Solutions in Sulphuric Acid. Part XVI. A Reconsideration of the Value of the Cryoscopic Constant.*

By R. J. GILLESPIE.

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It is shown that the cryoscopic constant k_f of sulphuric acid as defined in Part I (*J.*, 1950, 2473) is independent of the nature and concentration of any solute. A revised value of 6·12 is proposed. It is shown that Wyatt's claim (*J.*, 1953, 1175) that the cryoscopic constant varies with the nature and concentration of any solute results from a different, and it is believed less convenient, definition of this quantity.

RECENTLY new data on the heat of fusion of sulphuric acid have been published (Rubin and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 800), and Wyatt (*J.*, 1953, 1175) has criticised the value of the cryoscopic constant used in previous parts of this series (*e.g.*, Part I, *loc. cit.*), suggesting that this constant varies with the composition of the sulphuric acid

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* Part XV, *J.*, 1954, 7.

solvent and with the nature and concentration of any solute. The value and exact significance of this quantity are reconsidered.

If the standard state of the solvent is chosen to be the pure liquid solvent and if a_s is the activity of the solid at temperature T

$$\mathrm{d}\ln a_s/\mathrm{d}T = \Delta H^f/\boldsymbol{R}T^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where ΔH^f is the heat of fusion of the pure solvent at the temperature T (see Lewis and Randall, "Thermodynamics," McGraw-Hill, 1923, p. 282). Now for a *solution* at its freezing point T the activity of the liquid solvent a_1 is equal to the activity of the pure solid solvent a_s and hence

$$\mathrm{d}\ln a_1/\mathrm{d}T = \Delta H^f/\boldsymbol{R}T^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where ΔH^f refers, as before, to the pure solid solvent melting to the pure liquid solvent at the temperature T and is *not* the total heat change accompanying the fusion of the pure solid when it melts into the solution as was assumed by Wyatt (*loc. cit.*). This can be understood because the activity of the solvent in solution is equal to the activity of the pure solid phase with which it is in equilibrium, and the activity of the pure solid is determined only by the properties of the pure substance and not by those of the solution. Allowing for the variation of the heat of fusion with temperature and by integrating equation (2) we obtain

$$\ln a_1 = \frac{-1}{\boldsymbol{R}T_0^{\,2}}\left[\Delta H_0^f\theta + \left(\frac{\Delta H_0^f}{T_0} - \frac{\Delta C_p}{2}\right)\theta^2 + - - -\right] \quad . \; . \; . \; . \quad (3)$$

where ΔH_0^f is the heat of fusion of the pure solid solvent at the freezing point T_0 of the pure solvent, θ is the freezing point depression and ΔC_p is the difference between the heat capacities of the liquid and solid solvent (cf. Lewis and Randall, *op. cit.*). If the solution is ideal $a_1 = N_1$ and also

$$N_1 = [m_1 - s_2m_2]/[m_1 + (\nu_2 - s_2)m_2]$$

where m_1 is the molality of the solvent, m_2 the molality of the solute, s_2 the total number of solvent molecules required to react with the solute and to solvate the ions thus formed, and ν_2 is the number of ions formed. Substitution in equation (3) leads to

$$\frac{\Delta\,\theta}{\Delta m_2} = \nu_2\frac{\boldsymbol{R}T_0^{\,2}}{m_1\Delta H_0^f}\left\{1 - \left(\frac{2}{T_0} - \frac{\Delta C_p}{\Delta H_0^f}\right)\bar{\theta}\right\}\cdot\left\{1 + \frac{(2s_2 - \nu_2)\bar{m}_2}{m_1}\right\} \quad . \; . \quad (4)$$

where $\bar{\theta}$ is the mean freezing point depression and $\bar{m}_2$ the mean molality of the solute (Part I, *loc. cit.*). The factor $\boldsymbol{R}T_0^{\,2}/m_1\Delta H_0^f$ is a constant of the solvent called the cryoscopic constant k_f. Hence

$$\frac{\Delta\theta}{\Delta m_2} = \nu_2k_f\left\{1 - \left(\frac{2}{T_0} - \frac{\Delta C_p}{\Delta H_0^f}\right)\bar{\theta}\right\}\cdot\left\{1 + \frac{(2s_2 - \nu_2)\bar{m}_2}{m_1}\right\} \quad . \; . \; . \quad (5)$$

From this definition, the cryoscopic constant must be constant under all conditions and independent of the nature and concentration of any solutes, provided that the solid phase is the pure solid solvent.

