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XXXI. Osmotic pressure

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XXXI. *Osmotic Pressure.* By J. H. POYNTING, *Sc.D., F.R.S.,*
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SINCE the osmotic pressure of a solution is of the same order as the "gas pressure" of the dissolved substance at the same density, we are naturally tempted to think of it as an extra pressure produced by the motion of the dissolved molecules. But if we start from this supposition we soon find ourselves surrounded by the difficulties of the dissociation hypothesis. These are so great that it appears worth while to examine our ideas of liquid structure in the hope that they will suggest to us some hypothesis which will free us from the necessity of assuming dissociation.

I shall try to show in this paper that osmotic pressure may be accounted for as an indirect result arising, not from dissociation but from its very opposite, the greater complexity of the molecules in the solution, due to some kind of combination between salt and solvent.

The facts of liquid viscosity, diffusion, and surface conversion to vapour may apparently be represented by imagining a liquid to be, in the main, a solid structure, inasmuch as the molecules cohere and resist strain of any kind. But the molecules have so much energy, potential or kinetic or both, that they are not very far from instability. In a mass of connected molecules irregularly distributed and irregularly vibrating, concentrations of energy must occur, and at the

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points of concentration individual molecules may receive so much energy that they are able to do the work needed to free them from their immediate surroundings. Such molecules will travel off, and as they lose their energy will form new connexions with new surroundings. Thus the solid structure is continually breaking down and renewing itself. If we impose a shear strain on the structure, the strain will of course disappear with the structure in which it is produced. But the breaking down will always lag slightly behind the imposition of the shear, and the still surviving shear strain will be accompanied by a resistance the same in kind as the resistance to shear in a solid, though in a liquid it is only recognized as viscosity. This is the view first set forth by Poisson and developed by Maxwell, and it is to be noted that it gives an explanation of liquid viscosity entirely different from the diffusion explanation which so satisfactorily accounts for gaseous viscosity.

We may obtain an expression for the coefficient of viscosity by the following method, which is perhaps rather simpler than that of Maxwell. We must assume that a certain fraction, say λ , of the molecules of the liquid get free per second, and that this fraction remains practically the same when the liquid is sheared. Hence if s is the strain still existing at any instant, it is breaking down at the rate λs per second. If the liquid is moving steadily in parallel planes perpendicular to an axis along which x is measured, and if the velocity is v at a distance x from the reference plane, $\frac{dv}{dx}$ is the rate at which shear is being imposed on the liquid. But since the steady state is reached the rate of imposition equals the rate of decay, or

$$\frac{dv}{dx} = \lambda s. \quad (1)$$

If n is the coefficient of rigidity of the structure, the stress due to s is ns , and by our supposition this is the viscous stress, or

$$\eta \frac{dv}{dx} = ns, \quad (2)$$

where η is the coefficient of viscosity. Dividing (2) by (1) we obtain

$$\eta = \frac{n}{\lambda} (3)$$

We may compare the liquid breakdown here imagined with

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that which must occur in an electrolytic conductor. If D is the "displacement" or "induction" in an electrolyte, and if μ is the factor of decay per second, μD is the quantity disappearing per second and dissipating its energy as heat. This may be equated in the steady state to the new "displacement" or "induction" introduced per second per square centimetre, or to the current-density C . Hence

$$C = \mu D = \frac{\mu K E}{4\pi}, \dots \dots \dots (4)$$

where E is the slope of potential, and K is the specific inductive capacity. But Ohm's law gives us

$$C = \frac{E}{\rho}, \dots \dots \dots (5)$$

where ρ is the specific resistance; whence

$$\rho = \frac{4\pi}{\mu K} \dots \dots \dots (6)$$

Returning to equation (3), we see that if n is constant, η varies inversely as λ . For instance, when the temperature rises the molecules have more energy, the breaking down of structure is more frequent, and λ is greater. Probably n is not very much altered, though it doubtless tends to decrease. Hence η should decrease, and this is in accordance with observation. On the other hand, when a salt is dissolved in a liquid, if, as we are going to suppose, it makes the molecules on the average less energetic by partially combining the more energetic solvent molecules with the less energetic salt molecules, they are on the average rather further from instability, λ is less and η is greater. This again agrees with observation.

At the same time the specific electric resistance ρ is diminished. This would require that in (6) either μ or K , or both, should be increased, probably both; and this brings out a point which must be noted, that the factor of decay λ in (3) is not likely to be the same as μ in (6); for while one relates rather to the molecules and their relative positions, the other most probably relates to the atoms and their positions in the molecules.

