497. *Cryoscopic Measurements in Sulphuric Acid. Part I. Principles and Methods. The Cryoscopic Constant and Some Other Constants of Sulphuric Acid.*

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The experimental methods of cryoscopy in solvent sulphuric acid have been developed to a degree of precision sufficient for the evaluation of electrochemical equilibrium constants. The theoretical principles underlying a thermodynamically correct expression of the results are considered; and, van't Hoff's *i*-factors having led to confusions of concept which it seems impossible now to resolve, ν-factors are introduced, and are defined as a function only of numbers of solute particles, effects of forces being left for description by means of activity coefficients.

The methods and principles having been established, their first application was in a determination of the cryoscopic constant of sulphuric acid. This has not been satisfactorily measured hitherto, partly because the techniques were not accurate, and partly because substances were believed to dissolve without ionisation, which in fact are ionised in solution. We have found only two substances which dissolve freely in sulphuric acid without any apparent reaction, *viz.*, sulphuryl chloride and chlorosulphonic acid. Their use provides the first of three cryoscopic methods by which the required constant has been determined. The second method uses ionised sulphates, and the third employs certain organic oxygen-compounds which behave as infinitely strong bases. For most solvents, such a use of such solutes would be excluded by electrostatic non-ideality; but the dielectric properties of sulphuric acid are so extreme that, in certain concentration ranges, these solutes can be employed.

Revised values are given for the cryoscopic constant, for the heat of fusion, and for the melting point of sulphuric acid.

(1) *Principles and Methods.*

(1.1) *Aim of this Work.*—The experiments to be reported in this series of papers were originally undertaken with the object of elucidating by cryoscopic measurements certain ionogenic reactions in sulphuric acid, which had come to notice during kinetic studies on the mechanism of aromatic nitration. The formation of the nitronium ion from nitric acid in sulphuric acid was first clearly demonstrated by means of measurements of the depression of the freezing point of sulphuric acid by dissolved nitric acid (*Nature*, 1946, **158**, 480). However, the aim of the cryoscopic studies soon expanded beyond its originally contemplated limits: so many problems, in principle soluble by the cryoscopic method, presented themselves—problems concerning the behaviour of strong acids other than nitric acid, of aromatic nitro-compounds, and of other organic oxygen compounds, in solvent sulphuric acid. The original research thus has become greatly extended, although only those results which are most relevant to the nitration problem are now being published.

There has been one general aim in all this work. Hitherto, despite important improvements of method, the cryoscopic study of ionic equilibria in sulphuric acid has never been raised above a semi-quantitative status; it has not previously been possible to calculate reliable equilibrium constants from the cryoscopic results. An attempt has been made to improve this position. In order to do so it has been necessary to go carefully into such questions as the precise value of the cryoscopic constant of sulphuric acid, the degree to which ionic solutions in sulphuric acid attain ideality, the self-ionisation of sulphuric acid, and the value of the equilibrium constant for the fundamental proton-transfer reaction between solvent sulphuric acid and solute water. These subjects occupy much of the first few papers of this series.

