XXXV. THE EXTENSION OF THE GAS LAWS TO LIQUIDS AND SOLIDS. I.

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1. *The necessity of re-stating the Gas Laws.*

It was shown by van 't Hoff from Pfeffer's experimental data that in the case of dilute solutions of sugar and other non-electrolytes the osmotic pressure produced by the substance in solution is practically the same as the ordinary outward pressure it would exert if present by itself as gas at the same temperature and in the same concentration per unit volume as in the solution. In other words, if osmotic pressure is taken to represent gas pressure, Boyle's, Charles's or Gay Lussac's and Avogadro's laws for gases can be extended in some sense to substances in dilute solution. Nevertheless there is still no agreement as to how osmotic pressure can represent gas pressure, or how, if it does, the pressure is not in the opposite direction.

A very clear picture of the great divergence of opinion is afforded by the recent discussion on Osmotic Pressure at a meeting of the Faraday Society in May 1917 [Faraday Society, 1917]. Professor Porter defends van 't Hoff's kinetic theory that osmotic pressure is the bombardment pressure of the solute molecules, and therefore, in solutions sufficiently dilute to prevent complicating conditions, has the same value as if the sugar were present as a gas at the same temperature and concentration, with nothing else present in the same space, or only another gas at an ordinary pressure. He points out that the kinetic theory "is the *only one* which directly gives the experimentally ascertained values for dilute solutions." He is forced, however, to make the

assumption that molecules may be treated, not as "real molecules," occupying space, but as "massive points" without extension. Only on this condition does the van 't Hoff theory yield the experimental values for dilute solutions. As was pointed out by other contributors, we cannot, in view of the experimental facts as to highly compressed gases, make any such assumption. Moreover the osmotic pressure on this theory is in the wrong direction. If what is usually called "the osmotic pressure of a solution" were due to extra bombardment pressure caused by the solute molecules, it would be necessary to apply mechanical pressure from the side of the pure solvent in order to neutralise this pressure. Actually the pressure applied in measuring osmotic pressure is pressure on the solution itself—i.e. pressure in the *same direction* as the bombardment pressure of the solute molecules.

This latter objection is avoided by the theory, represented in the discussion by Mr Bousfield and other contributors, that osmotic pressure is equivalent to deficiency in the bombardment pressure of solvent molecules in the solution, in consequence of their dilution by the solute. When, however, we endeavour to obtain the experimental results in terms of this theory, the first objection (apart from other objections to the details of Mr Bousfield's theory) applies with the same cogency as to van 't Hoff's theory. The bombardment pressure inside a collection of molecules of the concentration of a liquid amounts to thousands of atmospheres, and the diminution in pressure owing to dilution of the solvent would be enormously greater than the actual osmotic pressure.

It is not necessary to follow at this point the details of the more purely mathematical discussions as to osmotic pressure. To understand the phenomena it is certainly necessary to return first to the fundamental gas laws and the kinetic theory of gases, and consider what must happen when real molecules are present at high concentrations such as exist in liquids.

According to Boyle's and Charles's laws the volume occupied by a given mass of any gas varies inversely as the pressure and directly as the absolute temperature. This is expressed in the equation $PV = rMT$, where P = pressure in atmospheres, V = volume in litres, M = mass in grammes, T = absolute temperature, and r = a constant which varies for the same mass of different gases¹. When we embody Avogadro's law in the equation it becomes

$$PV = \frac{22.4}{273} \frac{M}{W} T \quad \text{where } W = \text{molecular weight of the gas, and } 22.4 = \text{volume in}$$

¹ The particular units in which volume, mass, and pressure are expressed have been selected on the score of practical convenience.

litres occupied at 0°C . and 1 atmosphere pressure by the number of grammes of a gas which corresponds to its molecular weight. As $\frac{M}{W}$ = the relative number (n) of molecules (or the number of gramme-molecules) present in different masses of different gases, we can write the equation as $PV = \frac{22.4nT}{273}$, or, more simply, $PV = .082nT$. When n is constant and equal to 1, .082 is of course the R of the familiar equation $PV = RT$, when P and V are expressed in the units specified. The kinetic theory of gases has made it possible to deduce this equation from simple principles, and also enables us to realise some of its limitations.

The equation represents very satisfactorily the experimentally ascertained facts in the case of permanent gases or mixtures of them within common limits of pressure and temperature, but, as is well known, breaks down outside these limits, and cannot be extended, except in a very limited sense, to vapours, nor in any clearly intelligible sense, to liquids. The causes of these limitations must now be examined in connection with a proposed re-statement of the equation, so as to permit of its extension to vapours and liquids.

In the first place the molecules of the gas, or gas-mixture, may combine with one another chemically, or may dissociate, on altering the temperature or pressure. It is at once evident that the ordinary gas laws cannot be applied to a change of this character, although they apply, just as before, to the products of the change.

The second limitation of the equation becomes evident even at ordinary temperatures and pressures with gases consisting of large molecules, and at high pressures or low temperatures with all the permanent gases, as, for instance, hydrogen. With T and n constant the product PV sooner or later increases at a growing rate with increase of P ; and with P and n constant the quotient $\frac{V}{T}$ increases similarly with diminution of T . This is because, although, on an average, each molecule has an amount of free kinetic energy proportional to its absolute temperature, and therefore keeps clear at each temperature an average intermolecular space inversely proportional to the pressure, the space actually occupied by the molecules themselves in virtue of their relative impenetrability and incompressibility becomes an increasing fraction of the total space occupied by the gas. The volume at absolute zero cannot, therefore, be nothing, as the equation would imply; and with increasing pressure at constant temperature the specific gravity of the gas must increase less and less in proportion to the increase of pressure.

It is clear that the equation could only hold good for an ideal gas, the

molecules of which were points possessed of mass, but having no extension. Ideal molecules of this kind have, of course, been supposed to exist; but, like many other scientific ideals, they do not correspond with actual experience, the supposition that they exist being, for instance, completely at variance with the results of the experiments of Amagat and others on gases at high pressures.

We have thus reached a first point indicating the necessity of re-stating the gas-laws and the fundamental equation which embodies them. This re-statement, as will appear below, is essential for the application of the gas-laws to liquids. We must distinguish the intermolecular volume, or space kept clear by gas-molecules in virtue only of their movements, from the space they would still occupy if they had no movement capable of external transmission. If we call the latter space, in litres, v ,¹ we can then, in accordance with the kinetic theory, write the equation of a gas as $P(V - v) = \cdot082nT$.

When V is constant and = 1 litre, v is simply the proportion of occupied space and n is the relative number of molecules or separate particles in a litre, or the molecular concentration. Hence the equation for a gas becomes $P(1 - v) = \cdot082nT$. But $1 - v$ varies as n at any assigned value of P or of T , either in a pure gas or in any particular gas-mixture. Hence if we call N the molecular concentration or number of gramme-molecules in one litre at 0° and a given pressure, the equation $P(1 - v) = \cdot082NT$ will hold at all temperatures with the same pressure and at all pressures with the same temperature. This form of the general equation is of special convenience in connection with the extension of the gas laws to gases at very high pressure and liquids, and will therefore henceforth be used extensively in this paper, although, as will appear below, with an altered definition of P .

It is only at low pressures, where $1 - v$ is practically equal to 1 that P will vary as N when T is constant. Hence Boyle's law could only be practically true at low pressures and fairly high temperatures, and must become less and less true as the pressure rises or temperature falls. Boyle's law must also deviate more, or less, from truth according to the varying size of the molecule in different gases, and consequent varying value of v at the same

¹ It should be noted that v represents the volume occupied by the molecules when touching one another, and that this is more than the volume of the molecules themselves. In general v corresponds to the b of van der Waals's equation, but since, in the case of each individual gas, the value selected for the b of this equation depends on the value of the $\frac{a}{v^2}$, I have not adopted van der Waals's notation. It will be shown in a further paper that van der Waals's equation is defective.

pressure and temperature. Similarly, it is only when $1 - v$ is practically equal to 1 that with P constant N could vary inversely as T in accordance with Charles's law. Thus at a very high pressure equal volumes of different gases must contain very unequal numbers of molecules, as the experimental results show, and must also expand unequally with the same increments of absolute temperature.

Let us now consider the case of two or more gases present together at very high pressure P or low temperature. Let N_1 be the relative number of molecules and $1 - v_1$ the proportion of free space, or intermolecular volume, in a litre of a gas-mixture at 0° at very high pressure, n the number for a given gas in the mixture, N the number and $1 - v$ the intermolecular volume for the same gas in the pure state at the same pressure, and p its partial pressure in the mixture. It is evident that if the gas were present in the pure state the partial pressure p produced by n molecules would be to the total pressure P as n to N . If, now, without altering the pressure or temperature, we substituted for $N - n$ molecules of the pure gas an equal volume of the other gas or mixture of gases, there could be no change in the partial pressure exercised by the n molecules. But the number of molecules in the gas substituted would, as we have just seen, be different from the number displaced, since at the same temperature and pressure v differs for different gases, so that at very high pressures or low temperatures $1 - v_1$ differs correspondingly from $1 - v$. Hence p is to P , not as n to N_1 , but as n to N . This is a matter of great importance, as will appear below, in connection with the application of the gas laws to liquids.

Boyle's law could now be re-stated in the wider and more correct, though less convenient, form that the intermolecular volume of a gas varies inversely as the pressure when the temperature is constant. Charles's law would take the form that at constant pressure the intermolecular volume of a gas varies directly as the absolute temperature. For Avogadro's law the re-statement would be that the number of molecules in a given volume of any gas at the same pressure and temperature varies as the intermolecular volume.

As thus re-stated, and with the proviso that no chemical change occurs in the molecules, the gas laws would represent the experimental facts if it were the case that the molecules simply repelled one another on contact. One can imagine an ideal gas with molecules of this kind; and at ordinary temperatures hydrogen seems to behave in practically the same way as this ideal gas. Actually, however, it is clear from the experimental facts that the molecules, when close together, are powerfully attracted to one another,

so that, once more, the ideal fails to correspond with the reality. This brings us to a third limitation, involving an additional re-statement of the gas laws, but at the same time allowing them to be extended to liquids.

