

## THE VAN'T HOFF-RAOULT FORMULA

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By means of a thermodynamical cycle involving the use of a semipermeable piston, van't Hoff deduced in 1885 an equation<sup>1</sup> which can be written in the form

$$PV = RT \frac{N}{n} \log \frac{p_o}{p_i}.$$

In this equation  $P$  is the osmotic pressure,  $V$  the volume through which the piston moves in squeezing out the amount of solvent in which one molecular weight of the solute is dissolved,  $R$  is the gas constant,  $T$  is the absolute temperature,  $n$  is the grams of solute divided by the molecular weight of the solute in the solution,  $N$  is the grams of solvent per molecular weight of solute divided by the molecular weight of the solvent when in the form of vapor,  $p_o$  is the vapor-pressure of the pure solvent at the temperature  $T$ , while  $p_i$  is the partial pressure of the solvent in the solution at the same temperature.

In deducing this equation the assumptions were made that the vapor of the solvent followed the gas law and that the volume of the liquid could be neglected in comparison with that of the vapor when calculating the work done in an isothermal distillation. No other assumption is involved and the formula must be absolutely accurate except in so far as corrections due to the two explicit assumptions have to be made. The value of these corrections is easily determined in any particular case.

It is to be noticed that the volume  $V$  is not the molecular volume of the solution except for solutions<sup>2</sup> so dilute "that the volume occupied by the molecules of the solute is negligible in comparison with the volume of the solution."

<sup>1</sup> Kongl-Svenska Vetenskaps-Akademiens Handlingar, 21, 3 (1886); Zeit. phys. Chem., 1, 481 (1887).

<sup>2</sup> van't Hoff: Zeit. phys. Chem., 1, 483 (1887).

For two liquids such as carbon tetrachloride and benzene which are miscible in all proportions without contraction or expansion,<sup>1</sup>  $V$  will be the volume of the liquid which passes through the piston. If we mix 78 grams of benzene (about 68.6 cc at 20°) and 154 grams of carbon tetrachloride (about 245 cc at 20°) the volume  $V$  at 20° will be 245 cc in case the piston is permeable to carbon tetrachloride only and 68.6 cc in case it is permeable to benzene only. In neither case will it be 313.6 cc, the molecular volume of the solution. The usual definition of osmotic pressure is that it is the pressure which the solute would exert if it were present as a gas at that temperature, the volume being that of the solution. If we cling to this definition we cannot hold to the van't Hoff-Raoult formula

$$\frac{n}{N} = \log \frac{p_0}{p_1}$$

because the amount of solvent to be squeezed out is no longer  $N/n$ . If we stick to the van't Hoff formula, the osmotic volume becomes a physical fiction in some cases because it is difficult to think of 154 grams of carbon tetrachloride occupying a volume of 68.6 cc when no pressure we can apply would be sufficient to compress carbon tetrachloride into that volume either as liquid or as solid.

In spite of this difficulty the wise thing to do is to take the osmotic volume as defined by van't Hoff. An interesting confirmation of this is found in Cohen's<sup>2</sup> work on the inversion of cane sugar. Satisfactory results were obtained only when the concentration of cane sugar was referred to the volume of the water and not to the volume of the solution. Quite recently Morse and Frazer<sup>3</sup> have shown that their direct measurements of osmotic pressure come out better when the concentrations are referred to a constant volume of solvent. They consider this a discovery of their own, quite overlooking

<sup>1</sup> Brown: Jour. Chem. Soc., 39, 202 (1881).

<sup>2</sup> Zeit. phys. Chem., 23, 442 (1897).

<sup>3</sup> Am. Chem. Jour., 34, 1 (1905).

the fact that they have simply gone back to van't Hoff's original formulation. Having reached their conclusion empirically, Morse and Frazer have also overlooked that their method of expressing concentrations contains the tacit assumption that there is neither expansion nor contraction when the two components are mixed. For the general case we have the relation

$$V = \frac{NM_2}{n} \frac{\partial V}{\partial m_2},$$

where  $M_2$  is the molecular weight of the solvent as vapor and  $\frac{\partial V}{\partial m_2}$  the change in volume when 1 gram of the solvent is added to an infinitely large mass of the solution. In this paper  $V$  will always have this significance.

Returning to the original equation

$$PV = RT \frac{N}{n} \log \frac{p_0}{p_1},$$

we can obtain the van't Hoff-Raoult formula

$$\frac{n}{N} = \log \frac{p_0}{p_1}$$

by postulating the relation  $PV = RT$ . The conditions under which we may do this have been stated clearly and explicitly by van't Hoff. This relation can hold only in case the heat of dilution is negligible.<sup>1</sup> At that time it was important to test the simplest case and for infinitely dilute solutions the heat of dilution is negligible.