(1.2) *Previous Work on Cryoscopy in Sulphuric Acid.*—The earliest systematic measurements of the depression by solutes of the freezing point of sulphuric acid were those of Hantzsch (*Z. physikal. Chem.*, 1907, **61**, 257; 1908, **62**, 626; 1908, **65**, 41; 1909, **68**, 204; *Gazzetta*, 1909, **39**, i, 120; 1909, **39**, ii, 512; 1911, **41**, i, 645; *Ber.*, 1922, **55**, 953; 1930, **63**, 1782, 1789). He showed that the purity of the solvent sulphuric acid could not be adequately controlled by chemical analysis, and that the best criterion of its purity was the freezing point, which he found to have a maximum value of 10·46° (cf., however, Section 4), and to be sensitive to analytically undetectable amounts of water and sulphur trioxide. He discovered a number of substances which, on dissolution in sulphuric acid, had but little effect on its electrical conductivity; and they all gave about the same molal depression of the freezing point. He therefore assumed that they dissolved normally, that is, as simple non-electrolytes; and, from the freezing-point depressions which they gave, he deduced his value for the cryoscopic constant of sulphuric acid. Many solutes were found which considerably increased the electrical conductivity of sulphuric acid; and these gave larger molal depressions of the freezing point. Thus potassium hydrogen sulphate, water, alcohols, ethers, ketones, carboxylic acids, and amines gave about 1·5—2 times the normal depressions. Hantzsch assumed these compounds to dissolve with the formation of two ions, water and the organic oxygen compounds, as well as the amines, acting towards sulphuric acid as simple bases. Barium hydrogen sulphate, urea, and phthalic acid gave 2—2·5 times the normal depressions: and they were assumed to form three ions. Some substances, notably nitric acid and triphenylcarbinol, gave larger freezing-point depressions; and in these cases special explanations were suggested.

Similar measurements were recorded, largely in the same period, by Oddo and his collaborators (Oddo and Scandola, *Z. physikal. Chem.*, 1908, **62**, 243; 1909, **66**, 138; *Gazzetta*, 1908, **38**, i, 603; 1909, **39**, i, 569; 1909, **39**, ii, 1; 1910, **40**, ii, 163; Oddo and Cassalino, *ibid.*, 1917, **47**, ii, 200, 232; Oddo, *ibid.*, 1918, **48**, i, 17). They measured the cryoscopic constant of sulphuric acid in much the same way as Hantzsch had done, obtaining, however, somewhat different values. They also studied a wide range of organic and inorganic solutes and obtained results which, although broadly similar to those of Hantzsch, often differed quantitatively from his, essentially on account of the inaccurate experimental methods which constituted the best technique of that time. Some of Hantzsch's qualitative conclusions had to be altered: thus alcohols, which he had considered to behave as simple bases, were found by Oddo and Scandola to give a nearly three-fold depression of the freezing point, a clear indication that they become esterified with sulphuric acid (cf. Part VI). These authors were the first to recommend using as solvent, not pure sulphuric acid, but sulphuric acid containing a little water. However, they were not able to advance the correct reason for this procedure.

Reference will be made in acccompanying Parts of this series to the work of Poma (*J. Chim. physique*, 1912, **10**, 177) on the freezing points of sulphuric acid solutions of hydrogen sulphates (cf. Part IV), and to that of Robles and Moles (*Anal. Fis. Quim.*, 1934, **32**, 474; 1936, **34**, 331) on the depressions of the freezing point of sulphuric acid produced by nitric acid and perchloric acid (cf. Parts III and VI), and by the solutes water and sulphur trioxide (cf. Part II).

A definite improvement in experimental technique was achieved by Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900) and by Treffers and Hammett (*ibid.*, 1937, **59**, 1788). Their freezing-point cell was of better design than those employed earlier. As solvent they used sulphuric acid containing a small amount of water, explaining that this was necessary in order to repress the self-ionisation of the solvent; and they corrected their freezing points for supercooling. In their calculations they allowed for the non-proportionality of molality and mol.-fraction, and for the temperature-dependence of the latent heat of fusion of the solvent. For the cryoscopic constant they employed a value given by a calorimetric determination by Brönsted of the heat of fusion of sulphuric acid. They applied their methods mainly to the study of weak organic bases, and to the forms of ionisation undergone by carboxylic acids in solvent sulphuric acid.

