# ON VAN'T HOFF'S EQUATION AND THE MOLECULAR WEIGHTS OF LIQUIDS.

BY C. L. SPEYERS.

CONSIDER the equation

$$\frac{n}{N+n} = \frac{p-p'}{p} \text{ or } \frac{n}{N} = \frac{p-p'}{p'}, \qquad (1)$$

where $n$ is the number of gram-molecules of solute, $N$ is the number of gram-molecules of solvent calculated from the ordinary molecular weight, that is, the molecular weight of the solvent in the solution, *not* the molecular weight of the solvent in the vapor state between pressures $p$ and $p'$, and $p$ and $p'$ are the vapor-pressures of pure solvent and solution, respectively.

Consider also the equation

$$\frac{n}{N} = l\frac{p}{p'}, \qquad (2)$$

where $N$ is now calculated from molecular weight of the solvent in the vapor state between pressures $p$ and $p'$, the other letters being the same as for equation (1).

When $p'$ is only a trifle smaller than $p$, then the two equations are just about equivalent, but they are not at all equivalent when $p'$ is quite different from $p$. In the applications of these equations the difference $p-p'$ has hitherto been small and either equation has answered for the purposes desired. But recently the vapor-pressures of some concentrated solutions have been measured and for these solutions, equation (2) seems to fail lamentably while equation (1) seems to give excellent results.

The vapor-pressures have been measured by Noyes and Abbott,[1] by Goodwin and Burgess,[2] by Linebarger,[3] and by Lehfeldt.[4]

Noyes and Abbott, and Goodwin and Burgess, used solutions of naphthalene, azobenzene, benzophenone, and diphenylamin, in ether. The concentrations of their solutions ran up to about fourteen per cent. gram-molecules of solute.

When curves are plotted from equations (1) and (2) for which

1 *Ztschr. phys. Chem.*, 23, 56 (*1897*).

2 *Ibid.*, 28, 99 (*1899*).

3 This Journal, 17, 615, 690 (*1895*).

4 *Phil. Mag.*, 46, 42 (*1898*).

curves $p'$ is the ordinate and the per cent. gram-molecules is the abscissa, the values obtained from each curve agree pretty well with experiment, so long as the solutions are dilute, but as the solutions grow more concentrated, the deviation from observation increases, and the deviation increases more markedly with $p'$ calculated from (2) than with that calculated from (1). In making such comparison we must of course assign a molecular weight to the solute. I assigned a normal molecular weight to each solute. Had a different molecular weight been assigned to the solute, and I think for naphthalene at any rate we certainly ought to have done so, then the calculated values for $p'$ could be made to agree with the observed values. So these experiments do not declare strongly against either equation. But the observations of Linebarger and of Lehfeldt will compel us to reject (2) in favor of (1). They used liquids miscible in all proportions so that we can follow the molecular weights of solvent and solute from infinite dilution to complete purity. How equation (1) is to be applied, I have tried to show.[1]

Mixtures of chlorbenzene with benzene, chlorbenzene with toluene, brombenzene with benzene, carbon tetrachloride with toluene, when plotted with vapor-pressures as ordinates and per cent. gram-molecules as abscissas, all have partial vapor-pressures so nearly straight lines that we seem compelled to go further and put them as straight lines. This means that the molecular weight of the solute does not change at all with concentration; therefore, we must assume that the molecular weight of the solute in such solutions is normal, for whenever we can follow a molecular weight that is not normal, we find that it is variable with the concentration.

If we claim that equation (1) is not applicable but that equation (2) is the correct one to use, and that the molecular weight of the solute varies in such way that (2) is possible, then we are led to absurd values for the molecular weight of the solute.

Let $w$ be the weight of the solute, $W$ be the weight of the solvent, $m$ be the molecular weight of the solute, $M$ be the molecular weight of the solvent; then,

$$n = \frac{w}{m} \text{ and } N = \frac{W}{M},$$

[1] *J. phys. Chem.*, **2**, 347 (*1898*); This Journal, **21**, 282 (*1899*).

and we have from (1)

$$m = \frac{Mw}{W} \frac{p'}{p - p'}. \tag{3}$$

and from (2),

$$m = \frac{Mw}{W(lp - lp')}. \tag{4}$$

Let us apply these equations to the mixture of benzene and acetic acid at 35°, using data recalculated[1] from Linebarger's experiments. The following table contains these data :

| $HC_2H_3O$ per cent. gram-molecules. | $C_6H_6$ per cent. gram-molecules. | V. P. $HC_2H_3O_2$ (26.5). | V. P. $C_6H_6$ (146). | Mol. wt. $C_6H_6$ by (3). | Mol. wt. $C_6H_6$ by (4). | Mol. wt. $HC_2H_3O_2$ by (3). | Mol. wt. $HC_2H_3O_2$ by (4). |
|---|---|---|---|---|---|---|---|
| 10 | 90 | 2.8 | 140 | 78 | 312 | 156 | 158 |
| 30 | 70 | 8.0 | 127 | 78 | 152 | 172 | 184 |
| 50 | 50 | 13.2 | 109 | 78 | 112 | 177 | 205 |
| 70 | 30 | 18.7 | 85.8 | 78 | 87.7 | 199 | 263 |
| 90 | 10 | 23.8 | 45.0 | 78 | 84.1 | 241 | 459 |
| 93 | 7 | 24.6 | 34.3 | 78 | 78.9 | 245 | 550 |
| 96 | 4 | 25.2 | 22.5 | 78 | 63 | 262 | 770 |
| 98 | 2 | 25.9 | 12.6 | 78 | 68.7 | 278 | 1200 |

