

XXV. *The Solubility and Diffusion in Solution of Dissociated Gases.* By O. W. RICHARDSON, M.A., B.Sc., Clerk Maxwell Student and Fellow of Trinity College, Cambridge*.

THE solubility of gases which act chemically on the solvent, or which dissociate in solution, is treated in Van t'Hoff's Lectures on Theoretical Chemistry, pt. ii. p. 28 *et seq.* It is there pointed out, on theoretical grounds, that gases which dissolve without chemical action, or which associate with the solvent in such a way that each aggregate contains only one molecule of the dissolved gas, obey Henry's Law of proportionality between the pressure and the mass of gas dissolved. As all gases which have been examined appear to obey Henry's Law, with the exception of ammonia, sulphur dioxide, and hydrochloric acid in water, this subject has not hitherto attracted much attention. Phenomena of this kind appear, however, to characterize the absorption of hydrogen by palladium and platinum, and, probably, of other gases by other metals (for instance, carbon monoxide by iron). The recent experiments of Winkelmann on the variation of the rate of diffusion of hydrogen through hot palladium† and platinum‡, with the driving pressure, led him to the conclusion that the hydrogen was partly dissociated into atoms, and that only the atoms were capable of passing through the hot metal. A series of experiments on the rate of diffusion of hydrogen through platinum at different pressures and temperatures has just been carried out by the author in conjunction with Messrs J. Nicol and T. Parnell, and will shortly be published. This investigation, so far as the pressure relations are concerned, has yielded results similar to those of Winkelmann, and most of the phenomena appear to be capable of explanation on the view that the hydrogen dissolves in the platinum and then dissociates (partially, at any rate) into atoms. It was in seeking an explanation of these results that the author was led to examine into the theory of the solubility of a dissociating gas and to the results which are given in the present communication.

§ 1. *Solubility Relations.*

We shall confine our attention to the case of a gas in which each molecule dissociates into n similar molecules. The same methods could, of course, be applied to a more complicated case if it should occur. The reaction which we are considering is symbolized by a chemical equation of the

* Communicated by the Author.

† Drude's *Annalen*, vol. vi. p. 104.

‡ *Ibid.* vol. viii. p. 388.

type $X_n = nX$ and takes place, to a greater or less extent, both in the solution and in the surrounding gas. In the investigation given by Van t'Hoff (*loc. cit.*) certain relations are deduced by making the dissociated portion of the gas obey Henry's Law. It is evident, however, that for a steady state not only must there be equilibrium between the free and dissolved parts of the dissociated gas, but the undissociated portion must also be governed by a similar relation. It is not sufficient for equilibrium merely to postulate equality between the total amount of gas entering and leaving the solvent in a given time. It is necessary that the amount entering and leaving should be the same for each constituent. The only alternative is to suppose the gas to enter the solution in one form, to dissociate or recombine there and leave in the other form. Such processes involve a continuous transfer of heat at a rate depending on the value of the heat of dissociation. It is thus necessary that there should be a separate relation between the concentrations of the free and dissolved portions of each constituent; this reasoning is true whatever be the nature of the relation, quite apart from its assuming the special form of Henry's Law.

We have to take into account then four different equilibrium conditions. We have two equations which determine the relation between the undissociated and dissociated constituents of the dissolved, and undissolved, gas respectively, and two more equations which make the internal concentration proportional to the external concentration of each constituent. If these relations do not hold it is easy to see that perpetual motion is obtained.

Let the suffix 0 denote the gas outside, and ι inside the solution. Let C be the concentration of the undissociated, and c of the dissociated portion. The equations which determine the equilibrium between the dissociated and undissociated portions of the gas inside and outside the solution respectively are then:

$$\frac{c_0^n}{C_0} = k_0 \quad \text{and} \quad \frac{c_\iota^n}{C_\iota} = k_\iota,$$

where k_0 and k_ι are the dissociation constants of the free and dissolved gas respectively. In general k_0 will not be equal to k_ι , as for instance in the case of an acid gas like HCl where electrolytic dissociation occurs in solution. Applying Henry's Law to each of the two constituents we get two further equations, viz.:

$$C_0 = AC_\iota \quad \text{and} \quad c_0 = ac_\iota,$$

where A and a are the inverses of the solubilities of the undissociated gas and of the products of dissociation respectively.

