

sent is usually about 20 per cent., and a method of lowering the amount which has been employed recently is to admit exhaust gases into the producer in place of the usual water supply. The CO₂ then takes the place of H₂O as an energy absorber, and the chemical composition of the resulting gas is so greatly affected that the hydrogen sinks to less than 1 per cent. Another recent improvement in the suction gas producer is the regulation of the water admitted, so that the composition of the gas may be the same, no matter whether the "draw" of the engine is vigorous or slight. Without some such device the gas tends to become "wet" at the lower loads, and the producer to "go dead." To avoid this, the water supply to the producer has to be cut off, or greatly reduced, in proportion as the governor is cutting out working strokes in the engine.

Improvements in Class (c).

These are exceedingly numerous. The most recent decided change has been the adoption of the sleeve type of valve in the Daimler engine. Despite apparent drawbacks from the theoretical point of view, it has lately undergone an extremely severe test under the officials of the Royal Automobile Club, and has emerged victorious. It is understood that a number of other manufacturers are now considering the adoption of the slide type of valve.

Another innovation is the use of air pressure to force the fuel up from low-lying tanks to the carburettor. This is claimed to be an improvement on the exhaust pressure feed, as being less likely to choke. As regards heavy oil engines, the chief improvement to be noticed is the widespread use of water injection, which is even more useful here than in a gas engine on account of the very low pre-ignition point of mixtures of oil vapour and air.

Attempts have continually been made to produce an engine working on the two-cycle principle, and there would seem to be no reason why engines of this kind should not be as practically successful as any built to operate on the four-cycle principle. One would expect that in this way a lighter engine could be built, and lightness is a great asset, particularly in the most recent use to which the internal-combustion engine has been put, viz. *aéroplane* work. Wonderfully light engines have already been made for this purpose. The 50 horse-power engine on the *aéroplane Silver Dart* weighs only 220 lb. without oil and water, or 4.4 lb. per horse-power. The 50 horse-power "Wolseley" V-type eight-cylinder engine, built for *aéroplane* work, is reported to weigh only 340 lb., or 6.8 lb. per horse-power, although the engine is fitted with a water-cooling system. The somewhat similar 80 horse-power engine fitted to Mr. Moore Brabazon's *aéroplane* is reported to weigh only 366 lb., or 4.6 lb. per horse-power; this is also a water-cooled engine. The possibilities of the different types of engine have lately been summarised in the technical Press¹ as follows:—

Type of engine	Weight per brake horse- power lb.	Weight of 50-brake horse- power engine lb.
Four-cylinder vertical	8	400
Eight- " diagonal	6	300
Diagonal, with several cylinders grouped on one crank pin	4	200
Rotary	3	150

From this it appears that engines amply light enough for *aéroplane* work have already been built, and there is not much scope left for any improvement in this direction for which the two-cycle engine would be useful, although there is still room for general improvement by the avoidance of the use in the engine parts of all heavy materials of low mechanical strength. On the other hand, the lighter the engine the better, as it means the possibility of adding additional accessories that make for constancy of operation, such as duplicate ignition, ample water-cooling arrangements, &c. The *aéroplane* appears to offer little chance of an "altitude stop" to permit of the engine being adjusted, and constancy of operation is therefore the one essential thing so far as the motor is concerned.

Carburettors are continually being improved, but the ideal one, which will give a constant mixture at all speeds

¹ *Engineering*, April 16.

and all loads in all weather conditions, has yet to be invented. The high-water mark as regards fuel economy that has so far been reached is the performance of the White and Poppe carburettor in the 1907 Royal Automobile Club trials of commercial vehicles. This carburettor was fitted to a Maudslay car, and showed the very high "figure of merit" of 62 gross ton miles per gallon of petrol, which is nearly twice as good as was obtained from the average car of that time. In the last two years the average has, however, risen appreciably. This, with an assumed road resistance of 50 lb. per ton, would correspond to an efficiency of power transmission between the carburettor and the road wheels of no less than 15 per cent. What the road resistance really was is not known, but now, without doubt, such road resistances ought to be accurately measured and the results applied.

Conclusion.

