Semi-Permeable Films and Osmotic Pressure.

Lord Kelvin's very interesting problem concerning molecules which differ only in their power of passing a diaphragm (see Nature for January 21, p. 272), seems only to require for its solution the relation between density and pressure for the fluid at the temperature of the experiment, when this relation for small densities becomes that of an ideal gas; in other cases, a single numerical constant in addition to the relation between density and pressure is sufficient.

This will, perhaps, appear most readily if we imagine each of the vessels A and B connected with a vertical column of the fluid which it contains, these columns extending upwards until the state of an ideal gas is reached. The equilibrium which we suppose to subsist will not be disturbed by communications between the columns at as many levels as we choose, if these communications are always made through the same kind of semi-permeable diaphragm as that which separates the vessels A and B. It will be observed that the difference of level at which any same pressure is found in the two columns is a constant quantity, easily determined in the upper parts (where the fluids are in the ideal gaseous state) as a function of the composition of the fluid of the A-column, and giving at once the height above the vessel A, where in the A-column we find a pressure equal to that in the vessel B.

In fact, e have in either column

$$dp = -g\gamma dz,$$

where the letters denote respectively pressure, force of gravity, density, and vertical elevation. If we set

$$\frac{1}{\gamma} = F'(p),$$

we have

$$F'(p)dp = -gdz.$$

Integrating, with a different constant for each column, we get

$$F(p_A) = -g(z - C_A)$$
$$F(p_B) = -g(z - C_B)$$
$$F(p_A) - F(p_B) = -g(C_A - C_B).$$

In the upper region,

$$F'(p) = \frac{1}{\gamma} = \frac{at}{p}$$

$$F(p) = at \log p,$$

where t denotes temperature, and a the constant of the law of Boyle and Charles. Hence,

$$at \log p_A - at \log p_B = g(C_A - C_B).$$

Moreover, if I: *n* represents the constant ratio in which the S- and D-molecules are mixed in the a-column, we shall have in the upper regions, where the S-molecules have the same density in the two columns,

$$\gamma_A = (1 + n)\gamma_B \qquad p_A = (1 + n)p_B$$
$$g(C_A - C_B) = at \log(1 + n).$$

Therefore, at any height,

$$F(p_A) - F(p_B) = at \log(1 + n).$$

This equation gives the required relation between the pressures in A and B and the composition of the fluid in A. It agrees with van't Hoff's law, for when n is small the equation may be written

$$F'(p_A)(p_A - p_B) = atn$$

or

$$p_A - p_B = atn\gamma_A.$$

But we must not suppose, in any literal sense, that this difference of pressure represents the part of the pressure in A which is exerted by the D-molecules, for that would make the total pressure calculable by the law of Boyle and Charles.

To show that the case is substantially the same, at least for any one temperature, when the fluid is not volatile, we may suppose that we have many kinds of molecules, A, B, C, &c., which are identical in all properties except in regard to passing diaphragms. Let us imaging a row of vertical cylinders or tubes closed at both ends. Let the first contain A-molecules sufficient to give the pressure p' at a certain level. Then let it be connected with the second cylinder through a diaphragm impermeable to B-molecules, freely permeable to all others. Let the second cylinder contain such quantities of A- and B-molecules as to be in equilibrium with the first cylinder, and to have a certain pressure p'' at the level of p' in the first cylinder. At a higher level this second cylinder will have the pressure which we have called p'. There let it be connected with the third cylinder through a diaphragm impermeable to C-molecules, and to them alone. Let this third cylinder contain such quantities of A, B, and C-molecules as to be in equilibrium with the second cylinder, and have the pressure p'' at the diaphragm; and so on, the connections being so made, and the quantities of the several kinds of molecules so regulated, that the pressures at all the diaphragms shall have the same two values.

It is evident that the vertical distance between successive connections must be everywhere the same, say l; also that at all the diaphragms, on the side of the greater pressure, the proportion of molecules which can and which cannot pass the diaphragm must be the same. Let the ratio be 1 : *n*. If we write γ_A, γ_B, &c., for the densities of the several kinds of molecules, and *g* for the total density, we have for the second cylinder

$$\frac{\gamma_A + \gamma_B}{\gamma_A} = 1 + n.$$

For the third cylinder we have this equation, and also

$$\frac{\gamma_A + \gamma_B + \gamma_C}{\gamma_A + \gamma_B} = 1 + n$$

which gives

$$\frac{\gamma_A + \gamma_B + \gamma_C}{\gamma_A} = (1 + n)^2.$$

In this way, we have for the *r*th cylinder

$$\frac{\gamma}{\gamma_A} = (1 + n)^{r-1}.$$

Now the vertical distance between equal pressures between the first and *r*th cylinders, is

$$(r - 1)l.$$

Now the equilibrium will not be destroyed if we connect all the cylinders with the first through diaphragms impermeable to all except A-molecules. And the last equation shows that as γ/γ_A increases geometrically, the vertical distance between any pressure in the column when this ratio of densities is found, and the same pressure in the first cylinder increases arithmetically. This distance, therefore, may be represented by $\log(\gamma/\gamma_A)$ multiplied by a constant. This is identical with our result for a volatile liquid, except for the case we found the value of the constant to be *at/g*.