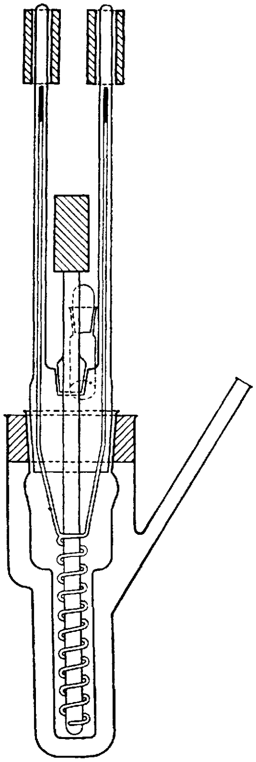
The investigation of carboxylic acids and their esters has been carried further by Newman, Ruivila, and Garrett (*ibid.*, 1945, **67**, 704), Kuhn and Corwin (*ibid.*, 1948, **70**, 3370), and Kuhn (*ibid.*, 1949, **71**, 1575). Three other recent reports on the freezing points of sulphuric acid solutions have appeared, one by ourselves dealing with solutions of nitric acid, dinitrogen pentoxide, dinitrogen tetroxide, and dinitrogen trioxide (*Nature*, 1946, **158**, 480), one by Kuhn concerning the first two of these solutes and also ethyl nitrate (*J. Amer. Chem. Soc.*, 1947, **69**, 1974), and one by Price on the properties of siloxanes as solutes (*ibid.*, 1948, **70**, 871).

(1.3) *Apparatus and Experimental Procedure.*—In principle, the Beckmann method was used in order to measure freezing points, although the usual apparatus was considerably modified in order to prevent error due to the intrusion of water vapour, and, generally, to secure a satisfactory standard of accuracy.*

The freezing-point cell (see Fig. 1), which was similar in type to that used by Treffers and Hammett, was designed to allow the use of a convenient quantity of sulphuric acid, to secure adequate immersion of the thermometer, to permit efficient stirring, and to provide suitable means for the introduction of liquid or solid solutes; and, in all circumstances, to keep out unwanted moisture. The ground-in head of the cell carried all necessary fittings, *viz.*, two standard ground joints, one accommodating the thermometer and the other a stopper, and two sealed-in, vertical, tubes, closed at the top, to act as guides for the electromagnetic stirrer. The stirrer consisted of a glass spiral joined at the top of two vertical glass rods, to the upper end of each of which a closed glass tube containing a soft-iron rod was sealed. The stirrer was actuated by two solenoids, supported one on each of the guide-tubes, and fed by an intermittent direct current, the period of which was controlled by a mercury switch, rocked by a rotating cam, driven by an electric motor. It was found unnecessary to provide cooling jackets for the solenoids, which produced no appreciable thermal disturbance.

FIG. 1.

Freezing-point cell for solutions in sulphuric acid.



In the early stages of this work an ordinary Beckmann mercury thermometer was used. It was fitted to the freezing-point cell by means of rubber tubing impregnated with paraffin wax. This thermometer was later replaced by a platinum-resistance thermometer, with which all the final sets of measurements recorded in these papers were made. Small differences of temperature could be measured (to 0·001°) equally well with either thermometer; but the measurement of temperature in an absolute sense (to 0·01°) was made much easier by the use of the resistance thermometer. Furthermore, this thermometer was designed and built as part of the equipment, so that its dimensions were optimal; and it had, sealed on to its hard-glass sheath, a standard ground joint by which it could be fitted to the cell-head; it was a definite advantage to be able to avoid the use of rubber in the apparatus. Calibrated at the National Physical Laboratory, this thermometer had the resistance 30·0435 ± 0·0005 ohms at 0°, and 41·802 ± 0·001 ohms at 100°. The resistance of the thermometer, which was of the potential-lead type, was measured with the aid of a Smith's difference-bridge.

The opening in the cell-head, which normally accommodated a stopper, provided a way for the introduction of solutes with the aid of suitable delivery apparatus. In order to prevent the incursion of water vapour during measurements, it was found essential to grease all ground-joints; and for this purpose Apiezon M grease was used.