With such a rapidly moving industry as that of the internal-combustion engine, prophecy is even more unsafe than it usually is. Writers have been bold enough to look forward to solid explosives being employed, but there one is faced with the difficulty of selecting any form of solid explosive that would have an entirely gaseous exhaust. When the gas turbine has taken practical shape, this consideration may be of less importance. Indeed, the combination of a solid explosive with a gas turbine promises this advantage, that the difficulty of the initial compression would thereby be removed. On the other hand, if we may judge by analogy with the steam turbine, provided that it were possible to keep the exhaust pressure sufficiently low, a high initial pressure would not be essential to economy. Whatever may be the outcome of the present experiments with gas turbines, or of gas producers, suitable for marine purposes on the one hand or to road transport on the other, one may be certain that the days of the external-combustion engine, the steam engine, are numbered, and that the engineers of the near future will not be satisfied with any less degree of efficiency than that which the internal-combustion engine will afford. One seems to see in the world of engineering the working of a continuous process leading to the supersession of those ideas, which, though old and tried friends, are found to produce less efficient results than those obtainable by more scientific methods. There is no reason that the writer can see to doubt the continued operation of this process during the present rivalry between the steam engine and the internal-combustion engine.

H. E. WIMPERIS.

OSMOTIC PHENOMENA AND THEIR MODERN PHYSICAL INTERPRETATION.¹

OSMOTIC pressure is a phenomenon of such importance in the theory of solutions, and in the interpretation of all vital processes, and so much valuable work has recently been directed to its elucidation, that, although it is a somewhat thorny and difficult subject, no apology is needed for any serious attempt, however inadequate, at its explanation.

One of the earliest recorded experiments on osmotic pressure is that of the Abbé Nollet, who found that a bladder containing alcohol, when immersed in water, absorbed water so greedily as in many cases to burst the bladder. The experiment illustrates in an imperfect manner the fundamental property of all animal and vegetable membranes of allowing some substances to pass through them by osmosis more easily than others. In many cases such membranes, while freely permeable to water, are practically impermeable to certain substances in solution, and play the part of sieves in directing and controlling diffusion. It will readily be understood that results of the greatest importance to biology have been obtained by studying this property of *semipermeability*, as it is called, but the application of natural membranes to the physical study of the subject is necessarily limited on account of the difficulty of obtaining sufficiently large and perfect membranes capable of withstanding any considerable pressure.

¹ Discourse delivered at the Royal Institution on Friday, February 26, by Prof. H. L. Callendar, F.R.S.

Artificial membranes of sufficient fineness to be impermeable to such substances as sugar in solution, were first prepared by Traube by means of precipitated pellicles of substances like copper-ferrocyanide. The first quantitative measurements of osmotic pressures of considerable magnitude were made by Pfeffer with membranes of this kind deposited in the pores of earthenware pots fitted with suitable manometers for indicating the pressure developed. Pfeffer found that when a semipermeable vessel, filled with sugar solution, was immersed in water, the membrane being freely permeable to water, but not to the dissolved sugar, the solution absorbed water through the membrane by osmosis until the internal pressure reached a certain magnitude sufficient to balance the tendency to absorption. The osmotic pressure developed in the state of equilibrium was found to be proportional to the strength of the solution, and to increase with rise of temperature at the same rate as the pressure of a gas at constant volume. A few years later van 't Hoff, reviewing these experiments in the light of thermodynamics, showed that the osmotic pressure of a dilute solution should be the same as the pressure exerted by a number of molecules of gas equal to those of the dissolved substance in a space equal to the volume of the solution, that it should be the same for all solutions of equal molecular strength, and that osmotic pressure followed the well-known laws of gas-pressure in all respects. This most important generalisation was hailed as the first step to a complete kinetic theory of solution, and the osmotic pressure itself has generally been regarded as due to the bombardment of the sides of the semipermeable membrane by the particles of solute, as though they were able to move freely through the solution with velocities comparable to those of the molecules of a gas. Such a view would not now be seriously maintained, but the fascinating simplicity of the gas-pressure analogy has frequently led to the attempt to express everything in terms of the osmotic pressure, regarded simply, but inaccurately, as obeying the gaseous laws, and has done much to divert attention from other aspects of the phenomena, which, in reality, are more important and have the advantage of being more easily studied. It was very soon discovered that the gaseous laws for osmotic pressure must be restricted to very dilute solutions, and that the form of the laws was merely a consequence of the state of extreme dilution, and did not necessarily involve any physical identity between osmotic pressure and gas-pressure. Many different lines of argument might be cited to illustrate this point, but it will be sufficient to take some of the more recent experimental measurements of osmotic pressure by the direct method of the semipermeable membrane.