Maxwell (Proc. Roy. Soc. cxlviii. 1873) gave an account of some experiments which he made to test this view of liquid viscosity by shearing a liquid and looking out for double refraction. He could only observe it in the case of Canada balsam, in which it had already been found by Mach, and here the "rate of relaxation" was so great that he could not

observe any double refraction after the shearing motion ceased. Kundt (*Ann. Phys. Chem.* xiii. 1881) made a series of experiments and found double refraction in many sheared liquids, notably in olive-oil, but never in a pure liquid with a definite chemical constitution. The more complex the molecules apparently the less is λ , and the greater is the shear strain still remaining at any instant of the motion. But in liquids such as water or glycerine, the decay is so rapid that no optically appreciable amount remains.

Still it is very possible that olive-oil is only an extreme case, and that water and other apparently inactive liquids would show the effect if we could sufficiently increase the shear, and I think Kundt's results may be claimed as supporting the hypothesis. Possibly, too, the observation of Quincke, that double refraction is observed in a liquid close to a very hot wire, gives further support. The unequal heating may perhaps be regarded as producing shear strains in the solid structure which are renewed by the supply of heat as fast as they break down.

In the case of breaking down of structure near the surface of a liquid the moving molecules may succeed in escaping altogether, and may fly off as gas molecules if they are directed upwards and have enough energy. Of course there may be many molecules able to move about and yet not able to evaporate; for though they may be able to travel when in the body of the liquid, they may not have energy enough to get clear away from their neighbours when these are all on one side and all pull in one direction as they do at the surface. In the case of practically non-evaporating liquids, such as mercury at ordinary temperatures, we must suppose that only a very minute fraction are thus able to do the work needed to overcome the large cohesion of their neighbours.

It will be convenient to use the term "mobility" to describe the number of "free" or "mobilised" molecules crossing a square centimetre per second in a liquid, where by "free" or "mobilised" we mean those which are changing their surroundings and forming new connexions. Evidently we may extend the term to a gas, remembering that then all the molecules are mobilised, and that the mobility is proportional to the pressure.

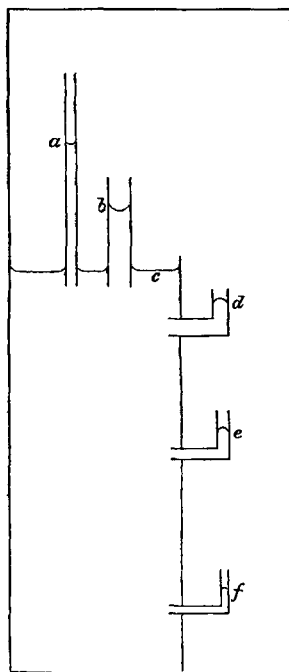
When a square centimetre is taken on the surface of a liquid, the mobility upwards is the rate of evaporation, and the mobility of the vapour downwards is the rate of condensation. When the two mobilities are equal the pressure of the vapour is the vapour-tension.

The mobility in the body of the liquid is probably far

greater than that at the surface for the reason already given; viz. that in the one case the neighbouring molecules entirely surround one which tends to get free, while at the surface they are all on one side and so tend to pull back and retain a molecule which may be inclined to move away. If, however, the internal mobility at a given temperature is altered, say by the pressure, or by the presence of some substance in solution, the surface mobility will be altered too. We shall assume that it is altered in the same ratio as the internal mobility, an assumption which appears to be justified by the account which it will enable us to give of the effect of pressure and of solution.

Let us now apply this idea to the familiar case of rise in a capillary tube standing in a liquid having only its own vapour above it. Or let us take the more general case of a liquid in a vessel with tubes which are wet rising above the flat surface, and with tubes which are not wet coming out of the side

Fig. 1.



and turning upwards, and of such diameters that the liquid does not rise to the top of the tube, as in fig. 1. Thomson's

theorem shows that there is ultimately a balance between evaporation and condensation at each surface, or that the vapour-tension is less at the surfaces *a* and *b* than the normal amount existing at *c*, while at *d*, *e*, and *f* it is greater. In other words, the surface mobility gradually increases as we go downwards. This is usually connected with the curvature of the liquid surface, but, as I have tried to show in a former paper (*Proc. Phys. Soc.* vol. iv. p. 271, *Phil. Mag.* July 1881), it should rather be connected with the increased pressure of the liquid just under the surface as we descend; the curvature of the surface is a non-essential accompaniment.