The freezing-point cell was supported in an air-jacket provided with an upward-sloping side-arm; and the air-jacket was surrounded by a water-bath containing a stirrer, a heater, and a cooling unit. The temperature of the bath could be quickly raised by the electric heater, or lowered by pumping cold alcohol through the cooling coils, and thus readily controlled to within 0·1°.

In order to make a series of freezing-point measurements, a weighed amount of sulphuric acid (about 120 g.) was introduced into the cell, and allowed to remain over-night, in order that any moisture present might be absorbed. By adjusting the temperature of the bath, the temperature of the sulphuric acid was then reduced until a supercooling of about 1·5° had been attained. The temperature of the bath was then brought to 1·2° ± 0·2° below the freezing point of the sulphuric acid, and crystallisation was

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* The earlier stages of development of the methods described in this section were carried through by Professor J. Graham and Dr. E. R. A. Peeling, whose basic work is gratefully acknowledged.

started by touching the outside of the cell with a small piece of solid carbon dioxide, inserted by means of a holder down the side-arm of the air-jacket. The temperature just before crystallisation was taken as the supercooling temperature; and the steady maximum of temperature, reached after crystallisation, was accepted as the freezing point. The measurement could be repeated as often as desired. Similar measurements were made after the introduction of successive weighed amounts of the solute. It was found that, provided that any necessary thermometric corrections were applied, and also the correction for supercooling as noted in Section 1.4, the freezing point could be reproduced to within 0·002° even after the solution had been allowed to remain in the cell for several days—a clear proof that the cell was moisture-tight.

Liquid solvents were introduced with the aid of a weight-pipette, one arm of which was long enough to reach down almost to the surface of the sulphuric acid. Some granular solids were added by means of a kind of weight-burette, having a tap with a wide bore, and a long, wide stem, which could be closed with a cap for weighing. Solids which were difficult to handle thus were introduced as concentrated solutions in sulphuric acid by the use of the weight pipette.

In some experiments the solvent was sulphuric acid having the maximal freezing point. In others, indeed in most, it was sulphuric acid to which sufficient water had been added to suppress the self-ionisation of the pure acid.

(1.4) *The Correction for Supercooling.*—To each observed freezing point a correction for the supercooling of the solution has to be added. Let T_0 be the freezing point of the pure sulphuric acid, and T the true freezing point of the solution, so that $\theta = T_0 - T$ is the true depression of the freezing point. Let T_1 be the observed freezing point of the solution, so that $\theta_1 = T_0 - T_1$ is the observed depression. Let T_s be the supercooling temperature, so that $S = T_1 - T_s$ is the amount of supercooling. Then the required correction for the supercooling is $\delta T = T - T_1 = \theta_1 - \theta$, and we shall show that it has the value $\delta T = 0{\cdot}012 S\theta_1$.

For, if the solute was dissolved in W g.-mols. of solvent before the crystallisation, but in only W_1 g.-mols. afterwards, then we have

$$\theta/\theta_1 = W_1/W$$

very approximately. Further, if ΔH^f is the molar heat of fusion of the solvent, and $C_p{}^l$ is its molar heat capacity in the liquid state, then, considering the heat balance, we can write

$$\Delta H^f(W - W_1) = C_p{}^l SW$$

in sufficient approximation. Eliminating W and W_1 between these two equations, we obtain the following formula for the supercooling correction:

$$\delta T = \theta_1 - \theta = (C_p{}^l/\Delta H^f)S\theta_1$$

If we take the value 32·1 cal. g.-mol.$^{-1}$ deg.$^{-1}$, extrapolated from the data of Rubin (cf. Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, New York, 1944, p. 337), as the molar heat capacity of liquid sulphuric acid at its freezing point, and a figure 2605 cal. g.-mol.$^{-1}$, deduced in Section 2.5, for the molar heat of fusion of sulphuric acid, then we obtain for the coefficient $C_p{}^l/\Delta H^f$ the value 0·012 deg.$^{-1}$, which appears in the formula given above.

