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ON THE APPLICABILITY OF RAOULT'S LAWS TO MOLECULAR WEIGHT DETERMINATIONS IN MIXED SOLVENTS AND IN SIMPLE SOLVENTS WHOSE VAPOR DISSOCIATES.

BY GILBERT NEWTON LEWIS.
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BECKMANN[1] has recently determined the molecular weights of several substances in concentrated sulphuric acid by the boiling-point method. Now the researches of Deville and Troost have shown that the vapor of sulphuric acid is completely dissociated into water and sulphur trioxide, and the question arises as to whether it is justifiable to apply to a case of this kind the simple laws of Raoult for the lowering of the vapor-pressure and the raising of the boiling-point.

The solvent used by Beckmann is described as follows: "Zu allen Versuchen wurde die verwendete reine Schwefelsäure aus einer Glasretorte fraktioniert destilliert. Nur der konstant bei 331.7° (unkorrigiert) übergehende mittlere Teil fand Verwendung." This sulphuric acid of constant boiling-point contains about 1.5 per cent. of water and must therefore be regarded, not as a simple liquid, but as a binary mixture. If instead of regarding it as a mixture of sulphuric acid and water we regard it as a mixture of sulphur trioxide and water, it is obvious that it does not differ essentially from any other binary mixture (such as a 20 per cent. hydrochloric acid solution for example) which has a constant boiling-point.

The following thermodynamic considerations lead to the interesting conclusion that, while pure sulphuric acid cannot be used for molecular weight determinations, the use of the constant boiling acid employed by Beckmann is entirely justifiable. In-

[1] Z. physik. Chem. 53, 129 (1905).

deed we shall find that the familiar equation for the molecular elevation of the boiling-point of a simple liquid may be applied equally well to any constant boiling mixture, composed of any number of constituents.

The equations of Raoult for the lowering of the vapor pressure and the raising of the boiling-point of a simple liquid may be written as follows:

$$N\frac{dp}{p} = -dn \qquad (1)$$

$$dT = \frac{RT^2}{Q}dn \qquad (2)$$

In (1) dp is the change in vapor-pressure when dn gram-molecules of solute are added to N gram-molecules of solvent. In (2) Q is the heat of vaporization of that quantity of the solvent in which dn gram-molecules of the solute are dissolved, dT is the change in boiling-point.

Corresponding to equation (1) Nernst[1] has obtained for a binary solvent the equation,

$$N_1\frac{dp_1}{p_1} + N_2\frac{dp_2}{p_2} = -dn, \qquad (3)$$

where p_1 and p_2 are the two partial vapor-pressures from a mixture containing N_1 gram-molecules of the first substance and N_2 of the second, and dp_1 and dp_2 are the changes in these partial pressures caused by dissolving in the mixture dn gram-molecules of a third substance.

In general, it is impossible to predict from this equation the change in the total vapor-pressure of the solvent when a given quantity of solute is added, but in the special case of a constant boiling solvent the equation may be simplified. It is a well-recognized fact that a constant boiling mixture must always have the same composition as the vapor phase with which it is in equilibrium. In such a case therefore

$$\frac{p_1}{p_2} = \frac{N_1}{N_2}$$

or by the principles of proportion,

$$\frac{N_1}{p_1} = \frac{N_2}{p_2} = \frac{N_1+N_2}{p_1+p_2}. \qquad (4)$$

Combining this equation with equation (3) gives

[1] Z. physik. Chem. **11**, 1 (1893).

$$\frac{N_1 + N_2}{p_1 + p_2}(dp_1 + dp_2) = -dn.$$

Now the total vapor-pressure, P, of the liquid is equal to $p_1 + p_2$, hence the last equation may be written,

$$(N_1 + N_2)\frac{dp}{p} = -dn, \tag{5}$$

which is the same as equation (1).

Similarly, it may be shown that the first law of Raoult is applicable to a constant boiling mixture of any number of constituents.[1]

If in place of the sulphuric acid of constant boiling-point we consider pure sulphuric acid, that is, a mixture of water and sulphur trioxide such that $N_1 = N_2$, then obviously equation (3) may be somewhat simplified but does not yield equation (1) and therefore to such a solvent Raoult's law cannot be applied.

Turning now from the lowering of the vapor-pressure to the raising of the boiling-point, we have a more complex problem.[2] Let us obtain first a general equation for the elevation of the boiling-point of any binary solvent.