Taking the pressure of the vapour at the flat surface *c* in fig. 1 as ϖ , and the densities of liquid and vapour as ρ and σ respectively, then at a level *h* below or above *c* the hydrostatic pressure is greater or less than at *c* by $g\rho h$, = P say, while the vapour-pressure is greater or less than at *c* by $g\sigma h = \frac{P\sigma}{\rho}$; or the increase in vapour-pressure at a surface as we descend is proportional to the increase in hydrostatic pressure just under that surface. This is accounted for if we suppose that the increased hydrostatic pressure results in increased mobility, and therefore increased evaporation from the surface. The vapour-pressure increases from ϖ to

$$\varpi + \frac{P\sigma}{\rho} = \varpi \left(1 + \frac{P\sigma}{\varpi\rho} \right);$$

or the coefficient of increase of its mobility is $\frac{\sigma}{\varpi\rho}$ per unit of hydrostatic pressure, and this is the coefficient we must assume for the increase of internal liquid mobility to account for the facts on this theory.

We have no direct evidence that increase of pressure does thus increase liquid mobility. The justification is to be sought in such explanations of known facts as that just given*.

It is perhaps worth noting that we obtain the true state of affairs externally if we picture the liquid in fig. 1 as a kind

* Liquid viscosity should decrease if mobility increases, and should therefore, in our view, decrease with increase of pressure were mobility alone concerned. But rigidity also comes in, and we must ascribe to this complication the result that, in water, pressure lessens the viscosity while in turpentine it increases it (*Cohen, Wied. Ann.* No. 4, 1892). But it would appear fair to seek support for the supposition of increased mobility in the "flowing" of solids under great stresses, as in the stamping and wire-drawing of metal, when the molecules undoubtedly change their positions with very greatly increased rapidity when under great strain.

of open framework, or as a spongy structure through which the molecules of vapour pass freely so that they are at the same pressure within and without the liquid at the same level. But this conception must be used only to give us the net result, and not as representing the actual condition.

If, in addition to the vapour, any soluble gas is present in the vessel, it too will exist both inside and out in quantities increasing as we descend, and it must be in equilibrium at all levels. So that if near the flat surface the density of the gas in solution is n times the density at the same level outside, the same ratio will hold at all depths. Again the net external result is the same as if we picture to ourselves a spongy structure through which the gas passes freely.

As a further illustration of the change of mobility with pressure, we may take the alteration of the melting-point which I have discussed in the paper mentioned above. Thus, in the case of water, water and ice are in equilibrium under 1 atmo. at 0° , and therefore have equal vapour-tensions and equal surface mobilities. If, however, we put on pressure, the coefficients of increase of mobility are, as we have just

seen, $\frac{\sigma}{\varpi\rho}$ and $\frac{\sigma}{\varpi\rho'}$, where ρ and ρ' are the densities of water and ice, and σ and ϖ the density and pressure of the vapour respectively. Since ρ is greater than ρ' the water mobility is increased less than the ice mobility, and so at the surface of contact the ice sends more molecules to the water than it receives in return, that is to say, it melts. Below 0° the vapour-pressures and mobilities at atmospheric pressure are different, the mobility of water being greater than that of ice. But if we put on sufficient pressure we may once more equalize the mobilities and so lower the melting-point to the new temperature. Thus if ϖ and ϖ' are the vapour-pressures of water and ice at $-d\theta$, and P is the pressure making the mobilities equal, or the pressure reducing the melting-point to $-d\theta$,

$$\varpi\left(1 + \frac{P\sigma}{\varpi\rho}\right) = \varpi'\left(1 + \frac{P\sigma}{\varpi\rho'}\right),$$

or

$$\varpi - \varpi' = P\sigma\left(\frac{1}{\rho'} - \frac{1}{\rho}\right), \dots \dots \dots (7)$$

a formula equivalent to that of Kirchhoff deduced by purely thermodynamic considerations. For using the ordinary formula for lowering of melting-point,

$$P\left(\frac{1}{\rho'} - \frac{1}{\rho}\right) = L\frac{d\theta}{\theta}, \dots \dots \dots (7a)$$

