

THE FORMULA FOR THE DEPRESSION OF THE  
FREEZING TEMPERATURE OF SOLUTIONS.

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THE formula first developed by van't Hoff for the depression of the freezing temperature of a solution below that of the solvent, and commonly used in comparing the results of experiment with the theory, is evidently only an approximate one. In view of the increasing accuracy with which this depression has been measured by Loomis, and the general confirmation of van't Hoff's law which his results furnish, it becomes a matter of interest to inquire whether the departures from the law exhibited by some of his results are due to the insufficiency of the formula or are to be ascribed to other causes. To carry out this inquiry we may use the thermodynamic method introduced by van't Hoff, and proceed to a closer approximation by noticing the circumstances :

1. That the cyclic process employed is not a simple or Carnot's cycle ; 2. That many of the quantities which enter the formulas are variable with the temperature.

The solution employed is made up by dissolving  $n$  gram-molecules of solute in  $N$  gram-molecules of solvent, both  $n$  and  $N$  being very large numbers. This solution is enclosed in a vessel furnished with a semi-permeable membrane and the following cyclic process is executed with it :

1. The solution being at the absolute temperature  $t$ , the freezing temperature of the solvent, a mass of the solvent  $w$  is expressed through the membrane. Work will be done by the pressure  $p$  required to force out the solvent. On the condition that the quantity of the solution is very great, the pressure will remain constant during this operation and the work done by it in reducing the volume of the solution by the volume  $v$  may be represented by  $p v$  to any required degree of approximation. At the same time heat will be

developed in the solution, which must be abstracted from the solution to keep its temperature constant. This may be expressed by  $\mu v$ , if  $\mu$  represents the heat which must be removed in this manner when the volume of the solution diminishes by unity at the temperature  $t$ . We may call  $\mu$  the latent heat of expansion.

2. Heat is then removed from the system at the temperature  $t$ , until the expressed solvent is solidified. If we represent by  $\lambda$  the latent heat of liquefaction of the solvent at the temperature  $t$ , the quantity of heat thus abstracted is  $w\lambda$ .

3. The temperature of the system is then lowered by the further abstraction of heat until its temperature becomes  $t''$ , the freezing temperature of the more concentrated solution. The heat removed may be represented by

$$s''(W - w)(t - t'') + \sigma w(t - t'')$$

if  $s''$  and  $\sigma$  represent the specific heats of the more concentrated solution and of the solid solvent respectively and  $W$  the mass of the original solution.

4. The solid solvent is then immersed in the solution and melted by the introduction of heat. As it melts the solution will become more dilute and the temperature will rise, until when the melting is completed it reaches the temperature  $t'$ , the freezing temperature of the original solution. The quantities of heat actually introduced to effect this change might be represented by symbols, and introduced explicitly in the final equations; but it is more convenient to proceed in another way. It has been assumed that the quantity of solvent employed is very great, so that the change in concentration caused by the melting of the solid solvent in it, and so also the rise of the freezing temperature, will be very small. We may therefore set  $t'' = t'$  and consider the latent heat of liquefaction as constant, to any desired degree of approximation. The heat introduced to melt the solid solvent will then be expressed by  $w\lambda'$ , where  $\lambda'$  is the latent heat of liquefaction at the temperature  $t'$ . The heat introduced to raise the temperature of the solution from  $t''$  to  $t'$  will be balanced in the final equations by that abstracted in lowering the temperature of the solid solvent and of the solution from  $t'$  to  $t''$  in operation 3 to a degree of approximation which may be made

as close as we please by the use of a very great amount of solution.

5. The solution is then raised to its original temperature  $t$  by the introduction of the quantity of heat represented by  $s'W(t - t')$ , if  $s'$  represents the specific heat of the original solution.