In 1894 Ewan<sup>2</sup> took up the problem again and worked out a formula for the relation between osmotic pressure and heat of dilution. This formula was said by the author to apply only to cases in which no dissociation and no chemical combination occur. This decreased the value of the paper very much because there is no way at present by which one can tell to what the heat of dilution is due. In consequence of

<sup>1</sup> Kongl-Svenska Vetenskaps-Akademiens Handlingar, 27, 13 (1886).

<sup>2</sup> Zeit. phys. Chem., 14, 417 (1894); 31, 22 (1899).

this and of a bad agreement between experiment and theory, these investigations of Ewan have fallen into undeserved oblivion. In 1898 Cady<sup>1</sup> found that sodium amalgam concentration cells gave electromotive forces which indicated abnormally low molecular weights. He showed that these peculiar results were due to the heat of dilution. He also showed that his results ran parallel with those of Ramsay<sup>2</sup> on the vapor-pressures of sodium amalgams; but he was not able to treat the simple case of the vapor pressures quantitatively. The general formulation, applicable to all cases, has recently been given by Trevor.<sup>3</sup>

The following derivation, also due to Trevor, seems to me more intelligible. Under all circumstances, for any fixed concentration, we have the relation

$$PV = Q + T \frac{d(PV)}{dT}$$

where  $Q$  is taken as positive if heat is evolved when the solution is diluted. This can be integrated if we know  $Q$  as a function of  $T$ . When  $Q$  is zero, the formula becomes

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \text{const.}$$

Experiment shows that one particular solution is the right one, namely

$$PV = RT.$$

When  $Q$  is independent of the temperature and is equal to a constant,  $A$ , we have

$$\frac{P_1 V_1 - A}{T_1} = \frac{P_2 V_2 - A}{T_2} = \text{const.}$$

In view of our experience with the previous case we adopt the particular solution

$$PV = RT + A.$$

If we assume that  $Q = A - BT$  and adopt the same solution we have

$$PV = RT + A + BT \log T.$$

<sup>1</sup> Jour. Phys. Chem., 2, 551 (1898).

<sup>2</sup> Jour. Chem. Soc., 55, 521 (1889).

<sup>3</sup> Jour. Phys. Chem., 9, 90 (1905).

We could go on indefinitely, assuming that  $Q$  was different functions of  $T$ ; but these three cases are enough to show the method.

Having established a relation between the osmotic pressure and the heat of dilution, it is now necessary to inquire what heat of dilution comes into the formula. From the van't Hoff deduction we see that the heat effect is that caused by the addition of  $N/n$  molecular weights of the solvent to an infinitely large mass of solution. This cannot be measured directly; but it is possible to get round the difficulty. If the heat of dilution be expressed, as is usually done, with reference to the molecular concentration,  $N/n$ , the heat required in the van't Hoff formula is given by the relation<sup>1</sup>

$$Q_H = \frac{\partial Q}{\partial \left(\frac{N}{n}\right)} \frac{N}{n}$$

$$Q_H = \frac{\partial Q}{\partial C} C$$

where  $C$  denotes the number of molecular weights of solvent per molecular weight of solute.

In this discussion  $Q_H$  has been taken as positive when there is an evolution of heat on diluting the solution. In any case where we have a marked evolution of heat on dilution we shall expect to find an abnormally high osmotic pressure and to calculate an abnormally low molecular weight. The first instance of this is sodium in mercury. Ramsay<sup>2</sup> found apparent molecular weights for sodium in mercury varying from 21.6 in dilute solutions down to 15.1 in the most concentrated. Cady<sup>3</sup> has measured the heat of dilution when a solution containing 20.2 molecular weights of mercury per molecular weight of sodium is changed to one containing 86.7 molecular weights of mercury per molecular weight of

<sup>1</sup> I propose the symbol  $Q_H$  to denote the van't Hoff or osmotic heat of dilution.

<sup>2</sup> Jour. Chem. Soc., 55, 533 (1889).

<sup>3</sup> Jour. Phys. Chem., 2, 562 (1898).

sodium. While this is altogether too wide a range over which to draw a tangent, we shall probably not be much in error if we assume that the mean value of  $\Delta Q/\Delta C$  or 13.2 gram-calories is not far from the value of  $\partial Q/\partial C$  for the concentration measured by Ramsay of 35.8 molecular weights of mercury per molecular weight of sodium. Assuming this and assuming that the heat of dilution is independent of the temperature, as shown by Cady for a short range, we get the following interesting result:

TABLE I

Apparent molecular weight of sodium.....	16.5
Correction for heat of dilution.....	6.2
Corrected molecular weight of sodium.....	22.7

Solutions of sulphuric acid in water show very large heats of dilution and correspondingly low apparent molecular weights. In Table II the first column gives the concentrations in molecular weights of water per molecular weight of sulphuric acid. In the second column are Dieterici's vapor pressure measurements at 0°. In the third column are the osmotic heats of dilution. Those in the upper part of the table are based on Ewan's interpolations from Pfaundler's measurements<sup>1</sup> while those in the lower part are based on Nernst's interpolations from Thomsen's results.<sup>2</sup> Nernst<sup>3</sup> believes that these heats of dilution may be considered as practically independent of the temperature. In the fourth column we have the apparent molecular weights calculated in the ordinary way. In the fifth column are the values obtained on the assumption that  $Q_H$  is independent of the temperature.

