

ON THE RELATION OF OSMOTIC PRESSURE TO THE INTRINSIC PRESSURE OF LIQUIDS

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The term "Intrinsic Pressure" was introduced by Lord Rayleigh¹ to represent an internal pressure in liquids arising from molecular attractions. The existence of such a pressure, together with estimates of its probable value had previously been shown by Young and by Laplace who represented it by the symbol K . The symbol K has been generally retained by later writers, but the term "intrinsic" has not been so generally accepted and retained. Careful examination will show that there are two distinct kinds of internal pressure in liquids, to one of which the term intrinsic seems particularly appropriate in contrast with extrinsic. The pressure exerted by an ideally perfect gas upon the walls of the containing vessel may appropriately be termed extrinsic pressure, but there is also in the interior of a body of gas what we may call an intrinsic pressure which is numerically equal to the extrinsic pressure. If we define the intrinsic pressure of a gas as the rate of change of momentum per unit area of the gas impinging on one side of an element of a plane area within the gas, the resultant change of momentum per unit time of all the molecular impacts resolved normal to the plane being regarded as the total pressure, the definition would make the intrinsic pressure numerically equal to the outwardly directed pressure on the containing walls. We may assume that the intrinsic and extrinsic pressures are numerically equal only in the absence of molecular attractions between the molecules, and that when the substance has reached such a degree of condensation that the molecular attractions are appreciable, the extrinsic pressure becomes less than the intrinsic, gradually diminishing as the liquid state is approached, becoming zero only in the case of a vaporless liquid. But from the fact that in the interior of

¹ Phil. Mag., 30, 288 (1890).

liquids, the molecular attractions on any given molecule during any appreciable interval of time will be equal in all directions; the freedom of motion, except as to the length of the mean free path, should not be interfered with; consequently the molecules should be capable of exerting a pressure within the liquid in any direction in which their freedom of motion is opposed. In that case the definition just given of intrinsic pressure should apply to liquids as well as to gases. It will be noticed that such a pressure, just as in a gas, must be proportional to the absolute temperature and density conjointly; consequently cannot be simply a change function of a gravitating force. Laplace's K is always assumed to be a function of the masses and distances of the molecules. Inasmuch, however, as the molecular attractions affect the densities, intrinsic pressure may be regarded as indirectly a function of the molecular attractions; but, as previously indicated, it does not vanish when the molecular attractions become zero.

That the general line of reasoning made use of in deducing the law of gas pressure from the molecular kinetic theory is applicable to the interior of liquids will be evident to anyone who will read carefully Maxwell's deduction of the law of gas pressure given in his *Theory of Heat* (10th ed., p. 319). The only additional hypothesis required will be that necessary to explain the absence of pressure on the walls of the containing vessel, and the approximate definiteness of volume of a liquid. This characteristic difference between a liquid and a gas is fully accounted for by the generally accepted theory of the unbalanced molecular attractions which cause the superficial tension in liquids. This unbalanced molecular attraction in and near the surface of liquids is sufficient to retain all the molecules having a translational energy below a certain definite value,—the escaping molecules constituting the vapor. Since the vapor is composed of those molecules which escape from the liquid in consequence of possessing, in the liquid, exceptionally high energy of translation it is not evident, without careful analysis,

how the average energy of translation per molecule can be the same in the liquid and vapor states. This conclusion, however, seems to be amply verified by experimental evidence and is an essential postulate in the deduction of the intrinsic pressure and intrinsic energy of liquids. The results of the assumption amply justify the hypothesis by enabling us to predict and compute results which are verified by experiment. The apparent improbability of the hypothesis may be made to disappear entirely by restating it in a different form as follows: The work which must be done by the molecules in passing from the liquid to the vapor state is just sufficient to deprive them of their excess of translational energy over the average in the liquid state.