Morse and Frazer in 1905 succeeded in preparing ferrocyanide membranes impermeable to sugar, and capable of withstanding pressures of more than 20 atmospheres. They operated by Pfeffer's original method, allowing water to diffuse into the solution in a porous pot until the maximum pressure was developed. There are many serious experimental and manipulative difficulties which the authors carefully considered and discussed in applying this method, but they succeeded in obtaining very consistent results. As a first deduction from their investigations they considered that they had established the relation that the osmotic pressure of cane-sugar was the same as that exerted by the same number of molecules of gas at the same temperature in the volume occupied by the solvent, and not in the volume occupied by the solution. In other words, the osmotic pressure of a strong solution was greater than that given by van 't Hoff's formula for a dilute solution in proportion as the volume of the whole solution exceeded the volume of the solvent contained in it. It was a very natural extension of the gas-pressure analogy to deduct the volume occupied by the sugar molecules themselves in order to arrive at the space in which they were free to move. Unfortunately, the later and more accurate series of measurements by the same experimentalists at 0° C. and 5° C. gave nearly the same osmotic pressures as at 24° C., and would appear to show either that there is little or no increase of osmotic pressure with temperature, and that the pressures at 0° C. are much greater than those given by their extension of the

gas-pressure analogy, or that one or other of the series of experiments are in error.

About the same time Lord Berkeley and E. J. Hartley undertook a series of measurements of the osmotic pressures of solutions of various kinds of sugar at 0° C. by a greatly improved experimental method, which permitted the range of pressure to be extended to upwards of 100 atmospheres. Instead of allowing the solvent to diffuse into the solution until the equilibrium pressure was reached, they applied pressure to the solution until balance was attained. The method of Lord Berkeley and Hartley possesses several obvious advantages, and it is impossible to study the original memoir without being convinced that they have really measured the actual equilibrium pressures with an order of certainty not previously attained or even approached. The pressures found were in all cases greatly in excess of those calculated from the gas-pressure of the sugar molecules in the volume occupied by the solution (according to van 't Hoff's formula for dilute solutions), or even in the restricted volume occupied by the solvent (according to Morse and Frazer's assumption).

Lord Berkeley endeavoured to represent these deviations on the gas-pressure analogy by employing a formula of the van der Waals type, with three disposable constants. Out of some fifty formulæ tested, the two most successful were those given in Table I. The constants A, a, and b were calculated to fit the three highest observations for each solution. Values calculated by the formulæ for the lower points were then compared with the observations at these points, with the results given in Table I. for cane-

TABLE I.—OSMOTIC PRESSURES OF CANE-SUGAR SOLUTIONS.

Osmotic Pressures calculated by various Formulæ.										
Van 't Hoff	Morse and Frazer	Lord B. (1)	Lord B. (2)	C.	Do. observed Lord B.					
35.6	...	53.2	...	68.4	...	67.7	...	67.6	...	67.5
27.6	...	37.4	...	45.0	...	43.4	...	43.7	...	44.0
19.7	...	24.4	...	27.7	...	25.4	...	26.8	...	26.8
11.2	...	13.3	...	14.6	...	12.2	...	14.1	...	14.0

Lord Berkeley's equations:—

$$(A/v - P + a/v^2)(v - b) = RT \quad \dots (1)$$

$$(A/v + P - a/v^2)(v - b) = RT \quad \dots (2)$$

sugar. It is at once evident that, even with three constants, the gas-pressure analogy does not represent the results satisfactorily within the limits of error of experiment. Moreover, with three constants the equation cannot be interpreted, so that the gas-pressure analogy becomes useless as a working hypothesis or as a guide to further research. On the vapour-pressure theory, to be next explained, the results are much better represented, as shown in column C, with but a single constant, and that a positive integer with a simple physical meaning.

Vapour-pressure Theory.

