316 EFFECT OF PRESSURE ON THE EQUILIBRIUM

DISCUSSION.

The **Chairman** considered that Professor Lewis had done a useful thing in laying emphasis on the distinct character of the two deductions referred to. In determining the theoretical value of the equilibrium constant the total volume and the temperature are to be kept constant. When the equilibrium constant has been obtained, its variation with pressure can then

CONSTANT OF A REACTION IN A DILUTE SOLUTION 317

be inferred; but this inference is an entirely distinct operation, and during it the volume varies, though the temperature is still to be maintained constant. In textbooks the matter is usually displayed in such an abbreviated way that the exact nature of the mathematical operations is left somewhat obscure.

When Professor Lewis proceeds to obtain these results by the method of maximum work, the Chairman felt that his proof was itself not free from obscurity. Each step in the argument requires further elaboration before its cogency could be appreciated. In particular he had doubts as to whether the final result obtained is correct as referring to the special equilibrium constant in which the concentrations are expressed in gram-molecules per unit volume as stated. In any case the first statement in the last paragraph can hardly be the correct specification of the meaning of the phrase "volume shrinkage," because if this phrase is so defined it becomes infinitesimal and vanishes in the limit when the two values of K (K_2 and K_1) approach to equality. This statement would seem to require revision.

Professor W. C. McC. Lewis (*communicated reply*): Professor Porter's criticism is valuable not only in connection with the mode of deduction which I attempted in the Paper, but also in connection with the more fundamental question as to whether, in the case of solutions, the equilibrium constant K actually employed alters with the external pressure at all. The equilibrium constant referred to is that in which the concentrations are expressed in number of mols per unit volume. As regards the first point, Professor Porter's remarks have led me to reconsider the process described, from which it appears that the method adopted in the Paper is an attempt at too great simplification, and in one stage is incorrect. A complete cycle, based on somewhat similar lines, but involving a greater number of steps, has since been worked out by Mr. J. Rice, and is contributed later to the discussion. It would appear that ultimately the same result is obtained as in the Paper itself, but Mr. Rice's method is much to be preferred. These considerations seem to indicate that the equilibrium constant referred to does vary with the external pressure. The whole question appears, however, to have been raised for the first time, and no general agreement has yet been arrived at.

Professor F. G. Donnan, F.R.S. (*communicated*): Suppose we think of an equilibrium in dilute solution between two molecular sorts—say the simplest type—

Let the volume of the solution be V , and the pressure and temperature P and T respectively. Let there be present in equilibrium n_1 mols of A_1 and n_2 mols of A_2 in the volume V . Consider an isothermal isobaric variation of the equilibrium state, whereby δn mols change from A_1 to A_2 .

Then—

$$\delta V = \delta n \left\{ \left(\frac{\partial V}{\partial n_2} \right)_{P, T, n_2} - \left(\frac{\partial V}{\partial n_1} \right)_{P, T, n_1} \right\}.$$

The right-hand side expression will not in general be zero, so that an increase of pressure producing a diminution of volume will in general cause an internal readjustment of the ratio $\frac{n_1}{n_2}$, the sign of which can be seen at once from Le Chatelier's general principle.

Now $\frac{n_1}{n_2} = K$, equilibrium constant in the limiting case of a dilute solution. The physical diminution of volume produced by an increase of the external

318 EFFECT OF PRESSURE ON THE EQUILIBRIUM

pressure does not *per se* change the ratio $\frac{n_1}{n_2}$, and therefore not the value of K . Hence we see that the effect of an increase of pressure must be to change K , since it necessarily changes the ratio $\frac{n_1}{n_2}$.

Mr. James Rice (*communicated*): The result obtained by Professor Lewis in his Paper appears to be correct, but the statement of the isothermal cycle is rather brief. The following is, I think, a rigorous description of the cycle:—

Consider three substances (A, B, C) which when dissolved in a definite solvent are connected by the reaction—

(The restriction to three substances is merely a matter of convenience in exposition; it involves no loss of generality in the reasoning.)