we obtain Kirchhoff's result,

$$\varpi - \varpi' = \frac{L\sigma d\theta}{\theta}.$$

Now let us consider the case of a dilute solution of a non-evaporating salt. We know by direct observation that the vapour-tension is reduced by the presence of the salt, and we must suppose, on the hypothesis here advocated, that this reduction is due to a decrease in the mobility of the liquid. Let us follow out this idea by imagining that we have in the same chamber maintained at a constant temperature two deep vessels, one containing the pure solvent the other a dilute solution. In this chamber we shall suppose that above the liquids there is only the vapour of the solvent. To begin with, we may suppose that each vessel is half full and at the same level. Then the pure solvent will distill over into the solution, and will continue to do so until the difference in level in the two vessels is such that each surface is in equilibrium with the vapour at its level. The hydrostatic pressure in the solution at the level of the surface of the pure solvent will then be the osmotic pressure. If we imagine a number of non-wettable tubes inserted, as in fig. 1, in the sides of the two vessels at various depths and turned upwards, the diameters being so adjusted that the liquid does not flow out of any of them, then in any pair at the same level we realize Fitzgerald's semi-permeable membrane; and at each level the two liquids must have equal vapour-tensions, which implies that their mobilities are equal at each level. This also comes out from our equations. Let ϖ, ϖ' be the flat surface vapour-tensions of solvent and solution, ρ the density of the liquid—practically the same for each—and H the final difference in level between the two surfaces, so that the osmotic pressure $P = g\rho H$. If M, M' be the mobilities at the surface-levels,

$$\frac{M}{M'} = \frac{\varpi}{\varpi'}.$$

Now as we descend in the solution the mobility increases, and the rate of increase is $\frac{\sigma}{\varpi'\rho}$ per unit pressure. For depth H this increase is $g\rho \frac{H\sigma}{\varpi'\rho} = g \frac{H\sigma}{\varpi'}$, or the mobility

$$\begin{aligned} M'' &= M' \left(1 + g \frac{H\sigma}{\varpi'} \right) = \frac{\varpi'}{\varpi} M \left(1 + g \frac{H\sigma}{\varpi'} \right). \\ &= \frac{M}{\varpi} (\varpi' + gH\sigma). \end{aligned}$$

But $\varpi = \varpi' + gH\sigma$,

whence $M''=M$, or at the level of the solvent surface the mobilities are equal. This equality will be maintained if we descend equal distances in the two liquids below that level. So that if we now connect the two vessels at any level by a horizontal tube with a semipermeable membrane in it, the solvent mobilities on the two sides of the membrane are equal, and therefore the solvent diffuses through at equal rates in the two directions.

We may then explain in the following general terms the rise which occurs when we place a semipermeable vessel containing a solution into a solvent. The solvent molecules are entering the membrane on both sides, but the mobility or number set free per second from the pure solvent is greater than the number set free from the solution. The membrane goes on absorbing the solvent from each side till it becomes saturated; *i. e.* holds so much that it returns as many molecules as it receives. It is receiving more from the pure solvent side, and therefore when saturated for that side it is supersaturated for the other. Consequently more molecules are sent into the solution than are received from it, and the solution grows until the growing pressure so much increases the mobility that it is equal on both sides of the membrane.

If the solution and solvent are in two vessels separated by an indefinitely produced vertical and semipermeable membrane, it is evident that ultimately the two will be in equilibrium at every level, whether in liquid or vapour.

We may apply the same idea to the change of melting-point in a solution. In the solution the solid mobility is unchanged, but that of the solution is lowered by the fraction $\frac{P\sigma}{\omega\rho}$, where P is the osmotic pressure; and to find the new melting-point, we must find the temperature $d\theta$ below the normal melting-point at which this is equal to the difference between the liquid and solid mobilities.

Taking pressures to represent mobilities,

$$\frac{\omega - \omega'}{\omega} = \frac{P\sigma}{\omega\rho}.$$

But

$$\omega - \omega' = \frac{L\sigma d\theta}{\theta},$$

whence we obtain the ordinary result

$$d\theta = \frac{P\theta}{L\rho}. \quad \dots \dots \dots (8)$$

Comparing the above result with the lowering due to pressure

(7 and 7a), we see that the lowering due to a given osmotic pressure in the solution is greater than that due to an equal pressure on the pure solvent in the ratio

$$\frac{1}{\rho} : \frac{1}{\rho'} - \frac{1}{\rho},$$

or

$$v : v' - v.$$

In the case of ice and water the ratio is $1 : 1.092 - 1$
 $= 1 : .092$
 $= 11 : 1$

It now remains to see if we can give any reasonable account of the decrease in mobility in a liquid when a salt is present in solution. If the molecules of salt were simply mixed with those of the solvent, or if they combined to form stable non-evaporating compounds with the solvent, which compounds were simply mixed, then the mixture should have the same vapour-tension as the pure solvent. For we might regard the salt or compound molecules at the surface as equally reducing the effective evaporating and the effective condensing area, somewhat as a perforated plate or gauze laid on the surface would do. But the salt probably combines with the solvent to form unstable molecules which continually interchange constituents, so that when near the surface they may serve equally with those of the pure solvent to entangle the molecules of vapour coming downwards, these descending vapour molecules taking the place of molecules attached to the salt. Probably, however, they are less energetic than the pure solvent molecules and do not contribute so much to evaporation. We shall make the supposition that they do not contribute at all.