On the vapour-pressure theory, osmotic equilibrium depends on equality of vapour-pressure, and not on an imaginary pressure which the particles of the dissolved substance would exert if they were in the state of gas at the same volume and temperature. The vapour-pressure of any substance is a definite physical property of the substance which is always the same under the same conditions of pressure and temperature and state, and is easily measured in most cases for liquids and solutions. Equality of vapour-pressure is one of the most general, as well as the simplest, of all conditions of physical equilibrium. Ice and water can only exist together without change under atmospheric pressure at the freezing point 0° C., at which their vapour-pressures are the same. Below the freezing point the vapour-pressure of water is greater than that of ice. Either is capable of stable existence separately within certain limits, but if the two are put in communication, the vapour, being mobile, passes over from the water at higher pressure to the ice at lower pressure until equality of vapour-pressure is restored by change of temperature, or until the whole of the water is converted into ice.

In the case of ice and water, equality of vapour-pressure can also be restored by a suitable increase of pressure.

This is the well-known phenomenon of the lowering of the freezing point by pressure. By considering the equilibrium of water and vapour in a capillary tube, Lord Kelvin showed that the vapour-pressure of water, or any other liquid, was increased by pressure according to a very simple law, the ratio of the increase of vapour-pressure, dp , to the increase of pressure, dP , on the liquid being simply equal to the ratio of the densities of the vapour and liquid, or inversely as the specific volumes, v and V . This relation, which may be written $Vdp = v dP$, is merely a special case of Carnot's principle, and was deduced by assuming the impossibility of perpetual motion. Assuming a similar relation to apply to ice, Poynting showed that when a mixture of ice and water was subjected to pressure, the vapour-pressure of the ice must be increased more than that of the water (since the specific volume of ice is greater than that of water). Consequently, some of the ice must pass over into water, and the temperature must fall until the vapour-pressures are again equal. The lowering of the freezing point by pressure, as observed by Lord Kelvin, and calculated by James Thomson, agrees precisely with that deduced as above from the condition of equality of vapour-pressure.

Similar considerations apply to the equilibrium between a solution and the pure solvent, or between solutions of different strengths. To take a simple case, the vapour-pressure p'' of a sugar solution is always less than the vapour-pressure p' of water at the same temperature, and the ratio p''/p' of the vapour-pressures depends simply on the concentration of the solution, diminishing regularly with increase of concentration and being independent of the temperature. If separate vessels containing solution and water are placed in communication at the same temperature by a tube through which the vapour has free passage, vapour will immediately pass over from the water to the solution in consequence of the pressure difference, and will condense in the solution. The immediate effect is to produce equality of vapour-pressure by change of temperature. This takes only a few seconds. The vapour-pressure then remains practically uniform throughout. As diffusion proceeds and the temperature is slowly equalised, the water will gradually distil over into the solution, but the process of diffusion is so infinitely slow compared with the equalising of vapour-pressure that the final attainment of equilibrium would take years unless the solution were continually stirred.

The reason why equality of vapour-pressure is so important as a condition of physical equilibrium is that the vapour is so mobile and so energetic as a carrier of energy in the form of latent heat. The first effect is generally a change of temperature, but if the temperature is kept constant there must then be a change of concentration. Thus if two parts of the same solution are maintained at different constant temperatures, the concentrations will change so as to restore equality of vapour-pressure, if possible. Thus in a tube of solution the two ends of which are maintained at different temperatures, the dissolved substance will appear to move towards the hotter end. What really happens is that the vapour, which is the mobile constituent, moves towards the colder end. If the tube is horizontal, with a free space above the liquid for the vapour, this transference will be effected with extreme rapidity. In fact, it will be practically impossible to establish an appreciable difference of temperature until the transfer is effected. If the vapour has to diffuse through the solution in a vertical column heated at the top, the process is greatly retarded, but the final effect is the same, and can be readily calculated from the relation between the vapour-pressure and the concentration.

In explaining the production of osmotic pressure as a necessary consequence of the laws of vapour-pressure, there is one difficulty which, though seldom expressed, has undoubtedly served very greatly to retard progress. How can an insignificant difference of vapour-pressure, which may not amount to so much as one-thousandth part of an atmosphere in the case of a strong sugar solution at 0°C ., be regarded as the cause of an osmotic pressure exceeding 100 atmospheres, or 100,000 times as great as itself? The answer is that the equilibrium does not depend at all on the absolute magnitude of the vapour-

pressure, but only on the work done for a given ratio of expansion, which is the same in the limit for a gram-molecule of any vapour at the same temperature, however small the vapour-pressure. Indirectly, the smallness of the vapour-pressure may have a great effect in retarding the attainment of equilibrium, especially if obstructive influences, such as other vapours or liquids, are present. Thus mercury at ordinary temperatures in the open air is regarded as practically non-volatile. Its vapour-pressure is less than a millionth of an atmosphere, and cannot be directly measured, though it may easily be calculated. When, however, we take mercury in a perfect vacuum, such as that of a Dewar vessel, the presence of the vapour is readily manifested by its rapid condensation on the application of liquid air in the form of a fine metallic mirror of frozen mercury. The least trace of air or other gas in the vacuum will retard the condensation excessively.