The accurate determination by Rubin and Giauque (*loc. cit.*) of the heat of fusion of sulphuric acid, $\Delta H_0^f = 2560$ cals., enables one to calculate the value of 6·12 for the cryoscopic constant. This value is definitely to be preferred to the value of 5·98 used previously in this series. This was a mean value determined from many cryoscopic measurements, since at that time (cf. Part I, *loc. cit.*), no accurate value for the heat of fusion of sulphuric acid was available.

Our definition and value of the cryoscopic constant are independent of the assumption of ideality made in deducing the above equations. If it is desired to allow for non-ideality of the solution this can be done most simply by introducing g, the rational osmotic coefficient of the solvent at the freezing point *of the solution*, and writing $\ln a_1 = g \ln N_1$ which leads to

$$g \ln N_1 = -\left[\Delta H_0^f\theta + \left(\frac{\Delta H_0^f}{T_0} - \frac{\Delta C_p}{2}\right)\theta^2 + \cdots\right] \bigg/ \boldsymbol{R}T_0^2 \quad . \quad . \quad . \quad (6)$$

and

$$\frac{\Delta\theta}{\Delta m_2} = g\nu_2 k_f \left\{1 - \left(\frac{2}{T_0} - \frac{\Delta C_p}{\Delta H_0^f}\right)\bar{\theta}\right\}\cdot\left\{1 + \frac{(2s_2 - \nu_2)\bar{m}_2}{m_1}\right\} \quad . \quad . \quad . \quad (7)$$

or, if it is wished to make solvation part of the general non-ideality and thus assume for simplicity that $s_2 = 0$, this reduces to

$$\frac{\Delta\theta}{\Delta m_2} = g\nu_2 k_f \left\{1 - \left(\frac{2}{T_0} - \frac{\Delta C_p}{\Delta H_0^f}\right)\bar{\theta}\right\}\cdot\left\{1 - \frac{\nu_2\bar{m}_2}{m_1}\right\} \quad . \quad . \quad . \quad . \quad (8)$$

Wyatt defined the cryoscopic constant as $\boldsymbol{R}T^2/(m_1\,\Delta H'_f)$ where $\Delta H'_f$ is " the heat which is absorbed when 1 mole of the solvent passes from the solid phase into the liquid," which is equal to the sum of the heat of fusion of the pure solid and the partial molar heat of mixing of the pure liquid with the solution. We will denote this cryoscopic constant by k'_f to distinguish it from k_f defined by equations (4) and (5); k'_f will necessarily vary with the composition of the solution because of changes in the partial molar heat of mixing. For an ideal solution the two cryoscopic constants become identical because the heat of mixing is zero. For a non-ideal solution Wyatt's definition of the cryoscopic constant leads to the following equation

$$\frac{\Delta\theta}{\Delta m_2} = g'\nu_2 k'_f \left\{1 - \left(\frac{2}{T_0} - \frac{\Delta C_p}{\Delta H_0}\right)\bar{\theta}\right\}\cdot\left\{1 - \frac{\nu_2\bar{m}_2}{m_1}\right\} \quad . \quad . \quad . \quad . \quad (9)$$

which is similar to equation (8) except that k'_f replaces k_f and g', the osmotic coefficient at the freezing-point *of the pure solvent*, replaces g. This equation has the apparent advantage of giving the osmotic coefficient at a constant temperature, namely the freezing-point of the pure solvent, rather than at the freezing-point of the solution, but it has the serious disadvantage that unless the heat of mixing is known k'_f is unknown and therefore g' cannot be calculated. While it cannot be said that k'_f as defined by Wyatt is incorrect it would seem that k_f as defined by equations (4) and (5) is more useful and therefore to be preferred. Both equations (8) and (9) may be written:

$$\frac{\Delta\theta}{\Delta m_2} = \nu_2 k_{ap} \left\{1 - \left(\frac{2}{T_0} - \frac{\Delta C_p}{\Delta H_0}\right)\bar{\theta}\right\}\left\{1 - \frac{\nu_2\bar{m}_2}{m_1}\right\} \quad . \quad . \quad . \quad . \quad (10)$$

where $k_{ap} = gk_f = g'k_f'$ may be called the " apparent cryoscopic constant." Since k_{ap} can be experimentally determined and since k_f is known, g can always be calculated. On the other hand, since in general neither g' nor k'_f is known neither can be calculated.

It is incorrect to attempt, as Wyatt has done, to interpret any observed variations in the apparent cryoscopic constant k_{ap} entirely in terms of variations in k'_f. This implies that g' is unity which can only be the case if the solution is ideal and k_{ap} is therefore constant.

The variations of the apparent cryoscopic constant observed experimentally by Wyatt may be given simple alternative explanations. In oleum solutions the apparent cryoscopic constant calculated from the freezing-point depression produced by 2 : 4 : 6-trinitrotoluene was found to be less than 6·12 and to decrease with increasing sulphur trioxide concentration in the oleum. 2 : 4 : 6-Trinitrotoluene probably behaves as a weak base (Gillespie, *J.*, 1950, 2542); hence it will partially ionise: $\mathrm{B} + \mathrm{H_3SO_4^+} = \mathrm{BH^+} + \mathrm{H_2SO_4}$. This does not increase the total number of solute particles and therefore 2 : 4 : 6-trinitrotoluene gives a smaller depression than the ideal value in oleum solutions. As the strength of the oleum is increased the apparent cryoscopic constant would be expected to decrease further because of the increased ionisation of 2 : 4 : 6-trinitrotoluene and also the presence in the oleum of an increasing concentration of polysulphuric acids (Gillespie, *J.*, 1950, 2516). In aqueous sulphuric acid the apparent cryoscopic constant was found to be greater then 6·12 and to increase with increasing water concentration. This may reasonably be attributed to the slight basic ionisation of the solutes used (2 : 4 : 6-trinitrotoluene and nitromethane) and to the neglect in the calculations of the effect of the ionisation and the solvation of the water on the mole fraction of the sulphuric acid.

When, as with sulphuric acid, the pure solvent is self-dissociated all the equations derived above and the definition of the cryoscopic constant k_f are still valid, and the osmotic coefficients that one obtains refer, as is usual, to the pure solvent as the standard state. However, where the added solute represses the self-dissociation of the solvent it may sometimes be more convenient to use instead of the pure solvent as the standard state a hypothetical non-dissociated solvent, or a hypothetical solvent that is dissociated to a different extent from the pure solvent. This is effectively what Wyatt has done in writing the heat of fusion term in the cryoscopic constant in the form $\Delta H_*^f + x\Delta H_d$ where ΔH_*^f is the heat of fusion of the hypothetical undissociated solvent, ΔH_d the heat of self-dissociation and x the degree of self-dissociation. This implies that the standard state is a hypothetical solvent in which the extent of self-dissociation is the same as that in the solution under consideration. It is less convenient to use this varying standard state but nevertheless in interpreting osmotic coefficients it may be preferable, particularly in the limiting case when sufficient solute is present to repress almost completely the self-dissociation.

Fortunately it is likely that for sulphuric acid it makes little practical difference which standard state is chosen. Thus Gillespie and Wasif (*J.*, 1953, 964) calculated that the heat of dissociation of sulphuric acid is approximately 2000 cals., and since x is approximately 0·002, $x\Delta H_d$ is approximately 4 cals., which is of the same order of magnitude as the experimental error in the heat of fusion (± 3 cals.), and may therefore be neglected.

In nitric acid however, where the self-dissociation is much more extensive, it is important to select carefully the standard state and this question will be fully discussed in forthcoming papers on cryoscopic measurements in nitric acid.

William Ramsay and Ralph Forster Laboratories,
University College, London.

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