The mutual attractions of the molecules of all gases are clearly shown by the fact that below a certain critical temperature, and with the assistance, if necessary, of a certain increase of pressure, all gases condense to the liquid form. If the gas laws as just restated were correct the formation of liquids and solids would be totally unintelligible, and substances would always behave as they do when high above their critical temperatures. But even when the molecules are, on an average, so far apart that there is no evident condensation, it must happen that the free kinetic energy of a certain proportion of them is for the moment so small that these molecules, in virtue of their mutual attraction, become associated or aggregated together for the moment in a manner analogous to the mutual association of comets or planets in a solar system, though with the molecules constantly colliding with, and not merely revolving round one another. With diminishing temperature or increasing pressure this must tend to happen more and more, and must thus cause a greater and greater deviation from the simple gas laws, even in their amended form: the effect being to diminish the external pressure which would exist but for the molecules becoming associated. When liquid is formed the great majority of the molecules are associated, so that the external pressure is very small.

Although with increasing association together of the molecules of a gas the external pressure exercised by it becomes less than it otherwise would be, yet the mean intermolecular pressure due to the mutual bombardment of the molecules, must remain the same as if no association had occurred, since the temperature, and consequently the mean kinetic energy of the molecules, is the same. Hence the fundamental gas equation still applies if we take P to mean, not external pressure, but the mean intermolecular pressure. When the gas begins to condense to visible liquid (or even, as will be shown later, to solidify) the equation will still hold good. The mean intermolecular pressure is then the "intrinsic" pressure of the liquid plus its vapour pressure, plus any additional external pressure. At lower temperatures the vapour pressure becomes so small in relation to the intrinsic pressure as to be practically negligible.

We must thus again re-state the gas laws by substituting "intermolecular pressure" for "pressure." In the fundamental gas equation $P(1 - v) = \cdot 082NT$ P now stands for intermolecular pressure, and v for the virtual volume of the

molecules in a litre of gas or liquid. We are thus in a position to extend the gas laws to liquids.

In accordance with the molecular conception of matter a liquid is regarded as a system of molecules held together by their mutual attraction, but free to move about within the system except in so far as they collide with one another. They are also kept in constant and very rapid motion by heat. The proportion of free space ($1 - v$) between the molecules in a litre of the liquid depends on a balance between the attraction of the molecules for one another and the mean free kinetic energy of the molecules. To apply the reasoning on which the kinetic theory of gases is based, this energy will vary, just as with gases, as the absolute temperature T , and will on an average be the same for any sort of molecule or other separate particle present. But since the attractions for one another of the molecules of different liquids vary, the intermolecular pressure, and consequently the free space between the molecules, will also vary in different liquids. The value of $1 - v$ in the fundamental equation is also no longer practically equal to 1, as in gases at ordinary pressures, but is much less than 1. The molecules themselves are also of unequal sizes. Hence equal volumes of different liquids contain very unequal numbers of molecules, and respond with very unequal changes in volume to changes of temperature and pressure. Van der Waals, with the help of his well-known equation, has calculated the value of P for water as about 10,500 atmospheres. If this estimate were correct, and no chemical combination existed among the molecules, the value of $1 - v$ for water would be about 0.118.

When we take P as signifying the intermolecular pressure, and N as the relative number of molecules per litre at 0° and the existing intermolecular pressure of any liquid, we can apply the same equation to liquids as to gases, or to systems of liquid and vapour or gas. If none of the molecules were associated together the external pressure (corresponding to vapour pressure) would be the same as the intermolecular pressure, and the gas would be an ideal or perfect one in the final sense reached in this paper. At temperatures sufficiently above their critical temperatures all the permanent gases approximate to this ideal gaseous state, so that until P becomes so high that $1 - v$ is sensibly less than 1, the gas laws in their crude original form correspond approximately with actual experience. If all the molecules were completely associated together in the liquid form there would be no vapour pressure. At temperatures not far above the melting point but far below the critical temperature this state is approximately realised.

At first sight it might seem that a re-statement of the gas laws in the wider form now given to them is a purely academic procedure, and deprives them of their practical utility, since there are two unknown terms in the re-stated equation, neither of which can be directly measured, though their product is known. It will be seen below, however, that the product of the two unknown terms may be used without either of them being known separately, and that for this reason the equation, in spite of the limitation just referred to, embodies a working hypothesis with very wide and important applications.

2. *Diffusion Pressure and Osmotic Pressure.*

We can now consider the theory of osmotic pressure tentatively suggested by van 't Hoff and accepted by many other writers. This theory has been generally felt, both by chemists and physiologists, to be unsatisfactory, but has become enveloped in a cloud of mathematical reasoning which seems to have hitherto protected it to a considerable extent against attack. Van 't Hoff suggested that the osmotic pressure of a liquid is pressure directly due to bombardment by the solute molecules¹; and he made the brilliant discovery that for dilute solutions the osmotic pressure corresponds to the external pressure which would be produced if the solute were present as a gas at the existing temperature and in the volume occupied by the solution, with nothing else, or only a gas at ordinary pressure, already occupying this volume.

Now when the solvent (for instance water) is present, the volume is already, as we have just seen, for the most part occupied, and the free space available for the solute molecules is only a small fraction of the total volume. There is thus no intelligible justification for the idea that the addition of the solute molecules would, if they were present under the same conditions as in a gas, add to the existing enormous intermolecular pressure a pressure equal only to what they would produce if the whole space were unoccupied, and they themselves occupied no space. Their actual pressure would be far greater. But even if, in some manner at present quite unintelligible, the intermolecular pressure were increased by an amount just equal to the osmotic pressure, this would give no explanation at all of why pure water should pass *inwards* into the solution through a semi-permeable membrane.

¹ On this subject van 't Hoff (quoted by Lewis [1916]) wrote as follows: "Regarding osmotic pressure as due to a kinetic cause (i.e. as produced by impacts of the dissolved molecules [upon the inside of the semi-permeable membrane]), there must exist a proportionality between the number of impacts in unit time and the number of molecules in unit volume. The proof is therefore exactly the same as that for Boyle's Law."

If a gas osmometer were furnished with a membrane permeable to hydrogen, but not to nitrogen, and if there were first of all pure hydrogen at atmospheric pressure both inside and outside the osmometer, and a little nitrogen were then forced in without altering the volume of gas inside the osmometer, the pressure inside would be increased, but there would be no passage of hydrogen inwards, as the partial pressure of the hydrogen inside would not be diminished. It would be just the same in the case of forcing into water a solute to which an ordinary semi-permeable membrane was impermeable. But if the *volume* of gas in the osmometer were increased, even very slightly, at the same time as the nitrogen was added, hydrogen would immediately begin to diffuse inwards, since the partial pressure of the hydrogen in the osmometer would be diminished in proportion to the increase in volume; and inward pressure proportional to this decrease of partial pressure would be developed.

Now when a solute goes into simple solution (without chemical change, such as hydrate formation) the volume of the liquid is always increased, so that the concentration of the solvent per unit volume is diminished. Just as in the case of the gas osmometer, it is this diminution in the concentration of the solvent that matters as regards osmotic pressure. Van 't Hoff's theory of osmotic pressure concentrated attention on the solute molecules, and not on the dilution of the solvent; and this is one reason for the failure of the theory to explain osmotic pressure.

The molecules of a gas are, apart from the almost negligible restraining influence of gravitation, free to move in all directions except in so far as they are stopped or diverted by collisions with other molecules. Now as all the molecules are in free movement, both of translation and rotation, the chances, whatever they may be, of any one molecule in travelling a definite distance in one direction undergoing a collision which will destroy, or partially destroy, its momentum in that direction, must vary as the proportion of occupied space to total available space, *i.e.* in proportion to v . The number of those which escape, or partially escape, will therefore vary as $1 - v$. The number of molecules of any one kind, which, for a given area of surface and unit of time, travel across this distance, must also vary in proportion to the rate of molecular bombardment of the area—*i.e.* in proportion to the total pressure P if only one kind of molecule is present, or to the partial pressure p of the kind in question if other kinds are present. Hence the rate at which molecules of any one kind penetrate through a given layer of the gas must vary as $P(1 - v)$ or $p(1 - v)$. The rate will of course depend also on the

size of the molecules and their mean velocity: also, when the diffusion is through a membrane, on the permeability of the membrane. But when we are only considering relative rates of penetration by the molecules of one particular gas these factors need not be considered, as they are constant. To put this conclusion into other language, *the diffusion rate of any particular gas through a layer of the gas of given surface area and thickness will vary as $P(1-v)$ or $p(1-v)$.*

In a gas at ordinary pressure the value of v is so small that it can be neglected where we are comparing variations of diffusion rates with variations of P . Hence in this case diffusion is simply proportional to the pressure P , or for each separate gas to its partial pressure p , where there is a mixture of gases. But in a gas at high pressure the value of v becomes a very appreciable fraction of unity, so that $P(1-v)$ will differ considerably from P . In a liquid such as water the value of $1-v$, as we have already seen, falls to a small fraction of unity. Hence the diffusion rate of water is proportional to only a small fraction of its intermolecular pressure.

We may now consider the case of a gas osmometer with hydrogen at equal but extremely high pressure P inside and outside the membrane, and containing N molecules per litre at 0° . If only pure hydrogen is present on both sides of the membrane the rate of diffusion of hydrogen both inwards and outwards through the molecular layer adjacent to the internal surface of the membrane will be proportional to $P(1-v)$, as we have just seen. But let us suppose that without altering the pressure a mixture containing n molecules of nitrogen to N_1 molecules of hydrogen and nitrogen per litre is substituted for the pure hydrogen in the osmometer and that the mixture is in the perfect gaseous state. In the mixture the value of $1-v$ will be altered to $1-v_1$ and since $\frac{P(1-v)}{P(1-v_1)} = \frac{.082NT}{.082N_1T}$, $1-v_1 = \frac{N_1}{N}(1-v)$. Hence the rate of diffusion of hydrogen inwards through the surface layer of molecules inside the osmometer will now be proportional to $\frac{N_1}{N}P(1-v)$ and since, as already pointed out, the partial pressure of any gas is proportional to the ratio of its actual concentration to its concentration in the pure state under the same pressure, the outward rate will be proportional to

$$\frac{N_1-n}{N}P(1-v) = \frac{N_1}{N}P(1-v) - \frac{n}{N}P(1-v).$$

Hence the inward rate is in excess in proportion to $\frac{n}{N}P(1-v)$, and as a direct consequence the inward diffusion pressure is in excess in proportion to $\frac{n}{N}P(1-v)$, since at equal temperatures, in accordance with the kinetic

theory of gases, the pressure in a given direction varies as the number of molecules passing in this direction in unit of time.