Under the conditions of an osmotic-pressure experiment we have solvent and solution in practical contact, separated only by a thin porous membrane. It will facilitate our conception of the conditions of equilibrium if we imagine the membrane to be a continuous partition pierced by a large number of very fine holes of the order of a millionth of an inch in diameter. If the holes are not wetted by the solution or the water, the liquid cannot get through unless the pressure on it exceeds 100 atmospheres, but the vapour has free passage. If the solvent and solution are under the same hydrostatic pressure the vapour-pressure of the solvent will be the greater, and the vapour will pass over into the solution. Since the surfaces are practically in contact, no appreciable difference of temperature can be maintained. If the solution is confined in a rigid envelope, so that its volume cannot increase, the capillary surfaces of the solution will rapidly bulge out as the vapour condenses on them, and the pressure on the solution will increase until condensation finally ceases, when the vapour-pressure of the solution is raised to equality with that of the pure solvent. The osmotic pressure is simply the mechanical pressure-difference which must be applied to the solution in order to increase its vapour-pressure to equality with that of the pure solvent. If any pressure in excess of this value is applied to the solution, the vapour will pass in the opposite direction, and solvent will be forced out of solution. The osmotic work required to force a gram-molecule of the solvent out of the solution is the product of the osmotic pressure P by the change of volume U of the solution per gram-molecule of solvent abstracted. In the state of equilibrium of vapour-pressure, this osmotic work PU must be equal to the work which the vapour could do by expanding from the vapour-pressure p' of the pure solvent to the vapour-pressure p'' of the solution. Neglecting minor corrections, we thus obtain the approximate relation

$$PU = R\theta \log(p'/p'').^1$$

From this point of view the osmotic pressure of a solution is not a specific property of the solution in the same sense as the vapour-pressure, or the density, or the concentration, but is merely the mechanical pressure required under certain special conditions to produce equilibrium of vapour-pressure when neither the temperature nor the concentration are allowed to vary. One might with almost equal propriety speak of the "osmotic temperature" of a solution, meaning by that phrase the difference of temperature required to make the vapour-pressure of the solution equal to that of the pure solvent. The observation of the elevation of the boiling point of a solution above that of the pure solvent is a familiar instance of a special case of such a temperature difference. It is just as much a specific property of the solution as the osmotic pressure, and would only require a perfectly non-conducting membrane for its production. No one would regard the rise of boiling point as being the fundamental property of a solution in terms of which its other properties should be expressed. By similar reasoning osmotic pressure should not be regarded as existing *per se* in the solution, and as being the cause of the relative lowering of vapour-pressure and other phenomena. This point of view does not detract in any way from the reality and physical

¹ Obtained by integrating $UdP = vdp$. Planck, "Thermodynamik," also *Zeit. Phys. Chem.*, xli. 212, 1902, and xlii. 584, 1903.

importance of the effects of osmotic pressure when it comes into play, but it puts the phenomena in their true light as consequences of the law of vapour-pressure.

Regarded as a verification of the laws of vapour-pressure, direct measurements of the osmotic pressure are of the highest value, but there are comparatively few cases known at present in which such direct measurements are possible. In other cases the osmotic pressure, if it exists, can always be calculated from a knowledge of the vapour-pressure. For the elucidation of osmotic phenomena and many other problems in the theory of solutions we are compelled to make a systematic study of the relations of vapour-pressure. Much has been done in this direction in the past, but, owing to the difficulty of the measurements, much remains yet to do. I may, therefore, be pardoned if I allude briefly to some of the methods which I have employed for this purpose, and some of the conclusions at which I have so far arrived.

