

Typed from print

THE THEORY OF SOLUTIONS.

As some recent *viva voce* remarks of mine have received an interpretation more wide than I intended, I shall be glad to be allowed to explain that when (now several years ago) I became acquainted with the work of van t' Hoff I was soon convinced of the great importance of the advances due to him and his followers. The subject has been prejudiced by a good deal of careless phraseology, and this is probably the reason why some distinguished physicists and chemists have refused their adhesion. It must be admitted, further, that the arguments of van t' Hoff are often insufficiently set out, and are accordingly difficult to follow. Perhaps this remark applies especially to his treatment of the central theorem, viz. the identification of the osmotic pressure of a dissolved gas with the pressure that would be exercised by the gas alone if it occupied the same total volume in the absence of the solvent. From this follows the formal extension of Avogadro's law to the osmotic pressure of dissolved gases, and thence by a natural hypothesis to the osmotic pressure of other dissolved substances, even although they may not be capable of existing in the gaseous condition. If I suggest a somewhat modified treatment, it is not that I see any unsoundness in van t' Hoff argument, but because of the importance of regarding a matter of this kind from various points of view.

Let us suppose that we have to deal with an involatile liquid solvent, and that its volume, at the constant temperature of our operation, is unaltered by the dissolved gas—a question to which we shall return. We start with a volume  $v$  of a gas under pressure  $p_0$ , and with a volume  $V$  of liquid just sufficient to dissolve the gas under the same pressure, and we propose to find what amount of work (positive or negative) must be done in order to bring the gas into solution reversibly. If we bring the gas at pressure  $p_0$  into contact with the liquid, solution takes place irreversibly, but this difficulty may be overcome by a method which I employed for a similar purpose many years ago.<sup>1</sup> We begin by expanding the gas until its rarity is such that no sensible dissipation of energy occurs when contact with the liquid is established. The gas is then compressed and solution progresses under rising pressure until just as the gas disappears the pressure rises to  $p_0$ . The operations are to be conducted at constant temperature, and so slowly that the condition never deviates sensibly from that of equilibrium. The process is accordingly reversible.

In order to calculate the amount of work involved in accordance with the laws of Boyle and Henry, we may conveniently image the liquid and gas to be confined under a piston in a cylinder of unit cross-section. During the first stage contact is prevented by a partition inserted at the surface of the liquid. If the distance of the piston from this surface be  $x$ , we have initially  $x = v$ . At any stage of the expansion ( $x$ ) the pressure  $p$  is given by

$p = p_0v/x$ , and the work gained during the expansion is represented by

$$p_0 v \int_v^x \frac{dx}{x} = p_0 v \log \frac{x}{v},$$

$x$  being a very large multiple of  $v$ . During the condensation, after the partition has been removed, the pressure upon the piston in a given position  $x$  is less than before. For the gas which was previously confined to the space  $x$  is now partly in solution. If  $s$  denote the solubility, the available volume is practically increased in the ratio  $x : x + sV$ , so that the pressure in position  $x$  is now given by

$$p = p_0v / (x + sV),$$

and the work required to be done during the compression is

$$p_0 v \int_0^x \frac{dx}{x+sV} = p_0 v \log \frac{x+sV}{sV}.$$

On the whole the work lost during the double operation is

$$p_0 v \left\{ \log \frac{x+sV}{x} + \log \frac{v}{sV} \right\},$$

And of this the first part must be omitted, as  $x$  is indefinitely great. As regards the second part, we see that it is zero, since by supposition the quantity of liquid is such as to be just capable of dissolving the gas, so that  $sV = v$ . The conclusion then is that, upon the whole, there is no gain or loss of work in passing reversibly from the initial to the final stage of things.

The remainder of the cycle, in which the gas is removed from the solution and restored to its original state, may now be effected by the osmotic process of van t' Hoff.<sup>1</sup> For this purpose one "semi-permeable membrane," permeable to gas but not to liquid, is introduced just under the piston which rests at the surface of the liquid. A second, permeable to liquid but not to gas, is substituted as a piston for the bottom of the cylinder, and may be backed upon its lower side by pure solvent. By suitable proportional motions of the two pistons, the upper one being raised through the space  $v$ , and the lower one through the space  $V$ , the gas may be expelled, the pressure of the gas retaining the constant value  $p_0$ , and the liquid (which has not yet been expelled) retaining a constant strength, and therefore a constant osmotic pressure  $P$ . When the expulsion is complete, the work done upon the lower piston is  $PV$ , and that recovered from the gas is  $p_0v$ , upon the whole  $PV - p_0v$ . Since this process, as well as the first, is reversible, and since the whole cycle has been conducted at constant temperature, it follows from the *second* law of thermo-dynamics, that no work is lost or gained during the cycle, or that

$$PV = p_0v.$$

<sup>1</sup> "On the Work that may be gained during the Mixing of Gases," *Phil. Mag.* vol. xlix. p. 311, 1875.

<sup>1</sup> *Phil. Mag.* vol. xxvi. p. 88, 1888.

The osmotic pressure  $P$  is thus determined, and it is evident that its value is that of the pressure which the gas, as a gas, would exert in space  $V$ .

The objection may perhaps be taken that the assumption of unaltered volume of the liquid as the gas dissolves in it unduly limits the application of the argument. It is true that when finite pressures are in question, an expansion (or contraction) of the liquid would complicate the results ; but we are concerned only, or at any rate primarily, with the osmotic pressure of *dilute* solutions. In this case the complications spoken of relate only to the second order of small quantities, and in our theory are accordingly to be dismissed.

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