But $\frac{n}{N} P (1 - v) = \frac{n}{N} \times .082 NT = .082 nT$. In other words the excess of diffusion pressure inwards owing to the dilution of the hydrogen with nitrogen in the osmometer varies as the outward pressure which the nitrogen would exercise if the molecules occupied no space, so that PV was constant. It is as if PV were constant, whereas it is $P (1 - v)$ that is constant. If the molecules were mere mathematical points repelling one another, so that PV was constant and Avogadro's and Dalton's laws held at all pressures the result would be the same with the same molecular concentration, since intermolecular pressure and diffusion pressure would then be identical. For instance, since PV would be constant and $= .082 NT$, P for a gas compressed to the same molecular concentration as water at 0° , would be $.082 \times 55.5 \times 273 = 1243$ atmospheres, instead of van der Waals's calculated value of about 10,500 atmospheres; and $\frac{n}{N} P$ would have the value which $\frac{n}{N} P (1 - v)$ has.

Now the ratio of excess of diffusion pressure inwards corresponds exactly in amount to what van 't Hoff showed to be the osmotic pressure of a very dilute solution; and this points clearly towards the conclusion that osmotic pressure is closely connected with excess of diffusion pressure of the solvent inwards over that outwards, and that the intermolecular pressure is the same in the solution as in the pure solvent, and remains the same with varying temperature, just as in the gas-mixture supposed.

Let us now consider what happens when we equalise the inward and outward diffusion pressure of the hydrogen by raising the pressure of the gas-mixture inside the osmometer, as in the ordinary method of measuring osmotic pressure. Let p_0 be the added pressure needed to equalise the diffusion pressure of hydrogen; and let N_2 be the molecular concentration of the gas-mixture at the increased pressure. The value of $1 - v$ in the gas-mixture will evidently be reduced to $(1 - v) \times \frac{P}{P + p_0}$, and the value of the added pressure of hydrogen, since the ratio $\frac{N_1 - n}{N}$ is not altered by compression, will be $\frac{N_1 - n}{N} p_0$. Hence the equation representing the equilibrium of diffusion pressure will be

$$\frac{N_1 - n}{N} P (1 - v) + \frac{N_1 - n}{N} p_0 = \frac{N_2}{N} P (1 - v) \times \frac{P}{P + p_0}.$$

At the ordinary low pressures of gas-mixtures $1 - v$ equals 1, and $N_2 \times \frac{P}{P + p_0}$ equals N_1 , in accordance with Boyle's law. Hence, since N cancels out, the equation becomes $(N_1 - n) P + (N_1 - n) p_0 = N_1 P$. On solving

this equation we find that $p_0 = \frac{n}{N_1 - n} P$. In other words we can equalise the two diffusion pressures of hydrogen by raising the pressure inside the osmometer by a fraction representing the ratio of nitrogen to hydrogen molecules in the mixture. This represents the familiar law of diffusion pressure or osmotic pressure at ordinary gas pressures.

At the other extreme of very high intermolecular pressures, such as those in liquids, the fraction $\frac{P}{P+p_0}$ differs hardly at all from unity until the value of p_0 becomes considerable. Thus if we accept van der Waals's estimate of P for water as about 10,500 atmospheres the value of $\frac{P}{P+p_0}$ will be about 0.998 when p_0 is 30 atmospheres. If the molecules are appreciably compressible¹ $N_2 \times \frac{P}{P+p_0}$ may still be equal to N_1 . But even if we consider them as incompressible we can practically simplify the equation into the form

$$(N_1 - n) P (1 - v) + (N_1 - n) p_0 = N_1 P (1 - v);$$

and from this it follows that $p_0 = \frac{n}{N_1 - n} P (1 - v)$, which, in its turn, is equal to $\frac{n}{N_1 - n} \times .082NT$. Even, therefore, though we do not know the exact value of P we can still calculate the osmotic pressure of the gas-mixture from its composition if its pressure is extremely high, and the osmotic pressure is very low in comparison.

It is clear also that even if we did not know the molecular concentration of the hydrogen or other "solvent" gas we could still calculate the osmotic pressure if we knew the mass of "solvent" gas in a given volume of the mixture, as compared with the mass in the same volume, and at the same pressure and at 0°, of the pure "solvent" gas, since any error in estimating N would apply equally to the estimate of $N_1 - n$, and would thus cancel out in the equation.

It follows from the equation that if we took P as signifying osmotic pressure and V as volume of "solvent" gas in the mixture, and if n were constant and equal to 1, PV would be equal to $.082T$, or to RT . If V were taken as volume of the mixture we should have an equation which could be expressed in the form $P(V - b) = RT$, since $V - b$ would correspond to $N_1 - n$. Sackur has shown empirically that an equation of the latter form gives the osmotic pressure of sugar solutions; but the b of this equation has evidently nothing to do with the b of van der Waals's equation. If the sugar molecules are hydrates the value of the b is of course increased, as the concentration of free water is diminished.

¹ This question will be discussed in a later paper.

When n is very small relatively to N , it is evident that $\frac{n}{N_1-n}$ becomes practically equal to $\frac{n}{N}$. Hence at great dilutions van 't Hoff's equation practically gives the osmotic pressure. But as n increases the value of $\frac{n}{N_1-n}$ diverges more and more from that of $\frac{n}{N}$. Hence van 't Hoff's equation for osmotic pressure gives a value which is increasingly too low, and particularly so if the molecules of the diluent gas are of large size.

If we substitute sugar for nitrogen in the osmometer, and water for hydrogen, the experimental results for osmotic pressure correspond to the values thus deduced theoretically. With very dilute solutions of sugar the results correspond almost exactly with the van 't Hoff equation; but as the strength of the solution increases the van 't Hoff equation gives results which are increasingly too low. Professor Morse and his fellow workers have shown experimentally in their extremely valuable series of researches [1901-1912] that the observed osmotic pressures increase, not in proportion to n , the molecular concentration of the sugar solution, but far more nearly in proportion to the ratio of sugar molecules to weight of water in the solution. This ratio is just the $\frac{n}{N_1-n} \times N$ of the equation deduced above¹. The reasoning on which the equation is based thus enables us to predict the experimental results if we assume that the conditions as regards diffusion in the sugar solution are essentially the same as in the very highly compressed gas mixture.

The experimental results for sucrose and dextrose of Morse and his co-workers show that at 0° the osmotic pressure increases with increase of concentration more rapidly than corresponds with the expression

$$\frac{n}{N_1-n} \times \cdot 082NT.$$

But as is shown in Table I, reproduced from one of their latest papers [1912], they found that (substituting $\cdot 0816$ for $\cdot 082$)² the accordance with the above expression becomes closer and closer as the temperature rises, and that at 80° the accordance is exact, even in a solution containing as much as 342 grammes of cane sugar per 1000 grammes of water, or about 28 grammes per 100 cc. of solution, this being the strongest solution of which they measured the osmotic pressure.

¹ When $N_1 - n$ is taken as 1000 (the weight in grammes of 1 litre of water at 0°) or when $\frac{n}{N_1-n}$ is multiplied by N , we obtain Morse's "weight concentration" or n . The n of the present paper corresponds, of course, with van 't Hoff's, and not Morse's n .

² Morse took 22.3, instead of 22.4, as the volume in litres occupied by one gramme-molecule of a gas at 0° and 760 mm. pressure. Hence $\cdot 0816$ is substituted for $\cdot 082$ in the equation in Table I.

TABLE I. *Osmotic Pressures of Cane Sugar Solutions*
(Morse and Co-workers).

Value of $\frac{n}{N_1-n} \times N$, assuming that no hydrates are pre- sent. (Weight nor- mal concentration of Morse.)	Ratio of observed osmotic pressure to osmotic pressure calculated from the equation $p_0 = \frac{n}{N_1-n} \times 0.816NT$ on the assumption that no hydrates are present.											
	0°	5°	10°	15°	20°	25°	30°	40°	50°	60°	70°	80°
0.1	(1.106)	1.082	1.082	1.082	1.084	1.084	1.000	1.003	1.000	1.000	—	—
0.2	1.061	1.063	1.060	1.061	1.062	1.059	1.020	1.011	1.002	1.001	—	—
0.3	1.061	1.058	1.059	1.061	1.060	1.060	1.031	1.024	1.009	0.999	—	—
0.4	1.060	1.059	1.060	1.059	1.060	1.059	1.040	1.038	1.017	1.000	—	—
0.5	1.069	1.067	1.066	1.068	1.067	1.065	1.050	1.046	1.025	1.006	1.000	—
0.6	1.077	1.074	1.073	1.073	1.073	1.071	1.060	1.054	1.032	1.015	1.002	—
0.7	1.083	1.084	1.083	1.083	1.084	1.083	1.069	1.059	1.041	1.020	0.999	—
0.8	1.093	1.093	1.092	1.093	1.093	1.093	1.081	1.067	1.049	1.027	1.008	1.001
0.9	1.104	1.102	1.102	1.102	1.103	1.102	1.089	1.076	1.059	1.033	1.015	1.000
1.0	1.115	1.115	1.113	1.115	1.115	1.113	1.101	1.085	1.071	1.044	1.023	1.000

TABLE II. *Osmotic Pressures of Cane Sugar Solutions at 0°.*

Values of $\frac{n}{N_1-n} \times N$, assuming that no hydrates of sugar are present.	Ratio of observed osmotic pressure to osmotic pressure calculated from the equation $p_0 = \frac{n}{N_1-n} \times 0.816NT$ on the assumption that no hydrates of sugar are present.		Calculated values of $\frac{n}{N_1-n} \times N$, assuming that the equation $p_0 = \frac{n}{N_1-n} \times 0.816NT$ is correct. (From Berkeley and Hartley's data.)*
	Berkeley and Hartley	Morse and Co-workers	
0.0992	1.008	1.098	1.000
0.2978	1.031	1.057	1.3070
0.6001	1.062	1.075	0.6372
0.895	1.096	1.099	0.9809
0.993	1.109	1.110	1.101
2.376	1.278	—	3.037
3.267	1.374	—	4.489
4.126	1.465	—	6.065

* If the values of $\frac{n}{N_1-n} \times N$ are calculated on the assumption that the sugar is present as a pentahydrate the values will be practically the same as in this column, except in the case of the last two values, which will be slightly higher.