It is often a difficult matter, when the difference of vapour-pressure between a solution and the solvent is small, to measure the pressure difference directly to a sufficient degree of accuracy. A method very commonly employed, which has been brought to a high degree of accuracy by Lord Berkeley and his assistants, depends on the observation of the losses of weight of two vessels, containing solution and solvent respectively, when the same volume of air is aspirated slowly through them in succession. To secure accurate results, the air must pass very slowly. One complete observation takes about a week to perform successfully, and involves many difficult manipulations. I have endeavoured to avoid this difficulty by measuring the temperature difference in place of the pressure difference, since the temperature difference remains nearly constant, while the pressure difference tends to diminish in geometrical progression with fall of temperature. The method adopted for this purpose is that indicated in the diagram of the vapour-temperature balance. The temperatures of solution and solvent, contained in separate vessels communicating through a tap, are adjusted until, on opening communication between them, there is no flow of vapour from one to the other, as indicated by a change in the reading of a pair of thermojunctions immersed in the solvent respectively. The corresponding difference of temperature is observed, and since the vapour-pressures of the solvent are known, it is easy to calculate the required ratio or difference of the vapour-pressures of solvent and solution at the same temperature. When the vapour-pressures are very small it may be difficult to observe the change of temperature on opening the tap unless the apparatus is very carefully exhausted. A more delicate method in this case is to observe the direction and magnitude of the current of vapour from solution to solvent, or *vice versa*, by means of the "vapour-current indicator," illustrated in the companion diagram. This consists of a delicately suspended vane, the deflections of which are read by a mirror, and will readily indicate a difference of pressure less than the thousandth part of a millionth of an atmosphere.

The vapour-current indicator is so constructed that its deflections are very accurately proportional to the pressure difference, much more so, in fact, than any form of electric galvanometer. It can also be employed for direct measurements of small differences of vapour-pressure. The chief difficulty in this case is to ensure the absence of air or other disturbing factors. A method of avoiding this difficulty is to work at atmospheric pressure, and to measure the pressure difference between two vertical columns of air saturated with the vapours of the solvent and solution respectively. The temperature difference may be adjusted to balance, and is preferably measured by means of a pair of differential platinum thermometers, which permits a higher order of accuracy to be attained than the thermoelectric method.

Vapour-pressure in relation to Molecular Constitution.

The well-known law of Raoult, according to which the relative lowering of vapour-pressure of a solution is equal to the ratio of the number of molecules n of the solute to the number of molecules of solvent N in the solution, has

¹ I first showed this experiment ten years ago, in illustration of the delicacy of the apparatus, at a Friday Evening Lecture at the Royal Institution.

thrown a great deal of light on the molecular state of the dissolved substance in dilute solutions, but fails notably in many cases when applied to strong solutions. In the case of homogeneous mixtures of two indifferent volatile substances, such as benzol (C_6H_6) and ethylene chloride ($C_2H_4Cl_2$), which mix in all proportions without mutual action, a slightly different but equally simple law is known to hold very accurately throughout the whole range of concentration from 0 per cent. to 100 per cent. The vapour-pressure of each ingredient is simply proportional to its molecular concentration. In other words, the ratio of the partial vapour-pressure p' of either constituent at any concentration to its vapour-pressure p'_0 in the pure state at the same temperature is equal to the ratio of the number of its molecules n' in the solution to the whole number of molecules $n'+n''$ of both substances in the solution. Such is evidently the form of the simple mixture law. For substances which form compounds in the solution, or the molecules of which are associated or dissociated, this simple law is widely departed from. In a recent paper, "On Vapour-pressure and Osmotic Pressure of Strong Solutions" (Proc. R.S.A., vol. lxxx., p. 466, 1908), I have endeavoured to extend this simple relation to more complicated cases by making the obvious assumption that, if compound molecules are formed, they should be counted as single molecules of a separate substance in considering their effect on the vapour-pressure. With this proviso the vapour-pressures of strong solutions are well represented by a natural extension of the simple mixture law, and it becomes possible to investigate the nature of the compounds formed in any case. To take a simple instance, suppose that each of the n molecules of the dissolved substance combines with a molecules of the solvent, the total number of molecules of the solvent being N . The ratio of the vapour-pressure p'' of the solvent in the solution to the vapour-pressure p''_0 of the pure solvent at the same temperature will then be the same as the ratio of the number $N-an$ of molecules of free solvent in the solution, to the whole number of molecules $N-an+n$ in the solution, each compound molecule being counted as a single molecule.

