerned is the heat effect when solid dissolves to form a saturated solution. It is not the heat effect when solid is dissolved in a large excess of solvent, and may differ so much from that effect as to have an opposite sign. Thus cupric chloride dissolves in much water with an evolution of heat, but when the solution is nearly saturated, it is cooled by taking up more of the solid.

In a very dilute solution no appreciable heat is evolved or absorbed when solvent is added, but such heat effects are generally found with more concentrated solutions. The result is to change the relation between tempera­ture and the osmotic pressure of a solution of constant concentration, a relation which, in very dilute solutions, is a direct proportionality.

The equation of available energy (see Energetics) A = U+ TdA/dT may be applied to this problem. The available energy A is the work which may be gained from the system by a small rever­sible isothermal operation with an osmotic cylinder, that is Pdv. If *l* is the heat of dilution per unit change of volume in a calorimeter where all the energy goes to heat, the change in internal energy U is measured by *ldv*. We then have

P<⅛=√<⅛+T^(P<⅛).

Neglecting the volume change with temperature this gives P =Z4-TdP∕dT for the relation required. In the case where *l* is negligible we have P∕dP = T∕dT, which on integration shows that the osmotic pressure, as in the special case of a dilute solution, is proportional to the absolute temperature.

*Theories of Solution.—*The older observers, noticing the heat effects which often accompany dissolution, regarded solutions as chemical compounds of varying composition. The physical investigation of osmotic pressure, and its correlation by Van’t Hoff with the pressure of a gas, brought forward a new aspect of the phenomena, and suggested an identity of physical *modus operandi* as well as of numerical value. On this view, the function of the solvent is to give space for the solute to diffuse, and the pressure on a semi-permeable membrane is due to the excess of solvent molecules entering over those leaving in conse­quence of the smaller number which impinge on the membrane from the side of the solution; the defect in the number must be proportional, roughly at any rate, to the number of solute molecules, present, that is, to the strength of the solution.

Whatever view, if any, be adopted as to the nature of a solu­tion, the thermodynamic relations we have investigated equally hold good. It is the strength and weakness of thermodynamic methods that they are independent of theories of constitution. The results are true whatever theory be in vogue, but the results throw no light on the problem of which theory to choose. All the thermodynamic relations we have deduced hold on any theory of solution and favour no one theory rather than another. Whether osmotic pressure be due to physical impact or to chemical affinity it must necessarily have the gas value in a dilute solution, and be related to vapour pressure and freezing point in the way we have traced. But for any theory of solution to be tenable, it must at least be consistent with the known thermo­dynamic relations, verified as those relations are by experiment.

On certain assumptions required for the extension of the methods of the kinetic theory of gases to liquids, L. Boltzmann offered a demonstration of the law of osmotic pressure in dilute solutions, based on the idea that the mean energy of translation of a molecule should be the same in the liquid as in the gaseous state. But, whether or not the assumption underlying this demonstration be accepted, the similarity between solution and chemical action remains, and the osmotic law has been examined from this side by J. H. Poynting and by H. L. Callendar. The fundamental phenomenon they take to be the identity of vapour pressure, and consider the combination necessary to reduce the vapour pressure of a solution to the right value. If each mole­cule of the solute combines with a certain number of molecules of the solvent in such a way as to render them inactive for evapora­tion, we get a lowering of vapour pressure. Let us assume that the ratio *p∣p'* of the vapour pressures of the solvent and solution is equal to the ratio of the number of free molecules of solvent to the whole number of molecules in the solution. Each molecular complex, formed by solution and solvent, is treated as a single molecule. If there are *n* molecules of solute to N of solvent originally, and each molecule of solute combines with a molecule of solvent, we get for the ratio of vapour pressures *p∣p'*=(N—*an)∣(N-an+n),* while the relative lowering of vapour pressure is *(p-p')∣p≈n∣(N~an).*

In the limit of dilution when *n* is very small compared with N this gives Raoult's experimental law that the relative lowering is n∕N, which we deduced from the osmotic law, and conversely from which the osmotic law follows, while for more concentrated solutions agreement is obtained by assigning arbitrary values to α, which, as we have seen, is 5 in the case of cane-sugar.

Certain solvents, such as water, liquid ammonia or liquid hydrocyanic acid, possess the power of making some solutes, such as mineral salts and acids, when dissolved in them, con­ductors of electricity. The special properties of these solutions are dealt with under Electrolysis and Conduction, Elec­tric, *§ In Liquids.* Attempts have been made to co-ordinate this ionizing power of solvents with their dielectric constants, or with their chemical properties. On the lines of Poynting’s theory of solution, each ion in electrolytes must combine with one or more molecules of solvent.

*Diffusion in Solutions.—*The passage of dissolved substances through animal and vegetable membranes was the subject of many early experiments. It was found that substances like mineral salts, which crystallize well from solution, passed such membranes with comparative ease, while the jelly-like substances such as albumen passed with extreme slowness if at all. The first to make systematic experiments on the free diffusion of dissolved substances with no separating membrane was Thomas Graham (1804-1869), who immersed in a large volume of water a wide-mouthed bottle containing a solution, and after some time measured the quantity of substance which had diffused into the water. Again the two classes of substances mentioned above were found to be distinguished, and Graham called the slowly diffusible non-crystalline bodies colloids, in contrast to the quickly diffusible crystalloids. Graham showed that the diffusion was approximately proportional to the difference in con­centration, and on these lines a theory of diffusion was founded on the lines of Fourier’s treatment of the conduction of heat.

The quantity of substance which diffuses through unit area in one second may be taken as proportional to the difference in con­centration between the fluids at that area and. at another parallel area indefinitely near it. This difference in concentration is proportional to the rate of variation—*dc∣dx* of the concentration *c* with the distance x., so that the number of gramme-molecules of solute which, in a time *dt,* cross an area A of a long cylinder of constant cross section is dN = -DA(dc∕dx)dZ, where D is a constant known as the diffusion constant or the diffusivity.

The osmotic pressure of a solution depends on the concentration, and, if we regard the difference in that pressure as the effective force driving the dissolved substance, through the solution, we are able to obtain the equation of diffusion in another form. When the solution is dilute enough for the osmotic pressure to possess " the gas ” value the equation becomes—

,, τ RT a *de j .*

i∕N \_ *f ⅛dχdti*

where R is the usual gas constant, T the absolute temperature, and F the force required to drive one gramme-molecule of the solute through the solution with unit velocity.