Note on the Vapour-Pressure of Solutions of Volatile Substances

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DISCUSSION.

Mr. BLAKESLEY observed that, as a rule, experiment preceded theory. He congratulated Mr. Whitehead upon having settled from theoretical considerations that the vertical position of the receiving coil is best.

Prof. EVERETT said that the very elaborate method of analysis adopted in the paper appeared to be very clearly stated. He would like to know whether the inducing coil ought to be vertical as well as the receiving coil.

Mr. APPLEYARD thought that the experiment had left no doubt as to the best position of both coils. The early investigations of Mr. Willoughby Smith and the later work of Mr. H. R. Kempe and Mr. Preece had proved that for the best effect both coils should be vertical. But large vertical coils were difficult to fix and expensive to maintain. It was this reason probably that led Prof. Lodge to try what could be done with coils placed horizontally.

Mr. WHITEHEAD, in reply, said that his final formulæ only applied to a horizontal inducing coil. He had not worked out the case of what would happen if the inducing coil itself was vertical. In the Flat Holm experiments both circuits were straight wires with their ends to earth, so that they really amounted to vertical coils.

XLVIII. *Note on the Vapour-Pressure of Solutions of Volatile Substances.* By R. A. LEHFELDT, D.Sc.*

THE change of vapour-pressure of a solvent due to the solution in it of a small quantity of volatile material has been calculated on the basis of Raoult's rule for the corresponding case of a non-volatile dissolved body, first by Planck, and later, more correctly, by Nernst; the formulæ obtained, and one experiment in support of them, are given in Ostwald's *Lehrbuch* (2. ii. 588). Further examples may be obtained from the measurements of vapour-pressures I have carried out on certain mixtures of organic liquids†; those measurements

* Read May 12, 1899.

† Phil. Mag. [5] vol. xlv. p. 46.

were made primarily with the object of following out the behaviour of liquids in solutions not dilute; but in the extreme cases the results obtained will serve as a test of the formulæ applying to dilute solutions.

Adopting the notation used in the memoir referred to, we have for a mixture of the two liquids A and B :—

π_A, π_B ,	vapour-pressure of A and B respectively,
p ,	" mixture
ζ ,	ratio of number of mols. of A to mols. of B in liquid,
η ,	" " " vapour.

Then the relation as expressed by Nernst becomes

$$\frac{\pi_B - p}{\pi_B} = \zeta - \frac{p}{\pi_B} \eta$$

for the case in which ξ is small, *i. e.* in which a small quantity of A is dissolved in B; π_B is therefore the vapour-pressure of the solvent. This equation may more conveniently be transformed into

[illegible]

When ζ , and consequently η , is very small, this becomes

$$\frac{p}{\pi_B} = 1 - \zeta + \eta,$$

the form in which Planck first gave the result, but which is less exact than the other when moderate concentrations are considered.

The expression in the above form (i.) is so simple that it is worth while to put it into words, thus:—

"When a volatile substance is dissolved in a liquid the vapour-pressure of the liquid is altered in the ratio of the molecular fractional amount of solvent (Molenbruch) in the liquid to that in the vapour."

When the dissolved substance is non-volatile, the latter fraction becomes unity, and we recover the well-known formula $p/\pi_B = 1 - \xi$.

It is perhaps worth remarking that the expression con-

sidered is a particular case of the thermodynamical relation applicable to any liquid mixtures, obtained by Duhem, Margules, and myself. The latter may be put * :—

$$(\eta - \xi) \frac{\partial \log \frac{\eta}{1 - \eta}}{\partial \log \frac{\xi}{1 - \xi}} = \frac{\xi(1 - \eta)}{p} \frac{\partial p}{\partial \xi},$$

whence

$$\frac{\eta - \xi}{\eta(1 - \eta)} \frac{\partial \eta}{\partial \xi} = \frac{1}{p} \frac{\partial p}{\partial \xi}.$$

If we integrate this for a small range from $\xi = 0$ and therefore $p = \pi_B$ we get

$$\frac{(\eta - \xi)\eta}{\eta(1 - \eta)} = \frac{p - \pi_B}{\pi_B},$$

or

$$\frac{p}{\pi_B} \eta - \xi = \frac{p - \pi_B}{\pi_B},$$

the formula in question.

In case of a dilute solution of B in A it is easily seen that equation (i.) becomes

$$\frac{p}{\pi_A} = \frac{\xi}{\eta} \dots \dots \dots \text{(ii.)}$$

The experiments made were on four series of mixtures, viz. :—alcohol with benzene and toluene, and carbon tetrachloride with benzene and toluene; so that, taking the end members of each series, we get eight cases of “dilute solution.” The second group of liquids, which were chosen as normal in character, give the following results :—

	η .	π (solvent).	p .	ξ (calc.).	ξ (obs.).
CCl ₄ in toluene	0.181	93.0	105.4	0.072	0.073
Toluene in CCl ₄	0.872	310.2	242.0	0.680	0.708
(A = carbon tetrachloride; B = toluene.)					
CCl ₄ in benzene	0.054	270.9	273.6	0.045	0.043
Benzene in CCl ₄	0.835	310.2	306.5	0.825	0.830
(A = carbon tetrachloride; B = benzene.)					

* *L. c.* p. 60.

Unfortunately no sufficiently dilute solution of toluene in CCl_4 was measured; that quoted contained (as may be seen from the value of ζ) 29·2 per cent. of the dissolved body, and it appears that the range of applicability of the formula is here exceeded: otherwise the agreement is good.

The mixtures containing alcohol, on the other hand, show maxima of vapour-pressures, and on this account the departure from the formulæ for dilute solutions is much more marked, and it is not possible to apply equations (i.) and (ii.) when the amount of dissolved body exceeds a very few per cent. The numbers are:—

	η .	π (solvent).	p .	ζ (calc.).	ζ (obs.).
Alcohol in benzene	0·281	270·9	350·4	0·070	0·088
Benzene in alcohol	0·668	219·5	315·0	0·958	0·886

(A = alcohol; B = benzene.)

Alcohol in toluene	0·591	93·0	199·5	0·123	0·138
Toluene in alcohol	0·902	219·5	233·5	0·959	0·946

(A = alcohol; B = toluene.)

Temperature, throughout = 50° C.

The quantity of dissolved substance in the liquid is less than that calculated, in each of the four alcohol mixtures. It is easy to show that for them the formula (i.) or (ii.) is less accurate than in the case of normal liquids, for a mixture in nearly equal parts may be looked upon either as a solution of A in B or of B in A. If it be calculated accordingly the results will of course differ, since the solution is not by any means dilute; but whilst in the case of the normal liquids the disagreement of the two results is small, in the alcohol mixtures it is egregious.

East London Technical College,
March 1899.