With the simple formula

$$p'/p'' = (N - an + n)/(N - an),$$

the values of the vapour-pressure are very easily calculated from the molecular concentration n for simple integral values of the hydration factor a . The osmotic pressures are also readily deduced from the ratio of the vapour-pressures (p'/p'') by the formula

$$PU = RT \log (p'/p'').$$

The value $a=5$ fits the osmotic pressures for cane-sugar very well, as shown in the column headed C in Table I. The value $a=2$ fits Lord Berkeley's observations on dextrose equally well up to pressures of 130 atmospheres. The same value $a=5$ for cane-sugar also fits the observations on the depression of the freezing point and the rise of the boiling point, as it necessarily must, since these phenomena also depend on the vapour-pressure. The freezing-point method is the easiest for getting the ratio of the vapour pressures to compare with the formula. At the freezing point of an aqueous solution the vapour-pressure of the solution must be the same as that of ice, provided that ice separates on freezing in the pure state. The ratio of the vapour-pressure of ice to that of water at any temperature below 0° C. is easily calculated. All the best recorded results, except those of a few associating substances, give simple positive integral values of a . Even in the case of associating substances, like formic acid and acetone, the curves are of the same type, but the value of a is negative. Dissociating substances, like strong electrolytes, present greater difficulties, on account of the ionisation factor; but, allowing for the uncertainty of the ionisation data, they seem to follow satisfactorily the same law of vapour-pressure.

It appears from the form of the proposed law that the hydration factor a makes very little difference to the vapour-pressure in weak solutions, which follow Raoult's law as a limiting case, but it makes a very great difference in strong solutions, when nearly all the free water is used up, and the denominator $N-an$ is small. Thus

the depression of the freezing point of a strong solution of calcium chloride is more than five times as great as that calculated from the number of ions present in the solution. Each ion appears to appropriate no less than 9 molecules of water. The factor $a=9$ gives a very good approximation to the freezing-point curve, as far as the uncertainty of the data permit. When $N=an$, the vapour-pressure would be reduced to zero, according to the formula, but the formula ceases to apply when the vapour-pressure of the compound molecules themselves becomes equal to that of the solution. At or before this point the molecules will dissociate with the formation of lower hydrates. Many analogous phenomena are already known, and a more complete study of the vapour-pressures of strong solutions may be expected to throw additional light on the subject.

The essential point of the theory here sketched is that the equilibrium existing in a solution is one between definite chemical compounds and the solvent, giving rise to a simple vapour-pressure relation by means of which the phenomena may be studied and elucidated. There is a great deal of work to be done before such a theory can be regarded as established, but in the meantime it may serve very well as a working hypothesis for correlating experimental results and suggesting new lines of investigation. Regarded in this light, the vapour-pressure theory may serve a useful purpose, and, judging by the experimental data at present available, I think I may fairly claim to have made out a good *prima-facie* case for the theory.

NOTE.—The vapour-current indicator is a development of the old smoke-jack. A light spiral vane with a mirror attached is suspended in a tube, which nearly fits it, by means of a quartz fibre. Joule (Proc. Phil. Soc., Manchester, vii., 35) employed a wire spiral suspended by a silk fibre for indicating air currents, but does not seem to have adapted it for purposes of exact measurement. The instrument shown in the lecture gave a deflection of 30° (500 mm. at 1 metre) for a velocity of air current 0.01 cm./sec. The sensitiveness might easily have been increased, but the above amply suffices for most purposes.

UNIVERSITY AND EDUCATIONAL INTELLIGENCE.

REUTER'S Agency states that the Hong Kong and Shanghai Bank has made a donation of about 4500l. to the Hong Kong University.

PROF. W. OSLER, F.R.S., will deliver the inaugural address of the winter session of the London School of Tropical Medicine on Tuesday, October 26.

MR. W. H. HADOW, fellow and tutor of Worcester College, Oxford, has been appointed principal of Armstrong College of Durham University at Newcastle-on-Tyne, in succession to Sir Isambard Owen, who has accepted the Vice-Chancellorship of Bristol University.

WE learn from *Science* that the College of Agriculture of the University of the Philippines, situated at Los Banos, opened on June 14 last with about sixty students. Prof. E. B. Copeland is dean and professor in botany; Prof. H. Cuzner, professor of agronomy; Prof. E. M. Ledyard, professor of zoology; and Prof. S. B. Durham, professor of animal husbandry.