By eliminating the concentration from these equations we obtain an interesting relation between the constants, viz. :

$$\frac{a^n}{A} = \frac{k_0}{k_i}.$$

In other words, the solubility of the products of dissociation is determined absolutely by the solubility of the undissociated substance, together with the two dissociation constants. In the simplest case, where the two dissociation constants are equal, the solubility of the dissociation products is the n th root of that of the original substance.

These results may be confirmed and extended by treating the subject thermodynamically. We can obtain a reversible cycle, at constant temperature, as follows :—Suppose we have a cylinder whose walls are perfect conductors of heat and supplied with a piston at each end. Across the middle of the cylinder is a slice of the solution we are considering. The two sides of the slice are bounded by semipermeable membranes, one end allowing only undissociated, and the other only dissociated molecules to pass. Initially the external gas is in equilibrium with that inside the solution at both ends. Since the diaphragms are only permeable to one of the two gases present, this does not necessarily imply equilibrium between the internal and external gas at any one end as regards both constituents, but only as regards one constituent. According to the result we obtained before, this would involve equality in the total pressures as well; since, as we have already seen, there is one total pressure for which the constituent gases are in equilibrium with the internal ones. We shall show that this equality follows thermodynamically; although any further proof cannot be regarded as strictly necessary, since the result is merely a particular case of Gibbs's general theorem regarding the equilibrium of mixed systems.

Let us suppose the partial pressures of the undissociated gas (X_n) and of the dissociated gas (X) on the side permeable to X_n are P_2 and p_2 respectively, the corresponding quantities on the other side being P_1 and p_1 . Then a volume V_2 of gas is forced through the X_n diaphragm, into the solution, a corresponding quantity being withdrawn through the X side so as to maintain the total internal pressure constant. Owing to the supposed difference of pressure on the two sides, the volume V_1 withdrawn will not be the same as V_2 , but is given by the modified law of Boyle and Charles for a dissociating gas, viz. :—

$$\left(P_1 + \frac{1}{n}p_1\right)V_1 = \left(P_2 + \frac{1}{n}p_2\right)V_2 = R\theta.$$

The work done by the gas in this part of the operation is evidently

$$(P_1 + p_1)V_1 - (P_2 + p_2)V_2 = \frac{n-1}{n}(p_1V_1 - p_2V_2).$$

The rest of the cycle consists merely in isolating a volume V_1 of the gas at pressure $P_1 + p_1$ and expanding it isothermally at θ° till its pressure and volume become $P_2 + p_2$ and V_2 respectively.

It is evident that we have now carried out a cycle at constant temperature which is perfectly reversible at every stage. We may therefore independently equate to zero the external work done, and the total heat absorbed, by the system. On account of the complicated nature of the integrals which arise in the general case, the calculation of the work done during the expansion from volume V_1 to V_2 isothermally, has only been carried out in the case where the pressure (p) of the dissociated gas is small compared with that (P) of the undissociated. The work done in this part of the cycle is evidently

$$\int_{V_1}^{V_2} (P + p) dV,$$

where the relation between P , p , and V is given by the modified gas equation above, together with the law of dissociation

$$p^n/k_0 = P + \frac{1}{n}p (=P \text{ approximately}).$$

To this approximation

$$p = (k_0 P)^{\frac{1}{n}} = \left(\frac{k_0 R \theta}{V}\right)^{\frac{1}{n}}.$$

When the above integral is evaluated on this basis we obtain

$$R\theta \log \frac{V_1}{V_2} + \frac{1}{n} (k_0 R \theta)^{\frac{1}{n}} \left(V_1^{\frac{n-1}{n}} - V_2^{\frac{n-1}{n}} \right).$$