Let there be a large quantity of the solvent, on the surface of which is exerted a pressure P .

In this mass of solvent let us have three large reservoirs containing respectively—

l mols of A at the concentration a mols per litre					
m	„	B	„	„	b „ „
n	„	C	„	„	c „ „

The sides of the reservoirs are permeable to the solvent, but not the dissolved substances.

Let us also have an equilibrium box containing the three substances in solution at the equilibrium concentrations α, β, γ mols per litre respectively. The box sides are also permeable to the solvent but not to A, B, and C.

By means of pistons, cylinders, and semipermeable membranes take λ mols of A from its reservoir and convert them into μ mols of B and ν mols of C in their respective reservoirs, via the box. If the reservoirs are very large, this leaves the concentrations a, b, c practically unchanged.

The external work of the system will be the sum of two terms—

(a) The work of the osmotic pressures during the passage of the substances into and out of the box, viz.,

$$RT \log K - RT \log (b^\mu c^\nu / a^\lambda) (1)$$

(b) If there is a change of volume due to the reaction, say from the volume V_1 of the whole system to the volume V_2 , the pressure on the solvent surface still remaining P , there will be work of the system during this change against the constant external pressure of amount

$$P(V_2 - V_1) (2)$$

This constitutes the first step in the cycle.

In the second step we gradually change the pressure on the solvent surface from P to P' and gradually change the volume of the system from V_2 to V'_2 . This will not involve a change in the concentrations a, b, c ; for although more solvent will be compressed into the reservoirs through the sides, yet the masses $l - \lambda, m + \mu, n + \nu$ will remain unchanged, and so volume concentrations will not alter. It may be otherwise for the box; for though compression of more solvent into the box will not alter the total mass of the dissolved substances inside it, yet it may affect the partial

CONSTANT OF A REACTION IN A DILUTE SOLUTION 319

masses of each substance and vary the equilibrium concentrations to α' , β' , γ' , and the constant to K' .

In this step the work of the system is—

$$\int_{V_2}^{V'_2} p dv_2 \dots \dots \dots (3)$$

where p is any value of the pressure between the values P and P' , and v_2 the corresponding total volume of the $l + \lambda$ mols of A , $m + \mu$ mols of B , $n + \nu$ mols of C , the solution in the box, and the mass of solvent outside reservoirs and box, all at pressure p .

In the third step, while maintaining the pressure at P' , we transform μ mols of B and ν mols of C into λ mols of A , via the box. This will involve a change of volume from V'_2 to V'_1 , and the system will do work which is the sum of two terms, as in the first step, viz.—

$$RT \log (1/K') - RT \log (a^\lambda / b^\mu c^\nu) + P'(V'_1 - V'_2)$$

or—

$$RT \log (b^\mu c^\nu / a^\lambda) - RT \log K' - P'(V'_2 - V'_1) \dots \dots \dots (4)$$

In the fourth step we gradually change the pressure back to P and the volume back to V_1 ; the work of the system during this change is—

$$\int_{V'_1}^{V_1} p dv_1 \dots \dots \dots (5)$$

where, as before, p is a pressure between P and P' , and v_1 is the total volume of solvent, l mols of A , m mols of B , n mols of C , and a mass of solution at equilibrium concentrations corresponding to the pressure p . [It is necessary to note that v_1 is not equal to v_2 ; i.e. it is not the same function of p as v_2 ; thus when $p = P$, $v_1 = V_1$, and $v_2 = V_2$; and when $p = P'$, $v_1 = V'_1$, and $v_2 = V'_2$.]