Table II embodies the very exact recent determinations of the Earl of Berkeley and E. G. J. Hartley for the osmotic pressures of cane sugar solutions at 0° C. and widely different concentrations, together with the corresponding results of Morse and his co-workers. The table is calculated from Table III in Berkeley and Hartley's paper [1916]. The first column shows the values which $\frac{n}{N_1-n} \times N$ would have if it were the case that no hydrates of sugar were formed, and that all the water in both pure water and sugar solution were present either as simple molecules of H₂O or as the same mixture of simple and more complex molecules of water.

It was suggested by Callendar [1908], who developed a previous suggestion of Poynting, that the reason why a cane-sugar solution at temperatures near 0° does not vary in a proportion nearly equivalent to "weight normal" concentration is that although no sugar hydrates have been isolated, hydrates nevertheless exist in solution. This is undoubtedly the true explanation, as will appear more fully below. On raising the temperature, or increasing the concentration of the sugar solution beyond a certain point, these unstable hydrates would naturally tend to be dissociated. At a temperature of 80° the dissociation seems, from Morse's data, to be complete, so that no sugar hydrates are present.

TABLE III. *Osmotic Pressures of Cane Sugar Solutions at 0°.*

Weight concentration.		Volume concentration.		Osmotic pressure in atmospheres.			
Grammes $C_{12}H_{22}O_{11}$ per 100 g. H_2O	Grammes $C_{12}H_{22}O_{11} + 5H_2O$ per 100 g. free H_2O	Grammes $C_{12}H_{22}O_{11}$ per 100 cc.	Gramme- molecules sugar per litre	Actually ob- served by Berkeley and Hartley	Calculated from the equation $p_0 = \frac{n}{N_1 - n} \times 0.82NT$, assuming that the sugar is present as pentahydrate	Calculated from the same equation, assuming that the sugar is not hydrated. (Morse's theory.)	Calculated from the equation $p_0 = 0.82nT$. (Van 't Hoff's theory)
3.393	4.33	3.32	0.097	2.23	2.24	2.22	2.17
10.18	13.21	9.59	0.281	6.85	6.85	6.66	6.29
20.525	27.39	18.26	0.533	14.21	14.17	13.44	11.95
30.61	42.04	25.81	0.754	21.87	21.80	20.04	16.90
33.945	47.07	28.13	0.822	24.55	24.40	22.22	18.41
81.26	130.54	54.24	1.585	67.74	67.66	53.19	35.48
111.73	199.70	66.14	1.933	100.13	103.50	73.14	42.20
141.11	282.97	75.33	2.201	134.84	146.66	92.37	49.31

Table III shows Berkeley and Hartley's values at 0°, as compared with values calculated from the equation $p_0 = \frac{n}{N_1 - n} \times 0.82NT$, on the assumption suggested by Callendar, that the sugar is present as the hydrate, $C_{12}H_{22}O_{11} + 5H_2O$, which of course leaves less free water present, and thus increases the value of $\frac{n}{N_1 - n}$. It will be seen that the calculated values agree very closely with those observed, until the concentration is so high that there is much more sucrose hydrate than water in the solution. The observed values then begin to fall below those calculated, just as might be predicted as probable on the hydrate theory. From Morse's data it appears that in solutions of lower concentration the whole of the sugar is present as pentahydrate until the temperature rises above 25°. The table also has columns showing the figures calculated on Morse's principle from the equation

$$p_0 = \frac{n}{N_1 - n} N \times 0.82NT$$

on the assumption that the sugar is not hydrated; also the figures calculated

according to van 't Hoff's theory of osmotic pressure from the equation $p_0 = \cdot 082nT$. These columns speak for themselves.

At very low concentrations the values obtained by Berkeley and Hartley diverge from those given by Morse and his co-workers for the same temperature, as shown in Table II; and in all the earlier results, which were obtained at temperatures below 25°, the values of the latter observers at very low concentrations present an anomaly which is very evident in Table I. This anomaly is absent in the results of Berkeley and Hartley at 0°; and it seems almost certain that it is due to a hitherto undetected source of error in the earlier experiments of Morse and his pupils. In these experiments a small proportion of ferrocyanide solution was purposely introduced into the sugar solution and the water, the assumption being that the effect of this on the osmotic pressure would cancel out. But the ferrocyanide, which is ionised and hydrated, must have, on the principles already laid down, the practical effect of increasing the osmotic pressure due to the sugar. Hence the osmotic pressure which would be caused by the sugar solution by itself is lower than the observed osmotic pressure, and in proportion more so at low sugar concentrations. It thus seems possible to account, not only for the general results of osmotic pressure determinations with sugar solutions, but also for the anomalies presented by the early results of Morse and his associates at low temperatures, as compared with the more correct results of Berkeley and Hartley, and of Morse and his associates in their later experiments at higher temperatures.

In so far as we have hitherto considered liquids we have considered solutions as if they were the same as mixtures of perfect gases at very high pressures. But the additional fact must be taken into consideration that the attraction for one another of different kinds of molecules is variable. Thus the different kinds of molecules cannot all come equally close to one another, and the mixture or solution is thus not homogeneous as regards its intermolecular spaces. The attraction of solute molecules for solvent molecules might be either less than, equal to, or greater than the mutual attraction of solvent molecules; and similarly the attraction of solute molecules for one another might be less than, equal to, or greater than their attraction for solvent molecules.

Let us consider the first case. In consequence of the attraction of solute molecules for solvent molecules being less than for solvent molecules to one another the mean-clear space round each solute molecule will be greater than round a molecule of solvent. But the result of this will be a surface conden-

sation of solvent molecules round each solute molecule, just as occurs at a free surface. There will thus be local surface tension tending to limit the mean clear spaces round the solute molecules; and the surface condensation will at the same time increase the intermolecular pressure and so diminish the free spaces round the solvent molecules in the area of condensation. Neither in ordinary "crystalloid" nor in "colloid" solutions, nor in gross suspensions, can the distribution of solvent in the space between solute molecules be even, unless solvent and solute molecules have equal attractions for one another.

Now the more the intermolecular pressure round the solute molecules is relatively diminished the more will intermolecular pressure round neighbouring water molecules be increased, provided that a sufficient excess of solvent molecules is present. As a consequence the *mean* intermolecular pressure in pure solvent and in the solution will be practically the same, as will also be the mean clear space per molecule. This would also be the case if the solute molecules had a greater attraction for solvent molecules than solvent molecules have for one another, and likewise if solute molecules had a less or greater attraction for one another than solvent molecules. If solute and solvent molecules had all equal attractions for one another both substances would be in the liquid state: they would be miscible in all proportions; and the intermolecular pressure would be the same at all concentrations. Hence, if P and P_1 be the mean intermolecular pressures in pure solvent and in the solution, P_1 will be equal to P ; and if $1 - v$ and $1 - v_1$ be the intermolecular volumes in one litre of pure solvent and of solution, $1 - v_1$ will be to $1 - v$ as N_1 to N (N_1 and N being the numbers of gramme-molecules in one litre of solution and of pure solvent at 0° respectively). The molecules in the two liquids as wholes can thus be treated statistically as if they were homogeneous mixtures of gas molecules at the same intermolecular pressure. In other words, *the intermolecular pressure up to high limits of concentration is the same in pure solvent and solutions in it.* All the experimental data for osmotic pressure and vapour pressure seem to correspond to this conclusion, and the best evidence in favour of it is furnished by this correspondence. The same experimental data show that over a wide range of temperature the intermolecular pressure P remains constant; and further direct experimental evidence on this point will be given in a succeeding paper.

Hence, by the same reasoning as was used in the case of a gas osmometer, the difference between the two diffusion pressures is

$$\frac{n}{N} P (1 - v) = \cdot 082 n T.$$

The osmotic pressure is therefore

$$\frac{n}{N_1 - n} P (1 - v) = \frac{n}{N_1 - n} \times .082NT,$$

as already shown to be the case from the experimental data. *Osmotic pressure is thus nothing but the excess of pressure required to equalise the diffusion pressure of the solvent from solution to pure solvent with that from pure solvent to solution; and this excess varies as the molecular concentration of the pure solvent, the absolute temperature, and the ratio of solute to solvent molecules.*

It appears that neither van 't Hoff nor succeeding investigators reached any clearly intelligible conception of what osmotic pressure is, though van 't Hoff showed that osmotic pressure is dependent in some way on the gas laws. So long, however, as these laws were embodied in the imperfect equation $PV = .082nT$, or $PV = RT$, instead of $P(1 - v) = .082NT$, or $P(V - v) = RT$, the real connection could not be established. Osmotic pressure is commonly referred to as if it were pressure added to a solution in virtue of the presence of the solute, whereas it is simply the increased pressure which must be applied to a solution in order to neutralise the excess in the diffusion pressure of the pure solvent over that of the solvent diluted with the solute. This increased pressure is exactly that required to neutralise the effect of the dilution, just as in the case of a gas mixture at an ordinary pressure; and it is in this indirect way that osmotic pressure depends on the concentration of the solute.