Adding this to the work done in the previous part of the cycle and equating the sum to zero, we obtain the following equation to determine the relation between V_1 and V_2 :—

$$\frac{V_1}{V_2} = \frac{e^{\frac{1}{n} k_0^{\frac{1}{n}} \frac{1}{n} (V_2/R\theta)^{\frac{n-1}{n}}}}{e^{\frac{1}{n} k_0^{\frac{1}{n}} \frac{1}{n} (V_1/R\theta)^{\frac{n-1}{n}}}} = e^{\frac{\frac{1}{n} p_2 V_2}{R\theta}} = e^{\frac{\frac{1}{n} p_1 V_1}{R\theta}}$$

Now $\frac{1}{n} \frac{p_1 V_1}{R\theta}$ and $\frac{1}{n} \frac{p_2 V_2}{R\theta}$ are the fractional amounts of the gas which are dissociated at volumes V_1 and V_2 respectively. By hypothesis n is ≤ 1 , *i. e.* the gas does not contract in dissociating. Hence, except when $n=1$, $\frac{1}{n} \frac{p_2 V_2}{R\theta}$ is $> \frac{1}{n} \frac{p_1 V_1}{R\theta}$

if V_2 is $> V_1$. When $n=1$, the value of $\frac{1}{n} \frac{pV}{R\theta}$ is independent of V . We see therefore that in both cases the only relation between V_1 and V_2 which satisfies the above transcendental equation is $V_1=V_2$. Hence $P_1=P_2$ and $p_1=p_2$, from which we conclude that portions of a dissociating gas which are separately in equilibrium with either of the constituents of the mixture in the same solution, are in equilibrium with one another.

We now come to the equation which is obtained when we equate to zero the sum of the quantities of heat given out in the various chemical and physical actions which take place during our cycle. We have seen already that owing to the modification in the "chemical potential" of the dissociated molecules produced by the solvent, the dissociation constant is not necessarily the same in the solution as in the free gas. For precisely similar reasons the heat given out for a given amount of dissociation is not necessarily identical inside and outside the solution. Let q_0 be the heat evolved when n gram-molecules of X unite to form X_n outside the solution, and q_i the corresponding quantity inside; let Q_x be the heat evolved when 1 gram-molecule of X gas dissolves in the solvent without recombination, and Q_{x_n} the corresponding quantity for 1 gram-molecule of X_n . By following the course of the cycle we evidently get

$$q_i + nQ_x - Q_{x_n} - q_0 = 0.$$

This equation shows, as we should expect, that q_0 is only equal to q_i in the special case when the heat of solution of n gram-molecules of X is equal to that of 1 gram-molecule of X_n .

For any reversible chemical action the variation with temperature of the reaction constant is given by the equation

$$\frac{d(\log k)}{d\theta} = \frac{Q}{2\theta^2},$$

where Q is the heat of reaction together with terms depending on the volume changes occurring. Applying this we obtain

$$\frac{d}{d\theta} (\log k_0 - \log k_i) = \frac{q_0 - q_i}{2\theta^2},$$

since the volume changes are the same for both internal and external dissociation.

But we have seen that

$$A \frac{k_0}{k_i} = a^n ;$$

whence

$$\frac{d}{d\theta} (n \log a - \log A) = \frac{nQ_x - Q_{x_n}}{2\theta^2},$$

or

$$\frac{a^n}{A} \left(= \frac{k_0}{k_i} \right) = C e^{\frac{-nQ_x + Q_{x_n}}{2\theta}},$$

where C is a constant. Thus the variation with temperature of the solubilities is determined entirely by the difference of the heats of solution of the dissociated and undissociated gas.

§ 2. *Calculation of the Rate of Diffusion.*

We now come to the problem, to which the preceding discussion is to a large extent a necessary preliminary, of the distribution, in the steady state, of a dissociating gas inside an infinite slab of solution of finite thickness, when one side of the slab is in contact with the dissociating gas at a finite pressure and the other is maintained at pressure zero. Naturally the resulting equations also lead to the rate of diffusion of the gas bodily through the slab.