Let then each of the salt molecules combine on the average with a of the solvent molecules, and in such a way that it prevents those a molecules from evaporating while the compound molecules formed will entangle returning molecules, each of the a being replaceable by a vapour molecule. Then we may regard the solution as solvent, having a number of molecules simply mixed up and inactive as regards evaporation but active in effecting condensation.

If N is the number of gramme molecules of solvent per litre, and n the number of gramme molecules of salt added, the number of solvent molecules left is $N - an$. Were the n compound molecules quite inactive both as regards evaporation and condensation the mobilities outwards and inwards would

be altered in the same ratio and the vapour-tension would be unaltered. But we are supposing that they are inactive for evaporation only and that their a molecules of combined solvent are still active for condensation. So that in the solution there are only $N-an$ active for evaporation, while there are still N active for condensation. Hence the vapour-tension is reduced in the ratio $\frac{N-an}{N}$. Or if ϖ and ϖ' are the solvent and solution vapour-tensions,

$$\frac{\varpi'}{\varpi} = \frac{N-an}{N}$$

and

$$\frac{\varpi - \varpi'}{\varpi} = \frac{an}{N}.$$

If each salt molecule takes one solvent molecule, so that $a=1$, we have

$$\frac{\varpi - \varpi'}{\varpi} = \frac{n}{N},$$

which is the usual result deduced for dilute solutions from the van't Hoff value of the osmotic pressure. We may, of course, work backwards from this result, and the work may be put in the following form:—

If P is the pressure in the solution necessary to restore its mobility to that of the solvent, *i.e.* to increase it in the ratio $\varpi : \varpi'$,

$$\varpi' \left(1 + \frac{P\sigma}{\varpi\rho} \right) = \varpi,$$

or

$$\frac{\varpi - \varpi'}{\varpi} = \frac{P\sigma}{\varpi\rho} = \frac{n}{N}$$

and

$$P = \frac{n\varpi\rho}{N\sigma}.$$

If M is the molecular weight of the solvent

$$\begin{aligned} \frac{\varpi}{\sigma} &= \frac{\varpi_0}{\sigma_0} (1 + at) \\ &= \frac{2}{M} \left(\frac{\varpi_0}{\sigma_0} \right)_H (1 + at) \end{aligned}$$

where $\left(\frac{\sigma_0}{\sigma_0}_H\right)$ is the value for hydrogen at 0° , and this is

$\frac{A}{\cdot 0000896}$ where $A = 1$ atmo.

Also $NM = 1000\rho$.

Substituting these values we obtain

$$\begin{aligned} P &= \frac{n}{N} \cdot \frac{2}{M} \cdot \frac{A\rho(1+\alpha t)}{0\cdot 0000896} \\ &= \frac{2nA}{0\cdot 0896} (1+\alpha t) \\ &= 22\cdot 3nA(1+\alpha t). \end{aligned}$$

If a has any other value than 1 we must put

$$P = 22\cdot 3anA(1+\alpha t),$$

whence we see that if each salt molecule combines with two or with three solvent molecules the osmotic pressure is double or treble the normal value.

The supposition here made is no doubt crude in its simplicity, but my attempts to introduce other considerations, such as change in density in the solution, have led to such complicated results that much more extravagant suppositions had to be made to reconcile these results with experiments. I therefore leave the hypothesis in this crude form, in which it will at least serve to show that it is not necessary to ascribe osmotic pressure to dissociation but rather to association or some kind of combination of salt and solvent.

XXXII. *Admittance and Impedance Loci.*

By FREDERICK BEDELL*.

THE quantities chiefly considered in the discussion of alternating currents are electromotive forces and currents, the values of these being determined for different conditions. Electromotive forces and currents are commonly represented by vector diagrams; and the change in these diagrams, as some one quantity is varied, is shown by the loci of the vectors which are altered thereby. What may be termed electromotive force and current loci are thus determined. The numerical values for which these are constructed necessarily depend upon some condition involving an assumed

* Communicated by the Physical Society: read June 26, 1896.