The cyclic process is then complete. It is a reversible process and we may accordingly write the equations of energy and entropy for it. Considering  $t'' = t'$ , these become

$$(a) \quad \mu v + w(\lambda - \lambda') + \{s''(W - w) - s'W + \sigma w\}(t - t') = pv.$$

$$(b) \quad \frac{\mu v}{t} + w \left( \frac{\lambda}{t} - \frac{\lambda'}{t'} \right) + \{s''(W - w) - s'W + \sigma w\} \int_{t'}^t \frac{dt}{t} = 0.$$

The integral  $\int_{t'}^t \frac{dt}{t} = \log \frac{t}{t'}$  which occurs in equation  $b$  may be expanded in a series of which it will be sufficient to retain the two terms,  $\frac{t - t'}{t'} - \frac{(t - t')^2}{2t'^2}$ . Dividing equation  $a$  by  $t'$ , combining the two equations and reducing, we obtain

$$(c) \quad (t - t') \left\{ \mu v + w\lambda + [s''(W - w) - s'W + \sigma w] \frac{t - t'}{2} \cdot \frac{t}{t'} \right\} = t'pv.$$

This equation is valid for any solution, whatever the solute may be, and however much dissociation or association there may be in the solution. It involves only the assumption that a definite pressure exists by which the solvent may be forced out of the solution through a semi-permeable membrane. The approximations involved in it, except that in which the third and subsequent terms of the expansion of  $\log \frac{t}{t'}$  are neglected, depend on the amount of the solution employed, and may be pushed to any degree required by the use of a sufficiently large amount of the solution.

The term in the parenthesis which is of the most importance is  $w\lambda$ . Neglecting the other terms in the first approximation we obtain van't Hoff's formula for the depression of the freezing temperature

$$(d) \quad t - t' = \frac{t'pv}{w\lambda}.$$

We may substitute this value of  $t - t'$  in the specific heat term

in the parenthesis, setting  $\frac{t}{t'} = 1$ , and obtain a formula for the depression of the freezing temperature which is correct to a second approximation.

In case the solution is one in which the osmotic pressure is proportional to the absolute temperature I have shown in a previous paper<sup>1</sup> that

$$(e) \quad \mu = p$$

and that

$$(f) \quad s''(W - w) - s'W + sw = 0,$$

where  $s$  represents the specific heat of the solvent.

In that paper it was shown by experiment that the relation embodied in equation  $f$  holds true for many solutions of non-electrolytes in water. For these solutions equation  $e$  will also hold true.

The general formula may therefore be modified for the case of non-electrolytic solutions into the form

$$(g) \quad (t - t') \left\{ w\lambda + pv + [\sigma - s] \frac{tpv}{2\lambda} \right\} = tpv.$$

If we set  $M$  for the mass of the solvent and  $n$  for the number of gram-molecules of solute dissolved in it, and assume that the mass  $w$  is the mass of solvent which is associated with one gram-molecule of solute in the solution, we obtain for the molecular depression in terms of a standard  $M$ ,

$$(h) \quad \frac{t - t'}{n} = \frac{tpv}{M\lambda + npv + (\sigma - s) \frac{ntp v}{2\lambda}}.$$

The volume  $v$  is the volume which contains one gram-molecule of solute in the solution.

This formula holds whether or not the osmotic pressure conforms to Boyle's law but requires a constant ratio between the osmotic pressure and the absolute temperature. If the osmotic pressure conforms to the laws, of gases, we may write  $pv = Rt$ , where  $R$  is the gas-constant, and may calculate the depression and examine the

<sup>1</sup> PHYSICAL REVIEW, Vol. IX., No. 2, August, 1899.

influence of the correction terms of the denominator upon its value. Setting  $R = 84490$ , in which the gram-weight is the unit of force,  $\lambda$  for water  $= 79.3$ <sup>1</sup> and  $M = 1,000$  grams we obtain in the first approximation  $\frac{t - t'}{n} = 1.855$ . Further, setting  $\sigma = 0.5$  calorie and  $n = 1$ , we find that the effect of the two correction terms, which are nearly equal and of opposite sign, is to reduce this value only by 0.001 or to 1.854; an effect far too small to be detected by the present methods of measurement. These terms will be of similar magnitude relative to the principal term of the denominator in any solution that is fairly dilute. It appears, therefore, that the first approximation gives us a formula which is sufficiently exact for our present needs and that the departures exhibited by many solutions from the law of proportionality between the depression of the freezing temperature and the concentration are to be accounted for on other grounds than the insufficiency of the ordinary formula.

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<sup>1</sup>Loomis, PHYSICAL REVIEW, Vol. IX., No. 5, November-December, 1899.