The molecular weight of benzene is not absurd as calculated by either formula, though suspiciously low by formula (4) in solutions dilute with respect to benzene. The molecular weight of acetic acid keeps within acceptable range as calculated by formula (3), while it runs far beyond acceptable range as calculated by formula (4).

Equation (4) as originally obtained by van't Hoff[2] was limited to solutions so dilute that the heat involved in removing the necessary quantity of solvent was negligible. This heat of course is not the heat equivalent of the osmotic work, but the heat of dilution at constant concentration minus the heat equivalent of the osmotic work.

Let us now deduce equation (4) again, following van't Hoff in a general way but using solutions as concentrated as we choose, only requiring that the quantity of solution shall be so great that no appreciable change in concentration may be made when the necessary quantity of solvent is removed or added. That component whose vapor-pressure is measured shall be considered as the solvent.

[1] *Loc. cit.*
[2] *Ztschr. phys. Chem.*, 1, 481 (1887).

We carry out an isothermal reversible cycle with the usual arrangement of a cylinder with frictionless piston, one end of the cylinder being closed by a diaphragm permeable to the solvent but not to the solute. Inside the cylinder is the large quantity of solution, outside the cylinder is the pure solvent. Temperature is equal to $T$. We press down on the piston. Thereby the solution is compressed until the pressure on it reaches the osmotic pressure $\pi$. Let $\beta$, be the coefficient of compression of the solution defined by

$$\beta = \frac{dv}{dp} \cdot \frac{1}{v}.$$

The work of this compression is

$$+\int_{p_2}^{\pi} V\beta_1 d\pi,$$

where $V$ is the initial volume of the solution and $p_2$ is the vapor-pressure of the solvent over the solution.

We continue pressing, and the pure solvent now passes out. The work is kept up until so much of the solvent has passed out as contained one gram-molecule of solute; that is, $N/n$ gram-molecules of solvent are pressed out. The work of this operation is

$$+\,\pi\varphi$$

where $\varphi$ is the volume of the $N/n$ gram-molecules of solvent.

After the solvent has passed through the diaphragm, it is released from the osmotic pressure and consequently expands, returning the work

$$-\int_{p_1}^{\pi} \varphi\beta_2 d\pi, \tag{5}$$

where $\beta_2$ is the coefficient of compression of the pure solvent, and $p_1$ is the vapor-pressure over the pure solvent. It seems to me from what I have previously said[1] that we should in each case consider the coefficient of compression of the pure solvent only as entering into the operations, and not that of the solution at all. However, even if we do make a distinction in the two coefficients, the difference thereby introduced is vanishingly small, and we need not discuss this matter in any detail.

[1] This Journal. 22, 579 (1898).

Heat energy, aside from the heat equivalent of the osmotic work, may be involved when the solution and solvent are separated, as already pointed out. Let $Q$ be the heat involved when one gram-molecule of solvent is added to the solution under consideration. Then the heat involved in separating solution and solvent in the above operation is

$$\pm \frac{N}{n} Q.$$

The $N/n$ gram-molecules of solvent are now vaporized isothermally at $T$. The work of this is

$$- p_1 v_1,$$

where $v_1$ is the volume of the vapor under $p_1$ pressure.

The vapor is now expanded isothermally to the volume $v_2$ corresponding to $p_2$ pressure. The work of this is

$$- \frac{N}{n} R Tl \frac{p_1}{p_2}$$

where $R$ is of course the gas constant.

The vapor is now brought into contact with the solution. But before this can be done, the pressure previously on the solution must be removed. In so doing the system returns nearly all the compression work. the slight deficiency in the return being due to the loss of the $N/n$ gram-molecules of solvent, a deficiency which is very small even when at its maximum value but which in the present case is still smaller since a large part of the compression work belonging to the removed solvent has already been returned by the system, (5). The compression work now returned by the system is

$$-\int_{p_2}^{\pi} ( V - \varphi ) \beta_1 d\pi.$$

The solution is now ready to receive the vapor. The work of driving it in is

$$+ p_2 v_2.$$

Now if heat is involved in separating solvent and solute osmotically in the first operation, then the same quantity of heat

but with opposite sign must be involved when the vapor is driven into the solution.   So we have

$$\mp \frac{N}{n} Q.$$

Of course, this heat has nothing to do with the heat of condensation.