The following demonstration of van't Hoff's law, which is intended to apply to existing substances, requires only that the solutum, *i.e.* dissolved substance, should be capable of the ideal gaseous state, and that its molecules, as they occur in the gas, should not be broken up in the solution, nor united to one another in more complex molecules.

It will be convenient to use certain quantities which may be called the *potentials* of the solvent and of the solutum, the term being thus defined: - In any sensibly homogeneous mass, the

potential of any independently variable component substance is the differential coefficient of the thermodynamic energy of the mass taken with respect to that component, the entropy and volume of the mass and the quantities of its other components remaining constant. The advantage of using such *potentials* in the theory of semi-permeable diaphragms consists partly in the convenient form of the condition of equilibrium, the potential for any substance to which a diaphragm is freely permeable having the same value on both sides of the diaphragm, and partly in our ability to express van't Hoff law as a relation between the quantities characterizing the state of the solution, without reference to any experimental arrangement (see *Transactions of the Connecticut Academy*, vol. iii, pp.116, 138, 148, 94)

Let there be three reservoirs, R', R", R''', of which the first contains the solvent alone, maintained in a constant state of temperature and pressure, the second the solution, and the third the solutum alone. Let R' and R" be connected through a diaphragm freely permeable to the solvent, but impermeable to the solutum, and let R" and R''' be connected through a diaphragm impermeable to the solvent, but freely permeable to the solutum. We have then, if we write μ_1 and μ_2 for the potentials of the solvent and the solutum, and distinguished by accents, quantities relating to the several reservoirs,

$$\mu_1'' = \mu_1' = \text{const.}, \qquad \mu_2'' = \mu_2'''.$$

Now if the quantity of the solutum in the apparatus be varied, the ratio in which it is divided in equilibrium between the reservoirs R" and R''' will be constant, so long as its densities in the two reservoirs, γ_2'', γ_2''', are small. For let us suppose that there is only a single molecule of the solutum. It will wander through R" and R''', and in a time sufficiently long the parts of the time spent respectively in R"and R''', which for convenience we may suppose of equal volume, will approach a constant ratio, say I : B. Now if we put in the apparatus a considerable number of molecules, they will divide themselves between R' and R" sensibly in the ratio I : B, so long as they do not sensibly interfere with one another, *i.e.* so long as the number of molecules of the solutum which are within the sphere of action of other molecules of the solutum is a negligible part of the whole, both in R" and R'''. With this we have, therefore,

$$\gamma_2''' = B\gamma_2''.$$

Now in R''' let the solution have the properties of an ideal gas, which give for any constant temperature (*ibid.* p. 212)

$$\mu_2''' = a_2 t \log \gamma_2''' + C,$$

where a_2 is the constant of the law of Boyle and Charles, and C another constant. Therefore,

$$\mu_2'' = a_2 t \log(B\gamma_2'') + C.$$

This equation, in which a single constant may evidently take the place of B and C, may be regarded as expressing the property of the solution implied in van't Hoff's law. For we have the general thermodynamic relation (*ibid.* p. 143)

$$v dp = \eta dt + m_1 d\mu_1 + m_2 d\mu_2,$$

where v and η denote the volume and entropy of the mass considered, and m_1 and m_2 the quantities of its components. Applied to this case, since t and μ_1 are constant, this becomes

$$dp'' = \gamma_2'' d\mu_2''.$$

Substituting the value of $d\mu_2''$ derived from the last finite equation we have

$$dp'' = a_2 t d\gamma_2''$$

whence, integrating from $\gamma_2'' = 0$ and $p'' = p'$, we get

$$p'' - p' = a_2 t \gamma_2'',$$

which evidently expresses van't Hoff's law.

We may extend this proof to cases in which the solutum is not volatile by supposing that we give to its molecules mutually repulsive molecular forces, which, however, are entirely inoperative with respect to any other kind of molecules. In this way we may make the solutum capable of the ideal gaseous state. But the relations pertaining to the constants of R" will not be affected by these new forces, since we suppose that only a negligible part of the molecules of the solutum are within the range of such forces. Therefore these relations cannot depend on the new forces, and must exist without them.

To give up the condition that the molecules of the solutum shall not be broken up in the solution, nor united to one another in more complex molecules, would involve the consideration of a good many cases, which it would be difficult to unite in a brief demonstration. The result, however, seems to be that the increase of pressure is to be estimated by Avogadro's law from the number of molecules in the solutions which contain any part of the solutum, without reference to the quantity in each.   J. WILLARD GIBBS.

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