The foregoing considerations would seem to indicate that we may be warranted in assuming that the interior of a liquid differs from the interior of a gas mainly in three different ways: (a) In the length of the mean free path; (b) In the degree of curvature in the path; (c) In density, or, in the number of molecules per unit volume. If, in addition we borrow a notion from astronomy, we may form a concrete conception of a liquid and of the critical state as a transition state lying between the liquid and gaseous conditions. In a planetary system of bodies satellites can exist only when the velocity of translation of the satellite is less than a certain definite maximum which gives a parabolic orbit. Less velocity than this maximum yields elliptical orbits, higher velocities lead to hyperbolic paths. Thus a comet may visit the solar system and then leave it never to return if its speed is sufficiently great, just as a molecule of vapor may leave a liquid mass never to return. Applying this notion to a molecular system with the understanding that the absolute temperature represents the mean square of the translational velocity of the molecules, we see that at a definite temperature the molecular attractions cease to be the controlling influence and the substance becomes essentially a gas irrespective of volume or proximity of molecules. In all cases, however, what is called the externally applied

pressure is supplementary to the molecular attractions which in the ideal gas is zero. On the other hand, we might define an ideal liquid as a vaporless liquid exerting no extrinsic pressure, the molecules being held within the given volume solely by molecular attractions. The term *ideal* may be understood as a state approached but never actually reached.

These preliminary remarks have been deemed necessary because the writer knows of no simple exposition covering the above ground, or of any generally accepted canon to which he could refer as to the relation of a vapor to its liquid. In order not to be misunderstood in what follows, it was considered necessary to state the point of view as to what constitutes a liquid so as to bring out clearly the meaning to be attached to the term intrinsic pressure of a liquid. In previous papers the writer has insisted, and offered evidence to show, that the experimental facts do not permit of introducing any special hypothetical forces of attraction or repulsion between solute and solvent, or of expansive force on the part of the solute, in our efforts to explain the dynamics of osmotic phenomena. And since it has been shown that the depression of the vapor-pressure of a solution is directly proportional to a corresponding depressed normal activity of a solvent, it is important to bring out definitely and define clearly just what constitutes this normal activity of a solvent before endeavoring to establish a definite relationship between it and osmotic phenomena.

Suppose we assume that the characteristic normal activity of a liquid at any temperature is due to its intrinsic pressure which may be obtained from its vapor-pressure at that temperature by simply multiplying the vapor-pressure by the ratio of the densities of the substance in the liquid and vapor phases. It will be found that what is known as the osmotic pressure bears a very simple relation to the intrinsic pressure as thus defined.

In a recent paper,¹ in discussing the conditions neces-

¹ Jour. Phys. Chem., 14, 260 (1910).

sary to produce osmotic equilibrium, I was led to the equation:

$$pv = PV = RT \dots\dots\dots (A)$$

where pv represented the product of the pressure and volume of a vapor and PV the product of the corresponding values for its liquid phase. At first sight the result seems absurd. The P representing pressure in the liquid phase cannot be interpreted in the same sense as that in which we interpret the p as applied to the vapor phase. In order to distinguish between the two pressures, I called the former the intrinsic pressure of the liquid, having in mind the intrinsic pressure of Lord Rayleigh and other writers, but stated that it did not necessarily represent an actual molecular pressure and at the same time briefly otherwise indicated an interpretation. Further examination of the matter has led me to the interpretation indicated above which confirms, but extends, the first impression. The name intrinsic is also retained as it seems particularly appropriate when its derivation is considered.

The equation (A) may also be interpreted simply as expressing an energy relation, since

$$p_1 = \frac{1}{3} n_1 m u^2 = \frac{2}{3} \frac{n_1 m u^2}{2}$$

On the assumption that the average molecular energy of translation is the same for the liquid and vapor phases, the intrinsic pressure $P_1 = \frac{2}{3} \frac{n_2 m u^2}{2}$, whence

$$P_1 = p_1 \frac{n_2}{n_1} = p_1 \frac{\rho_2}{\rho_1}$$

if the molecular weight is the same in the two phases.