Starting with a mixture containing N_1 gram-molecules of the first substance and N_2 of the second, in equilibrium with an infinitesimal quantity of the vapor-phase, at the boiling-point, let us add dn gram-molecules of a third substance and allow the temperature to rise to the new boiling-point, that is, until the total vapor-pressure is again equal to the original external pressure. If p_1 and p_2 represent the original vapor-pressures, and dp_1 and dp_2 their changes, then, since the total vapor-pressure is the same after the change as before,

$$dp_1 + dp_2 = 0. \tag{6}$$

The changes in p_1 and p_2 are caused in part by the addition of the solute and in part by the change in temperature. We may consider these effects separately and write,

$$dp_1 = d_1p_1 + d_2p_1, \; dp_2 = d_1p_2 + d_2p_2 \tag{7}$$

[1] This conclusion is of course valid only when the vapor of each constituent is normal and when the molecular weights in the vapor state are used in calculating the number of gram-molecules of the solvent.

[2] This problem has been discussed by Nernst (loc. cit.) with the aid of the provisional assumption that the addition of the solute causes the same percentage lowering of the two partial vapor-pressures of the binary solvent, but the experimental work of Nernst and Roloff (Z. physik. Chem. **11**, 7 (1893)) showed the incorrectness of this assumption.

where d_1p_1 and d_1p_2 are the changes produced merely by the addition of the solute; d_2p_1 and d_2p_2, by the change in temperature. For these changes we have the following equations:

$$N_1 \frac{d_1p_1}{p_1} + N_2 \frac{d_1p_2}{p_2} = -dn. \tag{8}$$

$$N_1 \frac{d_2p_1}{p_1} + N_2 \frac{d_2p_2}{p_2} = \frac{Q}{RT^2} dT. \tag{9}$$

The first of these equations is that of Nernst which we have used above. The second[1] shows the influence of temperature on the vapor-pressures of a binary mixture, when dT is the change in temperature and Q the total heat of vaporization of the mixture containing N_1 gram-molecules of the first substance and N_2 of the second.

Adding these two equations we have,

$$N_1 \frac{d_1p_1 + d_2p_1}{p_1} + N_2 \frac{d_1p_2 + d_2p_2}{p_2} = \frac{Q}{RT^2} dT - dn,$$

or by equation (7),

$$N_1 \frac{dp_1}{p_1} + N_2 \frac{dp_2}{p_2} = \frac{Q}{RT^2} dT - dn.$$

Hence by equation (6),

$$\left(\frac{N_1}{p_1} - \frac{N_2}{p_2} \right) dp_1 = \frac{Q}{RT^2} dT - dn. \tag{10}$$

This equation cannot be further simplified except with the aid of special assumptions. Evidently, therefore, the change in boiling-point does not depend solely upon the number of gram-molecules of solute. It can be predicted only when the effect of the solute upon the partial vapor-pressure of one of the constituents of the mixture is also known. In general therefore, we cannot speak of the molecular lowering of the boiling-point in the case of a binary solvent, since equivalent quantities of two different solutes may have very different effects on the boiling-point. In fact one solute may raise the boiling-point and another lower it.

When, however, we consider the special case of a constant boiling mixture a great simplification of equation (10) is possible, for then, as we have seen in equation (4), $\frac{N_1}{p_1} = \frac{N_2}{p_2}$, the first

[1] The equation in this form is, I believe, new. It is a simpler form of an equation obtained by Nernst ("Theor. Chem." (4th Edition), p. 117). The proof of it will be given in another place.

member of equation (10) becomes zero, and we have

$$dT = \frac{RT^2}{Q}\, dn,\qquad (11)$$

which is equation (2).

In the same way it may be proved that Raoult's law for the raising of the boiling-point applies to any constant boiling mixture, of any number of constituents.

In deriving equation (11) we have implicitly made use of two assumptions. The first is contained in equation (8) and is merely the assumption that the solute dissolves to form an ideal solution. The second is contained in equations (8) and (9). It is the assumption that the vapor obeys the gas laws. Now while the first assumption is fundamental and necessary, it is possible by a somewhat more general method than the one here adopted to dispense with the second assumption, and thus to show that equation (11) applies to all solvents, even to those whose vapors behave abnormally.

Our general conclusions are therefore as follows:

(1) The law of Raoult for the lowering of the vapor-pressure is applicable to an ideal dilute solution in any constant boiling mixture whose vapor obeys the gas laws.

(2) The law of Raoult for the raising of the boiling-point is applicable to an ideal dilute solution in any constant boiling mixture whatever.

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

BY GREGORY PAUL BAXTER, MURRAY ARNOLD HINES AND HARRY LOUIS FREVERT.

(SECOND PAPER.)

FROM a recent investigation of the atomic weight of cadmium[1] the value 112.469 (Ag = 107.930) for this constant was obtained, by analysis of cadmium chloride. Since this value is nearly one-tenth of a unit higher than the results of recent prior determinations by other investigators, in order to confirm or disprove the higher value, the analysis of cadmium bromide was undertaken.

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[1] Baxter and Hines: This Journal, 27, 222 (1905).