Summing up the various work terms given in (1) to (5), the result must be zero. Hence—

$$\begin{aligned} & RT (\log K - \log K') \\ & + P(V_2 - V_1) - P'(V'_2 - V'_1) \\ & + \int_{V_2}^{V'_2} p dv_2 - \int_{V'_1}^{V_1} p dv_1 \\ & = 0. \end{aligned}$$

By a partial integration—

$$\int_{V_1}^{V'_1} p dv_1 = P'V'_1 - PV_1 - \int_{P_1}^{P'} v_1 dp$$

and—

$$\int_{V_2}^{V'_2} p dv_2 = P'V'_2 - PV_2 - \int_P^{P'} v_2 dp.$$

320 EFFECT OF PRESSURE ON THE EQUILIBRIUM

Hence the above equation becomes, after cancellation of certain terms—

$$RT(\log K - \log K') = \int_{P'}^{P'} (v_2 - v_1) dP = \int_{P'}^P (v_1 - v_2) dP \dots \dots (6)$$

Had we carried out the operations described between the pressures $P + \delta P$ and P' , we should have had

$$RT [\log (K + \delta K) - \log K'] = \int_{P'}^{P + \delta P} (v_1 - v_2) dP = \int_{P'}^P (v_1 - v_2) dP + (V_1 - V_2) \cdot \delta P \quad (7)$$

where $K + \delta K$ is the constant for pressure $P + \delta P$. Therefore subtracting (6) from (7) we have—

$$RT [\log (K + \delta K) - \log K] = (V_1 - V_2) \delta P,$$

or proceeding to the limit—

$$RT \cdot \frac{d \log K}{dP} = V_1 - V_2.$$

The cycle described above seems to be correctly stated ; yet there is a discrepancy between this result and that deduced by Planck in his *Thermodynamics* (English translation, Chapter V).

The two results appear to agree until one observes that Planck's K and the K used above are defined differently. In defining K , Planck uses concentrations which are pure ratios, viz. the quotient of the number of mols of a dissolved substance to the total number of mols (*solvent mols included*) ; whereas in the K employed here, the concentrations are expressed in mols per litre. We have denoted the latter concentrations by α, β, γ above. Let us denote concentrations in Planck's sense by x, y, z ; let us also denote Planck's K by K_P and the K employed in the cycle by K_o .

Then—

$$K_o = \beta^\mu \gamma^\nu / \alpha^\lambda$$

and—

$$K_P = y^\mu z^\nu / x^\lambda.$$

If there are n_o mols of solvent, and n_1 mols of A, n_2 mols of B, and n_3 mols of C in the equilibrium box, which has a volume V (say), then—

$$x = \frac{n_1}{n_o + n_1 + n_2 + n_3} = \frac{n_1}{N}$$

$$y = \frac{n_2}{N}, \quad z = \frac{n_3}{N},$$

while—

$$\alpha = \frac{n_1}{V}, \quad \beta = \frac{n_2}{V}, \quad \gamma = \frac{n_3}{V}$$

$$\therefore K_o = K_P (N/V)^{\mu + \nu - \lambda}.$$

Hence—

$$\log K_o = \log K_P - (\mu + \nu - \lambda) \log v,$$

where—

$$v = V/N$$

and—

$$\therefore \frac{d \log K_o}{dP} = \frac{d \log K_P}{dP} - (\mu + \nu - \lambda) \frac{1}{v} \frac{dv}{dP}.$$

CONSTANT OF A REACTION IN A DILUTE SOLUTION 321

Hence the two pressure differentials should differ by a multiple of the compressibility of the solution when $\mu + \nu - \lambda$ is not zero. Yet according to the cycle above they should agree. It may be that a fallacy has crept in somewhere in the above cycle, although I fail to detect it; or it may be that the approximations used by Planck, as well as in the above analysis, are responsible for the difference; or as a third possibility it may be that the volume change considered by Planck and the volume change involved in the cycle are not the same, although I cannot satisfy myself that they are not.

This point certainly needs further discussion, and I hope this contribution will at all events serve the purpose of furthering it.