It is evident that with increasing concentration of a solution a point must finally be reached at which, if there are unequal attractions among the molecules, the mean intermolecular pressure begins to alter. Let us consider what must happen in a case not complicated by chemical combination between solute and solvent molecules, or by other chemical changes. The free space round each solute molecule will no longer be controlled by the surface tension resulting from a balancing condensation or rarefaction of solvent molecules round the solute molecule. As a consequence the free spaces round neighbouring solute molecules will finally run together and come to be controlled, not by the mutual affinities of the solvent molecules, but by those of the solute molecules. Unless, therefore, the solute molecules begin to form definite secondary compound molecules they will no longer be "held" in solution by the solvent. In other words the point of saturation will be reached, and the solute molecules can now only exist in the form of aggregates of molecules, whether these aggregates are solid, liquid, or gaseous.

A temporarily supersaturated solution can be prepared by cooling (or

heating) a saturated solution, or, in the case of a gas in solution, by lowering the external pressure of the gas. In this case the solute separates out, taking either the solid form as a precipitate, the liquid form as an emulsion, or the gaseous form as free aggregates of gas. It is evident also from the foregoing account that when two or more solutes are present together in simple solution each solute must diminish the solubility of the others. Hence it is possible to "salt out" one solute by adding another.

When solute molecules combine with water to form hydrate molecules this of course diminishes the concentration of free water molecules present in the solution. As a consequence the rate of diffusion of water from solution to pure solvent is diminished. But as the value $1 - v_1$ for the solution is correspondingly diminished as compared with $1 - v$, there is an equal diminution in the rate of diffusion from pure solvent to solution. The net result is that the excess of diffusion pressure of the pure solvent is the same as if no hydrate had been present. The osmotic pressure is, however, increased, since the value of $N_1 - n$ in the osmotic pressure equation is diminished as compared with what it would be without hydrate formation.

If, on the other hand, the solute molecules are partly or wholly ionised, it is equally clear that excess of diffusion pressure must be increased in proportion to the ionisation, provided that the membrane is impermeable to the ions. That increase of osmotic pressure, proportional to the ionisation in the case of very dilute solutions, is actually present was pointed out by Arrhenius. It seems probable that the process of ionisation in an aqueous solution, as was suggested by van der Waals, is a tearing apart of solute molecules owing to the affinity of their constituent atoms or atomic groups for water molecules, with formation of unstable hydrate molecules which cannot pass through the semi-permeable membrane. This hypothesis gets rid of the great difficulties associated with the assumption that ions are free atoms or completely unsaturated groups of atoms, and at the same time renders intelligible the influence of ionisation on osmotic pressure, the absence of any considerable absorption of heat in the process of ionisation, the relations between ionisation and dilution of a solution, and the action of water as a catalyst. The hydrate formation will add to the increase of osmotic pressure due to the mere splitting up of solute molecules in ionisation.

In the case of water, and to a less extent in that of other solvents, there is clear evidence that the molecules are to a large extent chemically combined with one another. This is shown, for instance, by the fact that as the temperature falls the contraction of water becomes less and less for each degree of

fall, quite out of proportion to the foregoing re-statement of Charles's law, and that below 4° there is an actual expansion. In this respect water presents a striking contrast to such liquids as mercury or alcohol. A similar anomaly appears in the compressibility of water. These anomalies correspond in direction with the expansion of about 10 per cent. on solidification to ice, so that when molecules of water unite with one another their virtual volume is increased.

Water must evidently be regarded as a solution of compound water molecules in simple H_2O molecules. In the solution the mean intermolecular pressure will therefore, in accordance with the principles already laid down, be the same as if no solute were present. But since the compound solute molecules are readily dissociable into simple H_2O molecules, they will be dissociated instantly in proportion to any fall in the diffusion pressure of the simple H_2O molecules owing to their dilution by an ordinary solute. Thus the compound H_2O molecules will reduce the fall which, but for their presence, would have occurred in the diffusion pressure of the H_2O molecules, and this reducing influence will be proportional to the concentration of the compound molecules. In other words, we must, in estimating the reduction of the diffusion pressure of the simple H_2O molecules, calculate, not from the original concentration of simple H_2O molecules, but from the original total concentration of H_2O molecules, combined or not combined with one another. We must therefore calculate from the "weight concentration" in Morse's sense, allowing only for any water which is present in relatively stable combination with the solute molecules. In calculating osmotic pressure we can thus neglect altogether the fact that the molecules of solvent are to a large extent combined with one another. Hence if we call M , M_1 , m , the masses of pure solvent, solution and solute in one litre at 0° , we can write the osmotic pressure equation as $p_0 = \frac{nM}{M_1 - m} \times .082T$.

The same considerations are valid also in the case of the osmotic pressure of gases at very high pressures. The molecules of the "solvent" gas may be to a large extent aggregated together, and this of course diminishes the external pressure which the same mass would otherwise exert; but in calculating osmotic pressures we have only to take account of the total concentrations of molecules.

In connection with osmotic pressure much confusion has arisen through failure to distinguish between the conditions which determine the amount of osmotic pressure and those which determine whether or not a membrane is permeable to a solute. This confusion occurs more particularly in connection

with the theory of I. Traube as to the cause of osmotic pressure, and its relation to the surface tensions of solutions and the intermolecular pressure. His data show an evident relation between lowering of surface tension of a solution and permeability of membranes by the solute, but none between surface tension of solutions and amount of osmotic pressure. It seems clear that the surface tension of a solution (as distinguished from a pure liquid) has no direct relation to its intermolecular pressure. Traube concluded that osmosis is due to the fact that a liquid of high intermolecular pressure absorbs, *ipso facto*, liquids of lower intermolecular pressure. This theory is inconsistent with the principles embodied in the kinetic theory of fluids.

The theory that osmotic pressure is essentially dependent on the existence of chemical combination between solvent and solute molecules has now almost ceased to be supported. It is perhaps, therefore, scarcely necessary to point out that this theory fails altogether to explain the connection between osmotic pressure and the gas laws. Of course molecular attraction plays an essential part in the explanation, but only in so far as it determines solubility.

3. *Vapour Pressures of Solutions.*

The vapour pressure of a substance is the pressure of its vapour at which inward diffusion balances the outward diffusion consisting in the flying off of molecules from the surface. In accordance with the conception of a liquid as a system of freely moving molecules held in proximity to one another by molecular attraction, and subject to the fundamental gas laws, the escape of molecules from the surface is due to the kinetic energy of a certain proportion of them being so great that they can fly off, thus producing external pressure. This proportion must vary inversely as the excess of kinetic energy required to overcome the molecular attraction which holds them; and this energy, as pointed out by van 't Hoff, will vary as the latent heat of vaporisation. The proportion must also depend on the number of molecules per unit of free surface, and on the absolute temperature, since this determines the mean energy of molecular movement.

Since anywhere near ordinary atmospheric pressure $1 - v$ is practically the same in a gas as 1, at these pressures the rate of escape of molecules from the surface will vary with the available excess of intermolecular over "intrinsic" pressure, there being in this reference no appreciable hindrance from the atmosphere. In accordance with the principles laid down in connection with osmotic pressure the rate of passage of vapour molecules from the atmosphere into the liquid must, other things being equal, vary as the

pressure of the vapour molecules and as the value of $1 - v$ for the particular liquid, just as in the case of liquid diffusion. Hence if we call the vapour pressure p , the inward diffusion pressure which balances the outward is $p(1 - v)$, and not p . The diffusion pressure of a vapour or gas into a liquid is thus only a fraction of the total vapour or gas pressure, just as the diffusion pressure of one liquid into another is only a fraction of its intermolecular pressure.

If, now, a solvent is diluted by the presence of a solute with no appreciable vapour pressure, and the temperature and intrinsic pressure are unaltered, the rate of passage, and consequently the pressure, of vapour molecules outwards will be diminished in the proportion of $\frac{N_1 - n}{N}$, where n , N , and N_1 denote relative number of molecules per litre of solute, pure solvent, and solution. As already seen, the values of $1 - v$ for the pure solvent, and $1 - v_1$ for the solution vary as N to N_1 so long as the intermolecular pressure is the same in pure solvent and solution. Hence if p be the vapour pressure of the pure solvent the diffusion pressure of the solvent outwards from the liquid will be diminished to

$$\frac{N_1 - n}{N} p(1 - v) = \frac{N_1}{N} p(1 - v) - \frac{n}{N} p(1 - v);$$

and the pressure inwards will be altered to $\frac{N_1}{N} p(1 - v)$. Hence the diffusion pressure outwards will be less by $\frac{n}{N} p(1 - v)$ than the previous inward pressure. The new vapour pressure will therefore be lower, and if the diminution of vapour pressure be designated p_d , $\frac{N_1 - n}{N} p(1 - v)$ must be equal to $\frac{N_1}{N} (p - p_d)(1 - v)$. From this equation it follows that $\frac{n}{N} p = \frac{N_1}{N} p_d$, so that $p_d = \frac{n}{N_1} p$. In other words, at equal temperatures *the depression of vapour pressure of the solvent is proportional to the ratio between concentration of solute molecules and of total molecules in the solution.*

Now this is the proportion discovered experimentally by Raoult. At great dilutions $\frac{n}{N_1}$ is practically equal to $\frac{n}{N}$, the proportion given in van 't Hoff's equation; but both the above theoretical deduction and the actual experimental results (as will be shown below) indicate that Raoult's equation is the correct one.

By similar reasoning it can be shown that if the vapour pressure of a solute in a given solution is p_1 , its vapour pressure in stronger or weaker solutions will vary as $\frac{n}{N_1}$.

It has been shown above that within the limits up to which osmotic

pressures have hitherto been measured, the osmotic pressure increases in proportion to $\frac{n}{N_1 - n}$, in accordance with the experimental results. But so long as n is small in relation to N_1 , as is the case with all existing measurements of osmotic pressure, the difference between $\frac{n}{N_1}$ and $\frac{n}{N_1 - n}$ is small, so that increase of observed osmotic pressure with increase of concentration of solute must run almost parallel with diminution of vapour pressure.

The same factors, such as combination among solute and solvent molecules (as in hydration), or ionisation, which cause increases in osmotic pressure will tell in the same direction, and, up to moderate concentrations, to nearly the same extent, in diminishing vapour pressure. It is evident, however, that the limiting value of p_d is p : whereas the limiting value of $\frac{n}{N_1 - n}$ is infinity. Hence depression of vapour pressure and increase of osmotic pressure must diverge more and more rapidly as the concentration increases, although up to moderate concentration they run nearly parallel.