<sup>1</sup> Zeit. phys. Chem., 14, 417 (1894).

<sup>2</sup> Theor. Chem. 3rd Ed., 164.

<sup>3</sup> Ibid.

TABLE II  
Dieterici, Pfaundler, Ewan

N/n	mm Hg.	$Q_H$	App. M. W.	Corr. M. W.
91.6	4.535	299	57.7	89.5
53.5	4.452	520	49.2	96.4
29.2	4.284	877	44.5	116.3
20.8	4.065	1183	36.9	117.4
14.7	3.664	1581	28.9	113.0
11.3	3.238	1928	24.4	111.3
9.9	2.952	2128	22.0	108.5
Dieterici, Thomsen, Nernst				
91.6	4.535	363	57.7	96.1
29.2	4.284	978	44.5	124.3
14.7	3.664	1739	28.9	121.0
9.9	2.952	2322	22.0	116.6
5.9	1.679	3215	16.4	113.1
4.8	1.206	3551	15.3	115.2
2.5	0.164	5073	11.7	104.8

With increasing concentration of sulphuric acid, the apparent molecular weight drops rapidly from 57.7 in a 5.6 percent solution to 11.7 in a 68.5 percent solution. If we introduce the correction due to the heat of dilution, this absurdity disappears and we get molecular weights increasing at first with increasing concentration and then remaining approximately constant. Owing to the inaccuracy of the thermal data and to the possibility that they may vary somewhat with the temperature, no importance can be attached at present to the fluctuations of the corrected molecular weight between 124 and 105. On the other hand, it is very gratifying to get so good a result over so wide a range of concentrations.

Beckmann's measurements<sup>1</sup> on resorcinol in alcohol show a molecular weight decreasing with increasing concentration. For concentrations of 0.1972, 0.5119 and 1.0375 grams resorcinol per 9.19 grams alcohol, the apparent molecular weights were 108, 105 and 100 respectively, the formula

<sup>1</sup> Zeit. phys. Chem., 8, 227 (1891).

weight being 110. Speyers<sup>1</sup> worked with the air-bubbling method and obtained an apparent molecular weight of 58.7 at 30° for a solution containing 20.3 grams resorcinol and 20.4 grams alcohol. Speyers<sup>2</sup> also showed that alcohol solutions of resorcinol evolve large amounts of heat when diluted.

The molecular lowering of the freezing-point of solutions of cupric chloride in water increases with increasing concentration.<sup>3</sup>

As a type of the reverse case in which there is a marked absorption of heat on dilution and a correspondingly high apparent molecular weight we may take solutions of ethyl alcohol in benzene. Beckmann<sup>4</sup> has found that the apparent molecular weight of ethyl alcohol increases from 45.9 to 318 as the concentration increases from 0.164 gram to 32.45 grams alcohol per 100 grams benzene. It has been shown by J. W. Walker<sup>5</sup> that there is a very marked absorption of heat when solutions of alcohol in benzene are diluted. The heat absorption is so great that we come out with impossible results if we assume that it is independent of the temperature. It is to be hoped that Mr. Walker will determine the heat-concentration curve for several temperatures so that we may be able to express the heat of dilution as a temperature function.

So far, we have been considering exceptional cases in which the heat of dilution is very large and the concentration relatively high. It may well be asked what is the value of the correction for dilute solutions and for the solutes most often studied. Calculation shows that at 0° the apparent molecular weight may be in error 10–15 percent if there is a heat effect of 1 gram calorie when 1 liter of pure solvent is added to 1 liter of a  $n/100$  solution. Small as this heat effect is, it is larger than what actually occurs in most solutions. From the tabulated heats of dissociation of electrolytes,<sup>6</sup>

<sup>1</sup> Am. Jour. Sci. (4), 13, 213 (1902).

<sup>2</sup> Jour. Am. Chem. Soc., 18, 146 (1896); Am. Jour. Sci. (4), 10, 449 (1900).

<sup>3</sup> Rüdorff: Pogg. Ann., 116, 70 (1862).

<sup>4</sup> Zeit. phys. Chem., 2, 728 (1888).

<sup>5</sup> Trans. Roy. Soc., Canada, 8, III, 105 (1902).