The equation (A) was derived from the proportion

$$\frac{p_1 - p_2}{p_1} = \frac{P_1 - P_2}{P_1} \dots\dots\dots (B)$$

on the assumption that a difference in vapor-pressure due to a difference in elevation, $h_2 - h_1$, is proportional to the

difference in pressure of the liquid columns due to the same difference in level. In consequence of the variation of density of the vapor with pressure this is not strictly true, but is approximately too small by about 1/2 percent for each hundredth, for values lying between 0 and $\frac{1}{10}$. Or, in symbols

$$\frac{p_1 - p_2}{p_1} < \log_e p_1 - \log_e p_2$$

by about the amount indicated above, for values not greater than $\frac{1}{10}$. For the ordinary differences encountered in actual measurements of depressed vapor-tensions the simpler expression introduces no appreciable error.

The intrinsic pressure of a liquid solvent was defined as $P_1 = p_1 \frac{\rho}{\rho'}$, where p_1 is the pressure and ρ' the density of the vapor of the solvent at some chosen temperature, ρ the density of the liquid phase of the solvent at the same temperature. For gram-molecules at the absolute temperature T , the above becomes, on writing RT for $p_1 v_1$, since $\frac{M}{v_1} = \rho'$, $P_1 = \frac{\rho RT}{M}$ where M is the molecular weight of the solvent. Therefore from formula (B)

$$P_1 - P_2 = \frac{p_1 - p_2}{p_1} \frac{\rho RT}{M}, \text{ or } \frac{\rho RT}{M} \log_e \frac{p_1}{p_2}$$

one of the standard forms of the equation for the osmotic pressure, the only symbols having any reference to a dissolved substance being p_2 the depressed vapor-tension of the solution, and P_2 its intrinsic pressure.

Boynnton,¹ working from purely molecular kinetic assumptions, derives the same equation for the osmotic pressure as the difference between two molecular pressures, but gives no estimate of their numerical values or otherwise suggests their physical significance. The above deduction is based

¹ Kinetic theory, p. 222 (1909).

upon a simple fundamental assumption involving the ratios of the pressures required to produce simultaneous equilibrium between vapors and liquids at different levels. The condition that the assumptions made should satisfy the necessary conditions of equilibrium, involving no contradiction of accepted dynamical laws is easily shown. The fundamental assumption made was that the ratio of the pressures of the vapor and liquid phases is the same for both solution and pure solvent. In the recent paper previously referred to, I assumed that

$$\frac{p_1}{p_2} = \frac{P_1}{P_2}, \text{ or } \frac{p_1}{P_1} = \frac{p_2}{P_2}$$

and independently, from conditions of equilibrium, derived the equations

$$p_1 - p_2 = \rho'gh \text{ and } P_1 - P_2 = \rho gh \dots (C)$$

The fact that the two sets are derived independently leaves the possibility that they may not be simultaneous. The two equations (C) are really equations of condition which must be satisfied simultaneously in order to prevent a possible assumption of a perpetual cycle. The ratios must satisfy the equations (C) or they are not simultaneous with the two equations.

From the equations (C) by division,

$$\frac{p_1 - p_2}{P_1 - P_2} = \frac{\rho'}{\rho}$$

In order to satisfy the condition that the equations of equilibrium (C) and the ratios shall be simultaneously satisfied it is sufficient to assume that

$$\frac{p_1}{P_1} = \frac{p_2}{P_2} = \frac{\rho'}{\rho}$$

then either set includes the other and the ratios satisfy the conditions of equilibrium. But this condition gives at once the definition of intrinsic pressure

$$P_1 = p_1 \frac{\rho}{\rho'}$$

previously given, or, on substituting volumes for densities

$$p_1 v_1 = P_1 V_1 = RT \dots \dots \dots (D)$$

as before, but more simply, without the process of integration.