In order to obtain the equations which determine the distribution of the gas in the solution, let us consider the rate of increase of the concentration inside an infinitesimal cube whose angular points are given by the necessary combination of the coordinates $x, y, z, x+dx, y+dy, z+dz$. Let C be the concentration and μ the coefficient of diffusion of the undissociated gas, c and μ_n being the corresponding quantities for the dissociated portion. Then the rate of flow of the

undissociated gas in at the x face of the cube is $-\mu \frac{dC}{dx} dy dz$.

Similarly the rate of flow in of this part of the gas at the $x+dx$ face is

$$\mu \left\{ \frac{dC}{dx} + \frac{d^2C}{dx^2} dx \right\} dy dz.$$

In this way we see that the rate of increase of the concentration C in the element of volume due to diffusion is

$$\mu \left\{ \frac{d^2C}{dx^2} + \frac{d^2C}{dy^2} + \frac{d^2C}{dz^2} \right\} dx dy dz.$$

But diffusion is not the only cause tending to change the concentration at a given point; the molecules are dissociating at a rate proportional to C and recombining at a rate proportional to c^2 . Hence the total rate of increase of C is given by

$$\frac{dC}{dt} = \mu \nabla^2 C - \beta C + \alpha c^2,$$

where α is the rate of recombination and β that of dissociation, and $\beta/\alpha = k_t$. Like considerations give us a similar equation for c , viz.:

$$\frac{1}{n} \frac{dc}{dt} = \frac{\mu_n}{n} \nabla^2 c + \beta C - \alpha c^2.$$

In the steady state

$$\frac{dC}{dt} = \frac{dc}{dt} = 0.$$

Returning to the one dimensional problem we started with let the faces of the slab be perpendicular to the axis of x and its thickness be d . Addition of the above equations gives

$$\mu \frac{d^2 C}{dx^2} + \frac{\mu_n}{n} \frac{d^2 c}{dx^2} = 0 \text{ (in the steady state),}$$

whence

$$\frac{\mu}{\mu_n} C + \frac{1}{n} c = A_1 x + A_2.$$

When $x = d$, $C = c = 0$, so that

$$\frac{1}{n} c + \frac{\mu}{\mu_n} C = A_1 (x - d).$$

When $x = 0$, Henry's Law gives $C_0 = AC$ and $c_0 = ac$. In addition to these we have the two following relations between C_0 and c_0 , viz.:

$$c_0^n = k_0 C_0 \text{ and } P_0 = C_0 + c_0,$$

if P_0 is the total external concentration. The equation for c_0 in terms of P_0 is therefore

$$c_0^n + k_0 c_0 = k_0 P_0.$$

Let λ_0 be a real root of this, then

$$C_0 = \frac{1}{k_0} \lambda_0^n.$$

If we determine A_1 and replace a by $\left(A \frac{k_0}{k_t}\right)^{\frac{1}{n}}$, we obtain

$$\frac{1}{n} c + \frac{\mu}{\mu_n} C = \left\{ \frac{1}{n} \left(\frac{k_1}{A k_0} \right)^{\frac{1}{n}} \lambda_0 + \frac{\mu \lambda_0^n}{\mu_n k_0 A} \right\} \left(1 - \frac{x}{d} \right).$$

The rate of flow through the unit area of the slab is therefore

$$-\left\{ \mu \frac{dC}{dx} + \frac{\mu_n dc}{n \frac{dx}{d}} \right\} = \frac{\mu_n}{d} \left\{ \frac{1}{n} \left(\frac{k_t}{A k_0} \right)^{\frac{1}{n}} \lambda_0 + \frac{\mu}{\mu_n k_0 A} \right\}.$$

This expression is independent of x , and therefore satisfies the equation of continuity.