(1.5) *i-Factors and ν-Factors.*—Results relating to the lowering of the freezing point of a solvent by a solute have often been expressed in terms of what are called van't Hoff's *i*-factors, but confusion has arisen through the use, explicitly or implicitly, of incorrect interpretations of such factors.

The van't Hoff *i*-factor is correctly defined as the ratio of the actual depression caused by a solute in the freezing point of the solvent to the depression which would be found in an equimolal solution of an ideal, non-solvated, non-electrolyte. When van't Hoff introduced his *i*-factors, he intended them to cover all deviations of the behaviour of real solutions from the equations, based on his ideal osmotic-pressure law, which applied to ideal solutions. No question then arose as to the physical origin of the deviations. However, following Arrhenius, it became usual to consider *i* as equal to the number of kinetically separate particles (molecules or ions) which are produced by the addition to the solution of one molecule of the solute. This interpretation remained customary until Lewis and Randall pointed out that it could not be correct ("Thermodynamics," McGraw-Hill, New York, 1923, p. 341), and that, for example, a degree of dissociation thus deduced from an *i*-factor was not the thermodynamic degree of dissociation. We now understand that an *i*-factor, as properly defined, is an over-all result arising from both the numbers of the different kinds of particles, and the forces they exert, or, in other words, from the concentrations of solute particles and the departure of the solution from ideality. In general, the *i*-factor measures an almost inextricable mixture of these two effects, and, as we shall see in more detail presently, even if a solution were strictly ideal, the precise relation between the *i*-factor and the number of solute particles would always have a complicated form, excepting in the special case in which $i = 1$. In spite of all this, van't Hoff's *i*-factors have been used in comparatively recent years in the sense of Arrhenius's partly incorrect interpretation.

In work on solutions in such a solvent as sulphuric acid one's chief interest is usually in the number of the solute particles, rather than in the effects of the forces they exert. For this reason, and in order to avoid confusion, we shall introduce another symbol to represent the average number of kinetically separate, dissolved, particles (molecules or ions) that are produced by the addition to the solution of one molecule of solute, calling this number the ν-factor of the solute.

In discussions concerning freezing-point measurements of low accuracy, the numerical differences between i-factors and ν-factors are of no practical consequence. However, when computing with modern cryoscopic data, it is desirable, for practical reasons, that a clear distinction between the two quantities should be maintained.

Theoretically, the distinction between i-factors and ν-factors is fundamental. On the one hand, the i-factor expresses, in a complicated and inexact way, a thermodynamic property of the solvent in the solution. On the other, the ν-factor expresses simply and exactly, a molecular property of the solute in the solution.

Lewis and Randall knew that the factor i has no simple thermodynamic meaning; but they were obviously trying to find some meaning for it when they wrote : " At best the factor i gives the ratio of the lowering of the activity of the solvent to the lowering which would be produced by a normal undissociated substance." However, even this is not correct; though it would be correct to say that the factor i is *approximately* equal to the ratio of the change in the ***logarithm*** of the activity of the solvent to the change in this quantity which would be observed in an equimolal solution of an ideal non-electrolyte.* From this it will be apparent that the factor i retains no very useful meaning, even in relation to the solvent. It certainly has none in relation to the solute, the properties of which are best defined by means of its ν-factor and the activity coefficients of the dissolved species. This method preserves as clear a distinction as is possible between the effect of the number of the solute particles and the effects due to their forces.