The derivation of equation (D) by different processes of reasoning and the fact that it enables us to derive well-known equations by exceedingly simple methods ought to convince us that the general gas equation may be applied also to liquids if we give to the symbol P_1 a proper interpretation. Perhaps intrinsic energy would be a better specification, but since it may be deduced by similar reasoning to that employed in deducing gas pressure, intrinsic pressure seems not inappropriate. When we consider its intimate relation to osmotic pressure it seems necessary to specify it in terms of pressure. Again when we consider the light, active molecule of water vapor and the enormous intrinsic pressure molecular aggregates may exert when condensed to a liquid, we receive a new insight into the significance and importance of water in the process of Nature. No other liquid is so generally a solvent, has so light and active a molecule and can consequently penetrate and exert its great pressure through so many septa throughout so wide a range of conditions.

In equation (D) P_1 represents what I have called the intrinsic pressure of the liquid solvent. But the osmotic pressure $P_1 - P_2 = P'$ (say) also satisfies the equation $PV = RT$; or, $P'V' = RT$ must also be satisfied. Since the second members of the equations are identical

$$\frac{P'}{P_1} = \frac{V_1}{V'}$$

If we assume the intrinsic pressure of the pure solvent to be due to N molecules and the intrinsic pressure of the solution to be due to $N - n$ molecules, we have

$$\frac{P_2}{P_1} = \frac{N - n}{N}, \text{ whence } \frac{P_1 - P_2}{P_1} = \frac{n}{N} = \frac{P'}{P_1} = \frac{V_1}{V'}$$

Therefore

$$V' = V_1 \frac{N}{n} \text{ and } P' = P_1 \frac{n}{N}, \text{ or } P'V' = P_1V_1$$

That is, the volume concerned in osmotic pressure is the volume of the solvent increased in the ratio $\frac{N}{n}$ while the pressure is diminished in the ratio $\frac{n}{N}$. This is equivalent to ascribing to the one- n th part of the solvent a volume n times as large as it actually occupies with a corresponding diminution in pressure. This fact explains the dual relation of osmotic pressure to the gas laws and to the volume of the pure solvent. The relation of osmotic pressure to the volume of the pure solvent was amply demonstrated by the extensive experiments of Morse and Frazer¹ who showed that for aqueous solutions of sugar the osmotic pressure was inversely proportional to the *volume of the solvent* containing the sugar and *not* to that of the volume occupied by the sugar.

This experimental fact is important and should not be ignored. The concentrations were carried up to 30 percent and showed conclusively that the volume in the equation $PV = RT$ *does not* relate to the volume occupied by the solute but to the volume of the solvent; and that therefore the pressure phenomena arose from the number of molecules of the solvent replaced by the non-volatile solid. *The general gas equation does not then apply to a dissolved solid but to the liquid solvent.* If each molecule of a liquid solvent has an average intrinsic energy, or pressure, equal to and just like that of a gas, except as to mean free path, then the presence of a foreign substance that dilutes the solvent or in any way interferes with its normal activity so as to depress it, causes the pure solvent to exhibit a greater activity than the solution just in proportion as the activity of the solvent in a unit volume of solution is lowered. It seems to me that the experimental evidence compels us to conclude that osmotic

¹ Am. Chem. Jour., 10, 141 (1906).

pressure enables us to measure the degree of depression of the normal activity of a liquid due to the presence of a foreign substance in solution and not the pressure exerted by the foreign substance itself.