The parallelism of depressions of vapour pressure with osmotic pressures of limited amount has been inferred by the well-known statical thermodynamical method of Arrhenius, or the cyclical thermodynamical method of van 't Hoff. But the mathematical deduction, with the help of these methods, of the vapour pressure equation $\frac{p_1 - p}{p_1} = \frac{n}{N}$ is imperfect in the absence of experimental proof that osmotic pressure is proportional to $\frac{n}{N}$; and as a matter of fact this proportionality, in whatever way n and N are defined, does not really exist, as already shown.

The approximate parallelism between depression of vapour pressure and osmotic pressure when the molecular concentration of solute is small as compared with that of solvent is shown by the following table constructed from the data of Berkeley, Hartley, and Burton [1909] for solutions of calcium ferrocyanide. It will be seen, however, that osmotic pressure increases more rapidly, in proportion, than depression of vapour pressure.

TABLE IV. *Depression of Vapour Pressure and Osmotic Pressure of Calcium Ferrocyanide Solutions at 0°.*

Grammes anhydrous calcium ferrocyanide per 100 g. water	Osmotic pressure in atmospheres	Percentage depression of vapour pressure of water	Relative values	
			Osmotic pressure	Depression of vapour pressure
31.388	41.22	3.210	1.000	1.000
39.503	70.84	5.400	1.719	1.682
42.889	87.09	6.557	2.113	2.042
47.219	112.84	8.397	2.737	2.620
49.966	130.66	9.674	3.170	3.014

The case of calcium ferrocyanide is of special interest, since not only is the molecule heavily hydrated ($\text{Ca}_2\text{Fe}(\text{CN})_6 + 11\text{H}_2\text{O}$), but, as pointed out in a further paper by Berkeley, Hartley and Stephenson [1909], it is associated in solution, besides being ionised to an extent varying with the concentration. In spite, therefore, of the complexity of the conditions, the expected relation between vapour pressure and osmotic pressure holds good generally, as will be shown in greater detail below (Table V).

When both solvent and solute have a sensible vapour pressure that of the solvent will (within wide limits of concentration) diminish, while that of the solute increases, as $\frac{n}{N_1}$. An interesting special case of vapour pressure is presented by solutions of gases. Here vapour pressure is represented by the partial pressure of the gas in equilibrium with its solution. Most of the common gases are relatively very insoluble in water and other liquids, the attraction of solvent for solute molecules being very small. Hence the value of n is very small in relation to N , so that N , N_1 , and $N_1 - n$ are sensibly equal, and it does not matter whether the variation of vapour pressure (or gas pressure) is taken as proportional to $\frac{n}{N_1}$, $\frac{n}{N}$, or $\frac{n}{N_1 - n}$. Henry's law, when put into the older form that the mass of a gas which goes into solution in a given mass of solvent varies directly as the partial pressure of the gas, implies that the vapour pressure of the solute varies as $\frac{n}{N_1 - n}$. The law holds better when stated in the more modern form that concentration of the dissolved gas varies proportionally to concentration of the free gas. This implies that the vapour pressure of the solute varies as $\frac{n}{N}$; and the value of $\frac{n}{N}$ is commonly nearer than that of $\frac{n}{N_1 - n}$ to $\frac{n}{N_1}$. The principles just laid down indicate, however, that concentration of the free gas varies as $\frac{n}{N_1}$, i.e. as the ratio of molecular concentration of dissolved gas to total molecular concentration of the solution. This appears, therefore, to be the correct form of Henry's law.

Another interesting special case is that of a vapour in contact with its own pure liquid. Here N_1 does not vary, however much of the vapour condenses. Hence the vapour pressure is constant if the temperature does not vary.

When the solvent liquid contains some other solute which does not enter into chemical combination with the gas, the solubility of the latter will be altered in accordance with Raoult's fundamental law of the relation of vapour pressure to molecular concentration of solutions. Hence most gases are

relatively insoluble in strong aqueous solutions of other solutes and particularly those which, like caustic soda or potash, or calcium chloride, are both very soluble and form hydrates. Such cases as that of sulphuric acid are of special interest in this connection. The commoner gases are about equally soluble in pure water and pure sulphuric acid, but relatively insoluble in solutions of the one liquid in the other, as Bohr found. This is clear evidence of the presence of hydrates in the solutions, with a consequent great diminution of molecular concentration, and therefore of solubility of a gas at a given pressure, since the value of $\frac{n}{N_1}$ is increased.

An important physiological application of Raoult's law is in connection with the solubility of gases in liquids, where there is no solute entering into chemical combination with the gas. Gases, where this condition is fulfilled, are considerably less soluble in blood and other physiological liquids than in pure water, since the molecular concentration, especially with large protein molecules, is considerably less than in water. Owing to certain ill-defined but very adhesive ideas which have become associated with "colloid" chemistry this matter has been much obscured in recent years.

Other inferences, of fundamental importance both in physiology and physical chemistry, are as follows. The diffusion pressure of a substance from its solution into the pure solvent is, in accordance with the reasoning in the previous section of this paper, equal to $\frac{n}{N} P (1 - v)$, where n is moles of the substance per litre, N is moles of the pure solvent; and $1-v$ the proportion of free space in the pure solvent. When the diffusion pressure of the substance is balanced by adding to the pure solvent, or to a solution in it, the requisite number (n_2) of moles of the substance, the diffusion pressure of the substance from the original solution is altered to

$$\frac{n}{N} P \times \frac{N_2}{N} (1 - v),$$

where N_2 is total moles per litre in the new solution. The diffusion pressure of the new solution into the old is $\frac{n_2}{N} P \times \frac{N_1}{N} (1 - v)$, where N_1 is total moles per litre in the old solution. These two values are equal. Hence $n_2 N_2$ must be equal to $n_1 N_1$, and therefore $\frac{n_2}{N_2}$ must be equal to $\frac{n_1}{N_1}$. Hence when the ratio of moles of solute to total moles per litre is equal in two solutions in the same solvent they are in diffusion equilibrium for the solute to which the value of n applies, $\frac{n}{N_1} P (1 - v)$, or $\frac{n}{N_1} \cdot 082 NT$ may be designated as the diffusion pressure of the substance. But the further deduction has already been made that the vapour pressure (at not too high a pressure) of

a solute varies as $\frac{n}{N_1}$. Hence the vapour pressure of a solute varies as its diffusion pressure when in solution.

Paul Bert was the first to show experimentally that, as has been abundantly confirmed by my own investigations, the physiological action of a gas depends (other things being equal) on its partial pressure. This implies, as already shown, that the action is dependent on the value of $\frac{n}{N_1}$ (n being the molecular concentration of the gas in free solution) in the blood and tissues, and is therefore dependent on the diffusion pressure of the dissolved gas. We have only to substitute "dissolved substance" for "dissolved gas," in order to give Paul Bert's law a far wider scope. It is evidently the variations in *diffusion pressure* of substances within the living organism which matter in a quantitative sense, and to which organic regulation responds. The delicacy with which the partial pressure of CO_2 in the alveolar air, and consequently the diffusion pressure of H_2CO_3 and its ions in the blood, is regulated was shown in 1905 by Priestley and myself in a well-known paper; and in 1912 definite experimental evidence was brought forward by Hasselbalch that it is hydrogen ion concentration to which the respiratory centre responds. It was further shown that there is an almost incredibly delicate regulation of the hydrogen ion concentration (more correctly hydrogen ion diffusion pressure) of the blood [Campbell, Douglas, Haldane and Hobson, 1913].

If we take n as signifying the molecular concentration of free water in an aqueous solution the diffusion pressure of water varies as $\frac{n}{N_1}$, just as does the diffusion pressure of any other substance of which n denotes the molecular concentration. We can then introduce into physiology and physical chemistry the conception of diffusion pressure of water. This is a clear quantitative conception based on the kinetic theory of fluids. The constancy of the depression of freezing-point for blood-serum is well known, and there must of course be a corresponding constancy for osmotic pressure. But depression of freezing-point and osmotic pressure are proportional to $\frac{n}{N_1 - n}$, and not to $\frac{n}{N_1}$, although for low molecular concentrations of a solute the two values are nearly the same. To speak of "the osmotic pressure" of blood and other physiological liquids is clearly, in the light of the conclusions reached above, meaningless except where mechanical pressure is concerned. Experiments recently published by Priestley and myself [1916] on the regulation of excretion of water by the kidneys indicate that diffusion pressure of water in the blood is regulated by the kidneys in a manner comparable as regards extreme delicacy with the regulation of hydrogen ion diffusion pressure.

To demonstrate the existence of blood changes to which the kidneys were re-acting during very rapid excretion of water Priestley had to employ the very delicate electrical conductivity method. This method gave, of course, no direct measure of the diffusion pressure of water in the blood, but in the absence of a sufficiently delicate direct method was very useful for indicating the existence of small changes in the concentration of ionised substances, and thus indirectly of the other substances, which affect the diffusion pressure of water. In this connection it should be noted that for a solution such as blood-plasma or tissue-fluid the value of $\frac{n}{N_1}$ is very different from that of $\frac{n}{N}$, and that for this reason the diffusion pressures of water and other substances are not practically proportional to their concentrations. The molecular concentration (n) of a given substance may differ considerably in different samples of blood-plasma and other physiological fluids, although the value of $\frac{n}{N_1}$ is the same.

4. *Boiling Points of Solutions.*

The connection between the boiling point of a solution and the molecular concentrations of solute and solution follows from the fact that when n gramme-molecules per litre of a solute without sensible vapour pressure are present, the reduction in diffusion pressure outwards of the solvent vapour is $\frac{n}{N} p (1 - v)$. To bring the solution to the boiling point the vapour pressure of the solvent must therefore be raised by the amount (p_r) required to neutralise the deficiency, and so raise the vapour pressure to the boiling pressure p . Hence $\left(\frac{N_1 - n}{N}\right) (p + p_r) (1 - v)$ must equal $\frac{N_1}{N} p (1 - v)$. It follows that p_r must equal $\frac{n}{N_1 - n} p$.