The most important case that arises is when the dissociation is small outside the solution. In this case we may take

$\lambda_0 = (k_0 P_0)^{\frac{1}{n}}$, when the equation for the distribution of the gas becomes

$$\frac{1}{n} c + \frac{\mu}{\mu_n} C = \left\{ \frac{1}{n} \left(\frac{k_t}{A} \right)^{\frac{1}{n}} P_0^{\frac{1}{n}} + \frac{\mu}{\mu_n A} \right\} \left(1 - \frac{x}{d} \right).$$

We see that the total flow consists of two terms, one of which is directly proportional to the pressure, and the other to its n th root. The relative importance of the two terms depends on the coefficients of diffusion, the solubility and the dissociation constant. It will therefore, in all probability, vary considerably with the temperature.

By substituting the value of C in terms of c and x from the above equation in the equation

$$\frac{\mu_n}{n} \frac{d^2 c}{dx^2} + \beta C - \alpha c^2 = 0,$$

and solving the resulting differential equation, we could obtain the distribution of the separate concentrations along the thickness of the slab, but this does not appear to be of any great interest, from an experimental point of view, in the present state of the subject.

There is, of course, no need to restrict ourselves to the case where the external concentration vanishes on one side of the slab. With the same notation, if the pressure be P_0 on one side of the slab and P_1 on the other, in the case where the external dissociation is small we obtain :

$$\frac{\mu}{\mu_n} (C - A P_0) + \frac{1}{n} \left(c - a P_0^{\frac{1}{n}} \right) = \left[\frac{\mu}{\mu_n} (P_1 - P_0) A + \frac{a}{n} \left(P_1^{\frac{1}{n}} - P_0^{\frac{1}{n}} \right) \right] \frac{x}{d},$$

whence we see that the rate of flow consists as before of two terms, one of which is proportional to the gradient of the pressure and the other to that of its n th root.

Case of a Gas which combines Chemically with the Solvent.

Another case may arise in which a gas is capable of diffusing through a solid partition, viz., when the gas is capable of combining in a reversible manner with the material of which the partition is composed. For instance, we might

imagine that a cylinder of hot lime, if it could be made airtight, would still be permeable to carbon dioxide. As a rule the disintegration produced by chemical action would prevent such partitions from being effective for any length of time, but still cases of this kind are possible and must therefore be considered.

The diffusion, which takes place in these cases by the gas particles being handed from one molecule to the other, follows in general the same kind of laws as those which have first been considered. There is, however, one very important difference conditioned by the fact that, the reaction being reversible, there is a definite dissociation pressure for each temperature. When the external pressure is \geq the dissociation pressure, the whole of the superficial layer is turned into the compound, so that the solid cannot transmit a pressure greater than the dissociation pressure. Hence, if we start with a very high pressure on one side of the diaphragm and zero pressure on the other side, the pressure on the low pressure side will rise until it is equal to the dissociation pressure, when no further transference will take place. On the other hand, if the pressure on one side is always kept at zero, whilst that on the other side is capable of taking all values, then the rate of flow through will be a uniform function of the pressure up to the dissociation pressure, at which there will be a discontinuity, and the rate of flow will be independent of the pressure for all higher pressures.

XXVI. *An Instrument for Drawing Conics.* By J. R. COTTER, M.A., Assistant to the Professor of Experimental Physics, Trinity College, Dublin*.

APROPOS of Prof. Karl Pearson's article in the 'Philosophical Magazine' for February, I should like to mention that in the year 1894 I designed an instrument for drawing conics which has the advantage of always keeping the drawing-pen parallel to the direction of the curve. The compasses will draw any kind of conic, given the foci and a point on the curve. The accompanying figure is drawn from the actual instrument, but as it is only a rough home-made model it is faulty in construction.

AGBF is a rhombus formed of four equal and freely jointed flat brass rods. The corner A slides freely along the slot of the bar BC. FH is another flat brass bar pivoted

* Communicated by Prof. John Joly, F.R.S.