The isothermal reversible cycle is now complete and so,

$$+\int_{p_2}^{\pi} V\beta_1 d\pi + \pi\varphi - \int_{p_1}^{\pi} \varphi\beta_2 d\pi \pm \frac{N}{n} Q - p_1 v_1 - \frac{N}{n} RTl \frac{p_1}{p_2}$$

$$- \int_{p_2}^{\pi} (V - \varphi)\beta_1 d\pi + p_2 v_2 \mp \frac{N}{n} Q = 0,$$

and since for our purpose,

$$\int_{p_2}^{\pi} V\beta_1 d\pi = \int_{p_1}^{\pi} \varphi\beta_2 d\pi + \int_{p_2}^{\pi} (V - \varphi)\beta_1 d\pi,$$

we have

$$\pi\varphi = \frac{N}{n} RTl \frac{p_1}{p_2}$$

or

$$\frac{n}{N} = l\frac{p_1}{p_2}$$

as before.

It would appear then that the compressibility of the solution need not be considered, neither need the heat of solution be considered so far as this is independent of the osmotic work, a conclusion which is not in accord with that of others.   Yet I cannot see what is wrong in my deduction, and I reach the same result when I follow Gouy and Chaperon,[1] for I cannot see how the vapor can be returned to the solution without releasing the pressure on it, nor how the solvent can be vaporized without releasing the pressure on it.   Likewise the heat of separation seems to cancel with heat of mixing when the vapor is driven into the solution in the last operation.

In Arrhenius' method[2] of getting the osmotic pressure, the com-

1 As given in Winkelmann's "Handb. d. Physik," 1, 633.
2 Ztschr. phys. Chem., 3. 115 (1889).

pressibility of the solution likewise seems to disappear. The column of solution rises to a certain height $h$. The osmotic pressure is

$$\pi = h s_0$$

where $s_0$ is the density of the solvent.[1] When the column is so high that the hydrostatic pressure is considerable, the lower layers of liquid become more dense and hence a greater mass of liquid in the vertical column and apparently a greater osmotic pressure. But the pure solvent as it passes through the diaphragm is compressed itself and so its concentration is increased which balances the increased concentration of the solvent in the solution, using the word concentration in the sense of mass in unit volume. Similarly the concentration of the solvent in any particular layer of the solution is greater than the concentration of the solvent in any layer above that particular layer, and therefore will exert a pressure from the lower layer upwards, which upward pressure is proportional to the difference in concentration of the two layers and therefore to the density. The solute itself is of course equally distributed throughout the column of liquid. So it would seem to me that, although the mass in the column of solution is increased by the compression, yet the solvent as it enters becomes compressed, its concentration is increased, and therefore its osmotic activity is likewise increased, and we have as the measure of osmotic activity, only the concentration of the solute whatever the compression may be.

I do not see therefore where we can find any substantial correction for equation (2) so as to bring it into accord with observation. A correction may be brought in by considering that $N$ refers to the molecular weight of solvent in the vapor state. In that state, the molecular weight is frequently somewhat greater than the simple chemical formula would give. Referring to formula (4) as applied to acetic acid as solute in benzene as solvent we see that an increase in $M$ only makes matters worse, but that as applied to benzene as solute in acetic acid as solvent an increase in $M$ would improve matters for solutions dilute in respect to benzene. Another correction may be brought in by considering that $RTl\dfrac{p}{p'}$ is only a true expression of work when

1 This Journal, 22, 579 (1898).

the gases are true gases, and the vapors we are considering are by no means true gases. However, for all vapors which I could follow in tables, the corrections coming from this source were trifling.

I do not mean of course that equation (2) is wrong; I only mean that it does not give results in harmony with our ideas concerning the molecular weights of liquids in concentrated solutions, while equation (1) does give excellent results, and I cannot find sufficient reason why (2) should fail unless we look upon the osmotic laws as ideal laws to be kept out of actual experimental work.

We cannot at present therefore base equation (1) on equation (2), but must seek some other way of justifying it, a conclusion not reached in a previous paper.[1]

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# HYDRASTINE HEXAIODIDE, AND THE ASSAY OF HYDRASTIS CANADENSIS BY MEANS OF STANDARD IODINE FOR HYDRASTINE AND OF STANDARD POTASSIUM IODIDE FOR BERBERINE.

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WHEN a solution of iodine in potassium iodide is added to a solution of a salt of hydrastine a dense precipitate falls out, of a color varying from light brown to a very dark brown. In this order of mixing the alkaloidal solution with the iodine solution, different periodides seem to be formed in mixture, no matter whether the addition of iodine is stopped while the alkaloid is yet in excess or carried till the iodine is in excess. Even in the first case, that is, when the addition of iodine is stopped long before all the alkaloid is precipitated, the body formed only approaches a triiodide in composition, but does not correspond to a triiodide exactly. As will be seen from the accompanying analysis the total iodine of the periodide formed under these circumstances agrees quite well with the theoretical amount required by hydrastine triiodide, but the additive iodine is considerably below the amount required by that body. It