Now although in liquids at the same temperature the total free or externally disposable energy is on an average the same per molecule at each temperature, and varies directly as the absolute temperature, yet the distribution of this energy among the individual molecules is uneven; and in liquids with an appreciable vapour pressure, i.e. with part of their molecules in the potentially gaseous state, the potentially gaseous molecules possess more kinetic energy than the liquid molecules. With a given rise of temperature, which of course increases the proportion of potentially gaseous molecules in the liquid, the rise in vapour pressure within the liquid is out of all proportion to the rise in mean intermolecular pressure, or to absolute temperature. If, however, we know the proportional excess of energy required to convert a gramme-molecule of the particular solvent into gas at the temperature

concerned we can calculate the elevation of temperature for a given increase of vapour pressure, as van 't Hoff showed. The expression he deduced for the elevation of temperature giving an increase in pressure of $\frac{n}{N} p$ is $\frac{.002T^2}{H}$, where H = heat of vaporisation per gramme of solvent at its boiling-point. Thus the elevation of boiling point required to give an increase of $\frac{n}{N_1-n} p$ is

$$\frac{n}{N_1-n} N \times \frac{.002T^2}{H}.$$

This corresponds with the experimental results, and the variable factor is not merely n , as in the van 't Hoff expression, but $\frac{n}{N_1-n} N$, corresponding to Morse's "weight-normal" concentrations. At great dilutions, however, it becomes, of course, practically indifferent which expression is used.

5. *Melting Points.*

When a crystal at its melting point is in equilibrium with the pure solvent from which it has crystallised we must assume that though molecules are constantly flying out from the crystal in consequence of the continuous molecular agitation due to heat, the number of molecules flying out is balanced by the number flying in from the liquid. Of the molecules which fly out we can further distinguish those which penetrate a given small depth of surrounding liquid from those which are stopped and turned back by collisions with other molecules. The former will be proportional to $1 - v$, in accordance with the reasoning already given; and if p denote the total pressure produced by the flying out of the molecules, the outward diffusion pressure produced by those which penetrate the liquid layer will vary as $p(1 - v)$. This will be balanced by a corresponding pressure in the opposite direction. The diffusion pressure will, in fact, vary just in the same way as if the layer of liquid were a completely permeable membrane.

Now let us suppose that without altering the temperature a solute is introduced into the liquid, and that n , N , N_1 denote gramme-molecules per litre of solute, pure solvent, and solution. The diffusion pressure outwards through the liquid layer will, in accordance with the reasoning in the case of osmotic pressure, alter to $\frac{N_1}{N} p(1 - v)$, and that inwards to $\frac{N_1-n}{N} p(1 - v)$. Hence there will be an excess outwards of $\frac{n}{N} p(1 - v)$, just as in the case of a semi-permeable membrane. The crystal will therefore melt away.

To make the crystal stable again, we must diminish the free energy of its molecules by lowering the temperature, just as in order to neutralise osmotic pressure we must raise the intermolecular pressure of the solution so as to

neutralise diffusion outwards. The lowering of temperature will, also, just as in the case of osmotic pressure, be proportional to $\frac{n}{N_1 - n}$. The actual lowering of temperature will, as van 't Hoff showed, depend on the latent heat of solution of the solvent, and is given by the expression $\frac{n}{N_1 - n} N \times \frac{-0.02T^2}{H}$, where H = latent heat of fusion, and T = melting point of pure solvent. This expression is the correct one, and differs from van 't Hoff's through the substitution of $\frac{n}{N_1 - n} N$ for n . When m , M , and M_1 are the masses of solute, pure solvent, and solution per litre, we can substitute $\frac{nM}{M_1 - m}$ for $\frac{n}{N_1 - n} N$, as shown above in the case of osmotic pressure.

When the solute, and not the solvent, crystallises out, the same reasoning applies, and the same equation with regard to alterations of crystallisation temperature with concentration of solute, H being taken as latent heat of solution at original temperature, n as existing concentration of solvent molecules, and N , $N_1 - n$ as original and existing concentrations of solute molecules. Hence if we know its solubility and latent heat of solution at any one temperature we can predict its solubilities at other temperatures, provided that no chemical interaction occurs among solute and solvent molecules.

6. *Experimental Verification of the Theory.*

If the foregoing reasoning with regard to osmotic pressure, diminution of vapour pressure, raising of boiling point, and depression of melting point is correct, it should be possible to deduce from any one of these values any of the others for the same concentration and temperature. Even when the concentration is so high that the intermolecular pressure of the solution has begun to alter it should still be possible to make this deduction, since the proportional effect on all the values will be the same. So long as the intermolecular pressures of solutions remain the same as those of the pure solvents it should also be possible, if the concentrations and specific gravities of the solutions are known, to decide as to the molecular weights of the solutes: in other words to deduce the "molecular" osmotic pressures and depressions of vapour pressure, boiling-point and melting-point. Unfortunately the accurate data at present available for testing the reasoning experimentally are somewhat limited, since comparatively few complete observations have been made on sufficiently concentrated solutions; but the chief of these data may now be considered.

As the relative depression of vapour pressure $\frac{p_d}{p}$ equals $\frac{n}{N_1}$, $\frac{p}{p_d}$ equals $\frac{N_1}{n}$,

and $\frac{p}{p_d} - 1$ or $\frac{p-p_d}{p_d}$ equals $\frac{N_1}{n} - 1$ or $\frac{N_1-n}{n}$. Hence $\frac{p_d}{p-p_d}$ equals $\frac{n}{N_1-n}$. Hence $\frac{p_d}{p-p_d} \times N$, or N multiplied by the ratio of depression of vapour pressure to vapour pressure of the solution, equals $\frac{n}{N_1-n} \times N$, or gramme-molecules of solute per weight in grammes of one litre of solvent at 0° , and therefore varies as the osmotic pressure, depression of melting-point and rise of boiling-point. Thus we can easily deduce any one of these values from the relative depression of vapour pressure. The molecular osmotic pressure, relative depression of vapour pressure, depression of melting point, and rise of boiling point, are given when the value of $\frac{n}{N_1-n} \times N$ equals 1. Hence with the molecular fall in the vapour pressure ratio the value of $\frac{p_d}{p-p_d} = \frac{1}{N}$, whereas on the van 't Hoff theory the molecular fall would be given when $\frac{p_d}{p} = \frac{1}{N}$.

Table V shows the osmotic pressures calculated in this way from the relative depression of vapour pressure, as compared with the osmotic pressure actually found by Berkeley, Hartley, and Burton in the experiments already referred to and tabulated in Table IV. For these experiments we have not the data for calculating the molecular weights of the calcium ferrocyanide and its ions.

It will be noticed that the agreement between the calculated values in column 2 and those found is very close, except for the last two observations. In connection with the latter a calculation from the experimental data shows that the observed depressions of vapour pressure must have been appreciably too great; as in spite of the precautions taken the final saturating solution must have increased slightly in concentration, and to an amount which would apparently account for the divergence between calculated and found values. Column 4 shows the increasing divergence between observed values and those calculated on the van 't Hoff theory.

TABLE V. *Depression of Vapour Pressure in relation to Osmotic Pressure.*

Grammes anhydrous $\text{Ca}_2\text{Fe}(\text{CN})_6$ per 100 g. of total water	Osmotic Pressure		
	Calculated on the theory that $\frac{p_d}{p-p_d} = \frac{n}{N_1-n}$, and that osmotic pressure $= \frac{n}{N_1-n} \times 0.82NT$	Found	Calculated on the theory that $\frac{p_d}{p} = \frac{n}{N}$, and that os- motic pressure = $0.82NT$. (Van 't Hoff's theory)
31.388	41.21	41.22	39.93
39.503	70.92	70.84	67.18
42.889	87.22	87.09	81.57
47.219	113.88	112.84	104.46
49.966	133.00	130.66	120.34

For aqueous sugar solutions we possess, besides the osmotic pressure observations of Berkeley and Hartley, and of Morse and his co-workers, the determinations by Smits of depressions of vapour pressure, and a series of determinations by various workers of depressions of freezing and elevations of boiling points¹. As has already been shown, the osmotic pressure results indicate that at 0° cane sugar is present as a pentahydrate in solutions up to high concentrations, but that with rise of temperature the degree of hydration diminishes, and that at 80° the sugar ceases to be hydrated. From similar reasoning it appears that dextrose is present as a di-hydrate at 0°. The following tables show the values calculated for molecular concentrations from the concentrations and experimental results, assuming that the sugar is present in the forms just mentioned. The molecular values are those calculated for a value of 1 of $\frac{n}{N_1-n} \times N$, or for one gramme-molecule of solute per 1000 grammes of water. The molecular osmotic pressures are divided by T .

Table VI is calculated from the observations by Berkeley and Hartley [1916] of osmotic pressures of cane sugar solution at 0°.

TABLE VI. *Osmotic Pressure of Cane Sugar at 0°.*

Grammes anhydrous sucrose per 100 g. of total water	Gramme-mole- cules sucrose pentahydrate per 1000 g. free water	Observed osmotic pressure (Berke- ley and Hartley)	Molecular osmotic pressure		
			Calculated from data in columns 2 and 3	Calculated from columns 1 and 3 on Morse's prin- ciple	Calculated from molecular concen- tration on Van 't Hoff's principle
3.393	0.1001	2.23	·0817	·0824	·0838
10.18	0.306	6.85	·0820	·0844	·0894
20.525	0.634	14.21	·0820	·0868	·0976
30.61	0.973	21.87	·0824	·0893	·106
33.945	1.089	24.55	·0823	·0909	·109
81.26	3.020	67.74	·0820	·105	·157
111.73	4.621	100.13	·0795	·112	·190
141.11	6.547	134.84	·0755	·120	·230

When the value of $\frac{n}{N_1-n} \times N$ (or gramme-molecules solute per weight in grammes of one litre of pure solvent) is 1, the value of $p_0 (= \frac{n}{N_1-n} \times .082NT)$ is 22.4 when $T = 273$ (0° C.). The molecular osmotic pressure is thus $\frac{22.4}{273} = .082$. It is evident, therefore, from the fourth column of Table VI (with which Table III should be compared) that up to concentrations of about 100 g. anhydrous sucrose per 100 g. of total water the whole of the sugar is present as pentahydrate when the temperature is 0°. At higher

¹ The latter data are collected in Landolt and Börnstein's *Physikalisch-Chemische Tabellen*, 3rd edition.

concentrations there is evidently a diminishing degree of hydration. It is clear also that consistent figures for molecular osmotic pressure cannot be obtained if the sugar is assumed to be anhydrous (Morse's principle), and that if the molecular osmotic pressure is calculated on van 't Hoff's principle there is no approximation to consistency, except at greater dilutions than the table shows.

