height of the column of solution would rise or fall and the equili­brium with the vapour be disturbed. A continual circulation might thus be set up in an isothermal enclosure and maintained with the performance of an unlimited supply of work. This result would be contrary to all experience of the impossibility of "perpetual motion,” and hence we may conclude that through such a semi-permeable wall, the solvent and the solution at the foot of the column would be in equilibrium under the excess of hydrostatic pressure repre­sented when the solution is very dilute by *P=(p-pl)p∣σ.* But such a pressure represents the equilibrium osmotic pressure discussed above. Therefore the equilibrium osmotic pressure of a solution is connected with the vapour pressure, and, in a very dilute solution, is expressed by the simple relation just given.

Another relation becomes evident if we use as a semi-permeable partition a "vapour sieve ” as suggested by G. F. Fitzgerald. If a number of small enough holes be drilled through a solid substance which is not wetted by the liquid, our knowledge of the phenomena of capillarity shows us that it needs pressure to force the liquid into the holes. A piston made of such a perforated substance, therefore, may be used to exert pressure on the liquid, while all the time the vapour is able to pass. By evaporation and condensa­tion, then, the solvent can pass through this perforated partition, which thus acts as a perfect semi-permeable membrane. When the solution and solvent are in equilibrium across the partition, the vapour pressure of the solution has been increased by the application of pressure till it is equal to that of the solvent. In any solution, then, the osmotic pressure represents the excess of hydrostatic pressure which it is necessary to apply to the solution in order to increase its vapour pressure to an equality with that of the solvent in the given conditions.

Similar considerations show that, since at its freezing point the vapour pressure of a solution must be in equilibrium with that of ice, the depression of freezing point produced by dissolving a sub­stance in water can be calculated from a knowledge of the vapour pressure of ice and water below the freezing point of pure water. But another method of investigation will illustrate new ways of treating our subject.

By imagining that a dilute solution is put through a thermo­dynamic cycle we may deduce directly relations between its osmotic pressure and its freezing point. Let us freeze out unit mass of solvent from a solution at its freezing point T—*dT* and remove the ice, which is assumed to be the ice of the pure solvent. Then let us heat both ice and solution through the infinitesimal temperature range *dT* to the freezing point T of the solvent, melt the ice by the application of an amount of heat L, which measures its latent heat of fusion, and allow the solvent so formed to enter the solution reversibly through a semi-permeable wall into an engine cylinder, doing an amount of work P*dv*. By cooling the resultant solution through the range *dT* we recover the original state of the system. The well-known expression for the efficiency of the cycle of reversible operation gives us *Pdv∣L = dT∣T* or dT = TPdt√L

as a value for the depression of the freezing point of the solution compared with that of the pure solvent.

The freezing point of a solution may be determined experimentally. The solution is contained in an inner tube, surrounding which is an air space. Then comes an outer vessel, in which a freezing mixture can be placed. This solution is stirred continuously and the tem­perature falls slowly below the freezing point, till the supersaturation point is reached, or until a crystal of ice is introduced. The solution then freezes, until the heat liberated is enough to raise the tem perature to the point of equilibrium given by the tendency of the solution taken in contact with ice to approach the true freezing point on one side and the temperature of the enclosure on the other. To get the true freezing point then, it is well to arrange that the temperature of the enclosure should finally be nearly that of the freezing point to be observed. One way in which this has been secured is by obtaining the under cooling by temporary cooling of the air space by a spiral tube in which ether may be evaporated, the outer vessel being filled with ice in contact with a solution of equivalent concentration to that within. Modifications of this method have been used by many observers, among others by Raoult, Loomis, H. C. Jones, and by E. H. Griffiths and T. G. Bedford, who compared directly the freezing points of dilute solutions with those of the pure solvent in similar conditions by the accurate methods of platinum thermometry.

Another application of the theory of energy enables us to co­ordinate the osmotic pressure of a dilute solution with the pressure of a gas occupying the same space. On the fundamental hypotheses of the molecular theory, we must regard a solution as composed of a number of separate particles of solute, scattered through­out the solvent. Each particle may react in some way on the solvent in its neighbourhood, but if the solution be so dilute that each of these spheres of influence is unaffected by the rest, no further addition of solvent will change the connexion between one particle of solute and its associated solvent. The only effect of adding solvent will be to separate further from each other the systems composed of solute particle as nucleus and solvent as atmosphere; it will not affect the action of each nucleus on its atmosphere. Thus the result will be the same whatever the nature of the inter­action may be. If solvent be allowed to enter through a semi- permeable wall into an engine cylinder, the work done when the solution within is already dilute will be the same whatever the nature of the interaction between solute and solvent, that is, whatever be the nature of the solvent itself. It will even be the same in those cases where, with a volatile solute, the presence of a solvent may be dispensed with, and the solute exist in the same volume as a gas. Now the work done by allowing a small quantity of solvent to enter reversibly into an osmotic cylinder is measured by the product of the osmotic pressure into the change in volume. Hence the osmotic pressure is measured by the work done per unit change of volume of the solution. The result of our consideration, therefore, is that the osmotic pressure of a dilute solution of a volatile solute must have the same value as the gaseous pressure the same number of solute particles would exert if they occupied as gas a volume equal to that of the solution.

The reasoning given above is independent of the temperature, so that the variation with temperature of the osmotic pressure of a dilute solution must be the same as that of a gas, while Boyle’s law must equally apply to both systems. Experimental evidence confirms these results, and extends them to the cases of non-volatile solutes—as is, indeed, to be expected, since volatility is merely a matter of degree. When the solution ceases to be dilute in the thermodynamic sense of the word, that is, when the spheres of influence of the solute particles intersect each other, this reasoning ceases to apply, and the resulting modifica­tion of the gas laws as applied to solutions becomes a matter for further investigation, theoretical or experimental. In the limit then, when the concentration of the solution becomes vanishingly small, theory shows that the osmotic pressure is equal to the pressure of a gas filling the same space. Experiments with membranes of copper ferrocyanide have verified this result for solutions of cane-sugar of moderate dilutions. But the most accurate test of the theory depends on measurements of freezing points.

A quantity of gas measured by its molecular weight in grammes when confined in a volume of one litre exerts a pressure of 22·2 atmospheres, and thus the osmotic pressure of a dilute solution divided by its concentration in gramme-molecules per litre has a corresponding value. But we have seen that the depression of dT of the freezing point of a dilute solution is measured by TPdv∕L. Putting the absolute temperature of the freezing point of water as 273°, the osmotic pressure P as 22·2 atmospheres or 22·4×106, C.G.S. units per unit concentration, L the latent heat as 79·4× 4·184×107 in the corresponding units, and *dv* the volume change