To illustrate: The intrinsic pressure of water at 0° C is 1235 atmospheres. A normal solution of sugar contains 1 mol of sugar to 55.6 mols of water. Therefore the osmotic pressure of such solution at 0° C is $1235/55.6 = 22.2$ atmos. If, at the same temperature, 46 grams of alcohol be substituted for the 342 grams of sugar, the osmotic pressure remains 22.2 atmos., if the membrane is not permeable to the alcohol molecule, and so on. In simple cases like these, the result is as if one molecule of solvent were removed, or replaced by, one molecule of the non-migratory solute. *The ultimate effect of the presence of the foreign substance is to bring about, and determine the direction of, certain energy transfers.* In this respect these comparatively simple phenomena are similar in their final result to those more obscure actions known as catalytic—a substance induces actions by its presence but seems otherwise to take no part and to suffer no change.

In dealing with the intrinsic pressure of liquids it is necessary to bear in mind the characteristic difference between it and pressure in gases and vapors. If this be done we can at once place the dissolved solid substance as belonging distinctly to the liquid state or phase; for while the molecules of the non-volatile solute may possess the average energy of translation and be distributed in space so as to give the requisite number of molecules per unit volume, they must lack the characteristic mean free path of a vapor. The great and distinct difference between a substance in dilute solution and a rarefied gas or vapor is found in the mean free path,—a quantity inversely proportional to the number of molecules in unit volume. Nernst's¹ equation showing the resistance to diffusion proves the extreme improbability of his theory of diffusion. It is impossible to suppose that

¹ Theoretische Chemie, 6th Ed., p. 158 (1909).

the mean free path of a non-volatile substance in dilute solution can increase with dilution to the extent it would have to do to occupy the volume and at the same time exhibit the pressure attributed to it. Those molecules at a distance greater than the free path could not exert any pressure, or have any influence in producing a pressure, on a dividing wall or membrane. But the number of molecules taking part in, or contributing to, the pressure in dilute solution cannot be the same as in the corresponding vapor unless the mean free path be the same in both. This is extremely doubtful, as shown by Nernst's equation.

Again, this peculiarity of intrinsic pressure,—its narrow range in consequence of the extremely limited mean free path,—throws light on a characteristic of osmotic pressure that has been insisted upon by some writers.¹ Osmotic phenomena through membranes are manifested only when the membranes are wetted by the liquid. For if not wetted by the liquid they are outside the liquid, and the molecules will be confined by the unbalanced pressure due to the superficial layer through which only the molecules, constituting a small percentage to form the vapor, can escape. That the semi-permeable membrane be *within the liquid* is evidently a *sine qua non*. There must be no unbalanced molecular attractions preventing free and untrammelled motion of the liquid. Therefore if the attractive force between the substance of the membrane and the liquid is equal to, or greater than, that of the liquid for itself, the superficial boundary confining the activity of the liquid extends into the substance of the membrane itself. Only under such conditions can a substance be said to be truly within a liquid.

In conclusion, it will be of interest to have a résumé of results with a complete separation of experimental facts and their dynamic interpretation from the hypothetical explanation of them.

(1) The maximum work obtainable by diluting a dilute solution is equal to a sum of elements each of which is just

¹ Kahlenberg: Jour. Phys. Chem., 10, 141 (1906).

sufficient to lift each element of mass of the solvent added, to a height which will equalize the difference in the vapor-pressures of the pure solvent and solution. This proves that the solute takes no active part in the production of the work,—the liquid solvent is the active agent.

(2) The requirements of dynamic equilibrium between the vapors and the liquids, (simultaneously), through a semi-permeable septum, impose the conditions (if the membrane be actually semi-permeable) that where the differences in vapor-pressures ($p_1 - p_2$ or Δp_1) be small, we must have

$$\frac{p_1 - p_2}{P_1 - P_2} = \frac{\Delta p_1}{\Delta P_1} = \frac{\rho'}{\rho} \dots\dots\dots (E)$$

where ΔP_1 represents the excess of pressure exerted through a semi-permeable septum by the pure solvent over that of the solvent in the solution, and ρ'/ρ represents the ratio of the density of the vapor of the pure solvent to the density of its liquid phase at the same temperature. In other words: The presence of the solute depresses both the vapor and liquid phases in exactly the same ratio. This is a dynamic requirement on the supposition that a semi-permeable septum is obtainable. Its validity may be confirmed as follows:

Recurring to the arrangement of an osmotic cell with an open top and semi-permeable bottom immersed to a depth, d , in the pure solvent,—the open top being at such height, h , as to equilibrate the vapors,—the depth to which the semi-permeable bottom is immersed in the pure solvent cannot affect the equilibrium. For suppose it does; then the pure solvent alone being able to pass in or out, a change in the concentration of the solution, in either case, will be produced at the bottom which will be opposed by the isothermal distillation at the open top thus setting up a never-ending cycle, so that no state of equilibrium, for a given concentration, is possible except one depending on the equilibrium of the vapors alone. But this requirement is entirely independent of the depth and consequent hydrostatic pressure on the semi-permeable bottom. Hence it follows as a corollary that *what-*

ever may be the pressure exerted by the dissolved substance it has no definite numerical relation to what is known as the osmotic pressure, which is a differential function of the solvent alone.

(3) The equation (E) may be stated in a more striking way by substituting words for the symbols of the effects.

$$\frac{\text{Depressed vapor activity}}{\text{Depressed liquid activity}} = \frac{\text{Depressed vapor tension}}{\text{Osmotic pressure}} = \frac{\text{vapor density}}{\text{liquid density}}$$

the temperature of liquid and vapor being the same and the liquids separated by a semi-permeable septum.

It should be noted that the dynamic requirement is entirely independent of the number of molecules or their nature, whether simple or complex, neutral or electrolyte, or whether dissociation occurs or not, the only essential requirement being semi-permeability. Measurements of osmotic pressure can then really determine little more than whether the septum is permeable or not to certain constituents of a solution. Depressed vapor-tension and osmotic pressure have a fixed definite ratio provided a semi-permeable septum can be secured. The depression of the vapor, the lowering of the freezing point, the elevation of the boiling point,—each gives us otherwise as much information as could the osmotic pressure.

(4) The above points, (1), (2), (3), relate to experimental facts and their dynamic interpretation. We may now be permitted, perhaps, to offer a hypothetical explanation of the observed facts.

The point requiring elucidation and one that would, if explained, throw light on a wide range of other facts is the equation (E) above. How can we explain the equality of action of the solute on both the vapor and liquid phases?

It was mentioned previously that the effect produced by the presence of the solute in certain simple cases was as if each molecule of solute had withdrawn from action one molecule of solvent. Perhaps this is the real explanation.

If solution is a chemical rather than a physical fact there must be some sort of chemical union when a substance dissolves. We have the analogous case of water of crystallization,—a loose but definite sort of chemical union between a salt and n molecules of water. Therefore when a substance is dissolved it may unite more intimately with one or more molecules of the solvent than with the remainder. The result would be to take out of action the molecules of solvent held by union with the solute with the result that both the vapor and liquid phases of a solution are less active in the same proportion than equal volumes of the two phases of the pure solvent. The facts discovered in connection with liquid crystals seem to point in the same direction.

It must also be evident that the dynamical facts are in opposition to the hypothesis of dissociation as an explanation of the abnormal depression of the vapor-tension of solutions of electrolytes unless we introduce the additional hypothesis that the solvent is also dissociated to the same extent by the formation of the ions. This latter form of the hypothesis seems to be unnecessary, for it has been shown by Prof. Poynting¹ that electrolytic conductivity may be accounted for by association rather than by dissociation. Taken all in all, the dynamic interpretation of experimental facts seems to indicate that the part played by the solvent in any tenable theory of solutions is of greater importance than the present dominant theory, in any adequate way sufficiently recognizes. This latter conclusion was also drawn by van der Waals² as a deduction from his analysis of certain experimental results.

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¹ Phil. Mag., 42, 289 (1896).

² Zeit. phys. Chem., 8, 215 (1891).