Table VII is calculated from measurements by different observers of depressions of freezing point, the first seven being quoted by Landolt and Börnstein, while the last four are from observations by Jones and Getman [1904]. This table confirms the conclusions drawn from Table VI. When the value of $\frac{nN}{N_1 - n}$ (molecules solute per 1000 g. water) is 1 the depression of freezing point ought, according to the foregoing reasoning, to be $\frac{0.01985T^2}{H}$ and as H (latent heat of fusion of ice) is 79.15, and T is 273, the value of $\frac{0.01985T^2}{H}$ (i.e. the molecular depression of freezing point) is 1.870. The mean of the values calculated for sucrose pentahydrate from the first eight observations is 1.872. In the case of the last three observations the calculated molecular depression diminishes, just as does the calculated molecular osmotic pressure at similar very high concentrations. The last two columns, which may be compared with the last two columns of Table VI, require no comment.

TABLE VII. *Depressions of Freezing-point of Cane Sugar Solutions.*

Grammes anhydrous sucrose per 100 g. of total water	Moles sucrose pentahydrate per 1000 g. free water	Observed depres- sion of freezing- point	Molecular depression of freezing-point		
			Calculated for sucrose penta- hydrate from columns 2 and 3	Calculated for an- hydrous sucrose from columns 1 and 3. (Morse's principle)	Calculated directly from molecular con- centration. (Van 't Hoff's principle)
0.4825	0.01409	0.0264°	1.874°	1.87°	1.87°
3.414	0.0999	0.1856°	1.858°	1.86°	1.86°
6.875	0.2014	0.378°	1.877°	1.88°	1.89°
2.231	0.656	1.230°	1.875°	1.89°	1.91°
4.465	1.320	2.450°	1.856°	1.88°	1.93°
29.82	9.44	1.768°	1.873°	2.03°	2.34°
56.18	1.923	3.630°	1.888°	2.21°	2.98°
68.90	2.461	4.612°	1.874°	2.29°	3.29°
84.46	3.178	5.800°	1.825°	2.35°	3.62°
101.99	4.077	7.230°	1.77°	2.43°	4.02°
122.14	5.27	9.13°	1.72°	2.54°	4.57°

Table VIII is calculated from the observations of Smits on the depression of vapour pressure of cane sugar solution at 0°. It will be seen that the observed depressions agree closely with those calculated on the assumption that the sugar is present as pentahydrate and that the depression (p_d) equals

$\frac{n}{N_1} p$, where p is the vapour pressure of pure water at 0° (4.620 mm. of mercury). The molecular depression ratio calculated from the equation $\frac{p_d}{p - p_d} = \frac{1}{N}$ is for an aqueous solution $\frac{1}{55.5} = .01802$. Column 3 shows that the molecular depression ratios as calculated from the experimental results on the assumption that the sugar is present as pentahydrate correspond with this value. If the depression is calculated on the van 't Hoff theory that $\frac{p_d}{p} = \frac{1}{N}$, or, as already shown in Table IV, on the theory that depression of vapour pressure runs parallel to the osmotic pressure, there is no such agreement.

TABLE VIII. *Depressions of Vapour Pressures of Cane Sugar Solutions at 0° .*

Grammes anhydrous cane sugar per 100 g. total water	Moles sucrose pentahydrate per 1000 g. free water	Observed depression of vapour pressure in mm. of mercury (Smits)	Calculated depression assuming that $p_d = \frac{n}{N_1} p$, and that the sugar is present as pentahydrate	Calculated molecular depression ratio, $\frac{p_d N}{p - p_d} \div \frac{n N}{N_1 - n}$
1.711	.0502	.00422*	.00416	.0182
5.896	.175	.01479	.0145	.0183
15.54	.473	.03972	.0391	.0183
34.52	1.104	.09074	.0906	.01806

* In Smits' paper there is an evident misprint (copied in Landolt and Börnstein's *Tabellen*) of 0.00242 for 0.00422.

Table IX, from the observations collected in Landolt and Börnstein's *Tabellen*, gives elevations of boiling point of cane sugar solutions. At temperatures over 80° cane sugar in solution, as pointed out above, is no longer hydrated. Hence the molecular elevation is calculated for anhydrous cane sugar.

TABLE IX. *Elevations of Boiling point of Cane Sugar Solutions.*

Grammes anhydrous sucrose per 100 g. water	Moles sucrose per 1000 g. of water ($\frac{nN}{N_1 - n}$)	Observed elevation of boiling-point. Degrees C.	Molecular elevation (observed elevation divided by $\frac{nN}{N_1 - n}$). Degrees C.
2.447	.0715	.035	.49
4.316	.1264	.064	.51
7.25	.212	.103	.49
11.02	.322	.164	.51
16.75	.490	.242	.495
21.68	.634	.317	.50
36.15	1.056	.55	.52
65.47	1.93	1.13	.59
103.4	3.02	2.06	.68
175.1	5.12	3.84	.75
276.2	8.07	6.71	.83

Taking the latent heat of evaporation of water at 100° as 539, the molecular elevation should be $\frac{.001985 \times 373^2}{5.39} = .512^\circ$. If allowance is made for the increased specific heat of water at 100° this figure is reduced to .506, which

agrees well with the mean of the figures calculated from the observations up to concentrations of 36 g. per 100 g. of water. At higher concentrations, however, the agreement ceases, presumably because the intermolecular pressure of the solution begins to increase.

Table X is for dextrose solutions, and is calculated from Berkeley and Hartley's determinations of osmotic pressure. They give the concentrations in grammes per litre. The concentrations in molecules per 1000 g. of water are calculated from the specific gravity determinations of Tollens, as given by Landolt and Börnstein. It is evident from the table that at 0° the dextrose is present as a di-hydrate, although, just as in the case of cane sugar, there appears to be some dissociation of the di-hydrate in the strongest solution observed.

TABLE X. *Osmotic Pressures of Dextrose Solutions at 0°.*

Grammes dextrose per litre of solution	Moles dextrose per litre of solution	Moles anhydrous dextrose per 1000 g. of total water	Moles dextrose di-hydrate per 1000 g. free water	Observed osmotic pressure in atmospheres	Calculated molecular osmotic pressure		
					For dextrose di-hydrate (columns 4 and 5)	For anhydrous dextrose (columns 3 and 5). Morse's principle	From molecular concentration (columns 2 and 5). Van 't Hoff's principle
99.8	0.554	0.591	0.604	13.21	.080	.082	.087
199.5	1.107	1.265	1.327	29.17	.081	.084	.096
319.2	1.772	2.215	2.407	53.19	.081	.088	.110
448.6	2.491	3.454	3.948	87.87	.082	.090	.129
548.6	3.046	4.669	5.612	121.18	.079	.096	.146

The foregoing tables show close agreement between observed values and those calculated on the new principles deduced in the present paper. The agreement affords strong support to these principles, with the corollary that the kinetic theory of fluids can be applied in a simple and direct manner, not merely to very dilute solutions, but also to strong solutions.

CONCLUSIONS.

Boyle's, Charles's and Avogadro's laws can be more correctly stated, and at the same time extended to liquids, in the form: *the intermolecular volume of a given volume of gas or liquid varies inversely as its mean intermolecular pressure, and directly as the absolute temperature, the concentration of gramme molecules, and a constant which is the same for all gases and liquids.*

This generalisation is an extension of the kinetic theory of gases, and is embodied in the equation $P(V - v) = \frac{22.4nT}{273}$, or $P(V - v) = .082nT$: where P = mean intermolecular pressure in atmospheres: V = volume in litres: v = volume virtually occupied by the molecules themselves, so that $V - v$ = virtual intermolecular volume: n = relative number of molecules

(gramme-molecules); and $22.4 = \text{value of } P(V - v) \text{ when } P \text{ and } n = 1 \text{ and } T = 273 (0^\circ \text{C.})$.

With the help of this equation new quantitative insight is obtained into diffusion pressure, the osmotic pressures, vapour pressures, boiling points, and melting points of solutions, and into other phenomena connected with gases and liquids. It can be shown that:

(1) Diffusion pressure of any one substance between one liquid or gas and another is proportional to the values of its partial pressure p in the one liquid or gas, and $1 - v$ in the other.

(2) The intermolecular pressure is the same for all solutions in the same solvent, up to high concentrations and with wide variations of temperature.

(3) Osmotic pressure is simply the increased intermolecular pressure required to neutralise the excess of diffusion pressure of a pure solvent inwards over that of a diluted solvent outwards, through a membrane permeable to the solvent but not to the solute which dilutes it. This excess is given, up to high concentrations, by the equation $p_0 = \frac{n}{N_1 - n} \cdot 0.82NT$, where p_0 = osmotic pressure, and n , N , N_1 = gramme-molecules of solute, pure solvent, and solution per litre.

(4) Diminution of vapour-pressure of the solvent and rise of vapour pressure of the solute are proportional to $\frac{n}{N_1}$.

(5) Elevation of boiling point and depression of melting point of the solvent are proportional to $\frac{n}{N_1 - n}$, and can be calculated respectively if the latent heats of boiling or melting of solvent are known.

(6) When the ratio $\frac{n}{N_1}$ is the same in different solutions with the same solvent the substances of which n denotes gramme-molecules per litre (including the solvent) are in diffusion equilibrium, and their mutual diffusion pressure is $\frac{n}{N_1} \cdot 0.82NT$. This diffusion pressure is of fundamental importance in physiology and physical chemistry, and has often, hitherto, been confused with osmotic pressure.

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