A CORRESPONDENT asks us to mention that a man with a science training and degree is wanted for a vacant post in an advanced mission college in South China. The Chinese are eager to acquire the secrets of Western power, and a teacher with the science qualifications required would have a fine opportunity of assisting to make history in that great land.

WE learn from the *Pioneer Mail* that on July 14 the Governor of Madras opened a new agricultural college and research institute at Coimbatore. The building is designed both for teaching and research work. A special set of rooms is set apart for chemistry, botany, entomology, and mycology. A physical laboratory is provided, as well as ample accommodation for the Madras herbarium

and a library. The cost of the new institution, including the surrounding farm, has been eight lakhs. The Governor, during the course of his remarks, said that as the demands of scientific agriculture grow and the necessity for expansion arises, the Government will not hesitate to increase the capacity of the institution.

SOCIETIES AND ACADEMIES.

PARIS.

Academy of Sciences, August 9.—M. Bouquet de la Grye in the chair.—The thermal effects of moistening soils: A. Müntz and H. Gaudechon. Certain dry soils, when moistened, give out an appreciable amount of heat, and it is possible that this thermal phenomenon may have an effect on the growth of plants. Measurements with different soils gave an evolution of heat varying from 0.9 to 6.6 calories per kilogram, and a systematic levigation showed that the finest particles caused nearly all the heat evolution.—Magneto-anodic phenomena: M. Gouy. The phenomenon described accords to a certain extent with the theory of M. Fortin, which regards the magneto-kathode rays as formed of spirals of electrons.—Discontinuous singularities of uniform analytical functions: A. Denjoy.—Tides and the crust and the elasticity of the terrestrial globe: Ch. Lallemand. The author has shown in a previous note that the principal modes of determination of the rigidity of the globe lead to different results. The theory developed in the present paper removes this anomaly.—The different species of asymmetrical intensities, observed for the magnetic components, polarised circularly, of the absorption bands of uniaxial crystals: Jean Becquerel.—The decomposition of carbon dioxide by the ultra-violet rays: H. Herchefinkel. The decomposition of carbon dioxide into oxygen and carbon monoxide by the action of the ultra-violet rays has been proved; a similar result has been obtained with the radium emanation, confirming the observations of Ramsay and Cameron.—The intervention of osmotic pressure in dyeing: M. Rosenstiehl.—A method for the rapid estimation of metallic aluminium: E. Kohn-Abrest. The metal is heated to 300° C. first in hydrogen, and then in pure hydrochloric acid gas, followed again by hydrogen. The aluminium is volatilised as chloride, and the metal determined indirectly by a determination of the chlorine.—Attempts at benzidation in the diphenyl, diphenylamine, and diphenylethane series: H. Duval.—The ethyl acetal of tetrolic aldehyde: P. L. Viguer. Dibromo butyric aldehyde was obtained by the addition of bromine to crotonaldehyde; the application of Claisen's method to this aldehyde gave, not the tetrolic aldehyde desired, but its ethyl acetal.—Some parasitic diseases of *Cinnamomum zeylanicum* of Ceylon: D. Bois and C. Gerber.—Vaccination of cattle against tuberculosis: M. Rappin. The bacilli used in these injections were modified by the action of sodium fluoride; it has been shown that the resistance of the animal to tuberculous infection is increased by the treatment almost to the point of immunisation.—The glucoses of the urine: F. Landolph. Each species of glucosuria or diabetes corresponds, in the urine, to the presence of mixtures of several kinds of sugars, and it may be supposed that these differences correspond to diseases of different organs.—The preservation and increase of digestibility of distillery pulps and of green ensilage by a rational fermentation by inoculation: J. Croibois.—The suprarenal capsules and their exchanges between the blood and tissues: J. Athanasiu and A. Gradinesco. The experiments on a dog and a cat described lead to the conclusion that the death of animals deprived of the suprarenal capsules is due to the arrest of the exchanges between the blood and the tissues.—Contribution to the study of urinary indosis in diabetic subjects: H. Labbé and G. Vitry.—The variation of an oxidising enzyme during metamorphosis in *Limnophilus flavicornis*: Xavier Roques.

CAPE TOWN.

Royal Society of South Africa, June 16.—Dr. R. Marloth in the chair.—Some points in the morphology and biology of a new species of Haworthia: Dr. S. Schönland. The author gives a full description of the only species of Haworthia with strictly distichous arrangement