<sup>6</sup> Landolt-Börnstein: Meyerhoffer Tabellen, 466.



we see however that heat effects of one-tenth to one-twentieth this value are quite common. At  $0^{\circ}$  the apparent molecular weights of potassium chloride, potassium bromide and hydrochloric acid may easily be in error from 0.5 to 1.5 percent in  $n/100$  solutions. Under these circumstances, it is a waste of time to speculate about variations from the dilution law until we have eliminated the known errors in the determinations. It is quite possible that the difference between strong electrolytes and weak organic acids is due chiefly to a difference in the heats of dilution.

Practically all calculations of the electromotive forces of concentration cells are in error to a greater or lesser extent because Nernst's formula is based on the assumption that the heat of dilution is zero. All calculations as to the existence of hydrates in concentrated solutions are also in error because they are based on the apparent molecular weights which are themselves necessarily wrong. This criticism does not affect the existence of hydrates in solution. It merely emphasizes the fact that formulas assigned to account for erroneous molecular weights cease to have any justification as soon as it is recognized that the molecular weights in question are wrong.

In connection with this we must consider the case of sodium chloride and water. While sodium in mercury, sulphuric acid in water, resorcinol in alcohol, and alcohol in benzene behave as they should, sodium chloride in water shows a decreasing apparent molecular weight with increasing concentration<sup>1</sup> in spite of the fact that there is an absorption of heat when the solution is diluted. The correction, which must be applied, will make the molecular weights more unsatisfactory than they now are. The only way out of the difficulty seems to be to assume that, owing to the formation of hydrates in solution, the apparent concentrations are very different from the real ones.

Under certain circumstances we may have an abnormally

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<sup>1</sup> Kahlenberg: Jour. Phys. Chem., 5, 362 (1901).

low molecular weight even though there is an absorption of heat on dilution. If  $Q_H = A - BT$  we have  $PV = RT + A + BT \log T$ . When  $T_1 = A/B$ ,  $Q_H$  is zero and  $PV = RT + A + A \log T$ . In this case we have an abnormally high osmotic pressure even though the heat of dilution is zero for the temperature  $T_1$ . When  $T_1 > A/B$ , the heat of dilution changes sign but the osmotic pressure is higher than the normal and the molecular weight lower than the normal. Sodium chloride and water do not come under this head though there is some reason to suppose that resorcinol and alcohol may at higher temperatures.

We must now face another question. If an apparent molecular weight of 15 or less for sodium in mercury means a real molecular weight of 23, what does an apparent molecular weight of 29.3 mean for sodium chloride in aqueous solution? There is one fundamental difference between the two cases. The apparent molecular weight of sodium in mercury is 23 for infinite dilution so that it then agrees with the formula weight. For infinite dilution the apparent molecular weight of sodium chloride is 29.3 or half the formula weight. At infinite dilution the change of the heat of dilution with the concentration becomes zero and the correcting term becomes zero. The apparent molecular weights at infinite dilution are therefore true molecular weights. Since we must postulate a dissociation for sodium chloride in dilute aqueous solution, there is no point in postulating anything except an electrolytic dissociation. We come back to the conclusion that the electrolytic dissociation theory must hold absolutely for infinite dilution, which is exactly what experiment has shown. On the other hand we see that all determinations in finite solutions have been in error by amounts varying from a fraction of a percent up to several hundred percent. All of our experiments, which involve molecular weights in solution, must be redetermined. While this seems a bit discouraging at first sight, it must be kept in mind that when we have done this we shall probably be able to break loose from the tyranny

of dilute solutions and to develop a quantitative physical chemistry which shall apply to all concentrations.

We can now reconcile Kahlenberg's point of view with that of the orthodox physical chemist. Kahlenberg has worked with finite solutions and has found that one must consider the specific nature of solvent and solute. The majority of physical chemists have worked with very dilute solutions and have obtained results which were independent of the nature of solvent and solute—within certain limits. For finite solutions the heat of dilution is a factor and it varies with the specific nature of solvent and solute, just as Kahlenberg has found. For infinitely dilute solutions, the heat of dilution becomes negligible and the effects due to the specific nature of solvent and solute become unimportant—within certain limits. Kahlenberg has not really been fighting the electrolytic dissociation theory. He has been fighting the false applications of the electrolytic dissociation theory, and there have been many of these.

The general results of this paper are:

1. It has been shown how the osmotic pressure varies with the heat of dilution.
2. The abnormal molecular weights for sodium in mercury, sulphuric acid in water, resorcinol in alcohol, cupric chloride in water, and alcohol in benzene are due wholly or in part to the heats of dilution.
3. The abnormal molecular weights for sodium chloride in water are not due to the heat of dilution.
4. The molecular weights at infinite dilution are correct but all others are in error to a greater or lesser extent.
5. It is probable that a quantitative theory of concentrated solutions can be worked out if we make corrections for the heat of dilution.

*Cornell University,  
December, 1905.*