(1.6) *Calculation of* ν-*Factors*.—In order to reduce the following calculation to the simplest possible form, we shall at the outset introduce a conclusion, which actually was reached only after a fairly extensive study of freezing points of solutions in sulphuric acid; and of necessity we shall defer until later the presentation of the supporting evidence. It was pointed out by Hammett and Deyrup (*loc. cit.*) that inter-ionic forces in sulphuric acid solutions must be unusually small. The present conclusion is that they are completely negligible. More specifically, it is concluded that, to the best standards of accuracy that we can attain experimentally, dilute solutions in sulphuric acid, even solutions of ionised solutes, can be considered ideal. This implies that inter-ionic activity effects are so weak as to require that the dielectric constant of sulphuric acid shall be very much greater than that of any solvent whose dielectric constant has yet been measured. Such a " ferroelectric " dielectric constant is not inconceivable, if we may assume co-operative orientation in suitably associated structures (and there is, of course, plenty of evidence of association). A direct test of this deduction is being undertaken by one of us (R. J. G.) in association with Dr. D. J. Millen. In the meantime we shall reduce our cryoscopic results on the basis that the solutions can be treated as ideal, *i.e.*, that the relevant activity coefficients may be set equal to unity. It should perhaps be stated here that the assumption of ideality does not wipe out the numerical differences between ν-factors and i-factors (except for dilute solutions of a non-solvated non-electrolyte, for which $\nu = i = 1$). This will become clearer as we proceed to calculate ν.

Consider the equilibrium between the pure solid solvent and solutions of variable concentration at a constant pressure of one atmosphere. Let us denote activities by a, mol.-fractions by N, and molalities by m, with subscripts 1 and 2 referring to the solvent and solute, respectively. The basic equation for the variation of the activity of the solvent as the freezing point varies is

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

but, in view of our conclusion concerning the ideality of the solutions in which we are interested, we can replace this equation by the following :

$$\mathrm{d}\ln N_1/\mathrm{d}T = \Delta H^f/\boldsymbol{R}T^2$$

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* This follows from a consideration of the equation $\mathrm{d}\ln a_1/\mathrm{d}T = \Delta H^f/\boldsymbol{R}T^2$, where a_1 is the activity, and H^f is the heat of fusion, of the solvent in a solution of freezing-point T. Comparing two such equations, one for a solution of a real solute, and the other for an equimolal solution of an ideal solute, we derive the statement in the text by taking the right-hand sides as equal. A general approximation of this form involves neglecting all terms after the first in the expansion of $\Delta H^f/\boldsymbol{R}T^2$ about its value in the pure solvent, $\Delta H_0{}^f/\boldsymbol{R}T_0{}^2$, in powers of the freezing-point depression $T_0 - T$.

Since we usually express the composition of solutions in terms of the molality of the solute, rather than the mol.-fraction of the solvent, it becomes convenient to transform this equation as follows:

$$\mathrm{d}T/\mathrm{d}m_2 = (\boldsymbol{R}T^2/\Delta H^f)(\mathrm{d}\ln N_1/\mathrm{d}m_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We have now to calculate the two factors on the right, so let us consider the factor $\mathrm{d}\ln N_1/\mathrm{d}m_2$. In many of our experiments the solvent was pre-treated with a small amount of water before addition of the solute in which we were interested; and for this and other reasons it is convenient here to consider the general case in which two solutes A and B are employed. Suppose that one molecule of the solute A interacts with s_2 molecules of sulphuric acid to form a total number ν_2 of dissolved ions and non-ionised molecules, and that one molecule of solute B reacts with s_3 molecules of sulphuric acid to give ν_3 dissolved ions and molecules:

$$\mathrm{A} + s_2\mathrm{H_2SO_4} = p\mathrm{P} + q\mathrm{Q} + r\mathrm{R} + \ldots\ldots$$

$$p + q + r + \ldots = \nu_2$$

$$\mathrm{B} + s_3\mathrm{H_2SO_4} = x\mathrm{X} + y\mathrm{Y} + z\mathrm{Z} + \ldots\ldots$$

$$x + y + z + \ldots = \nu_3$$

Then, if m_2 is the molality of the solute A and m_3 that of B, we may write the following expression for N_1:

$$N_1 = (m_1 - s_2m_2 - s_3m_3)/\{m_1 + (\nu_2 - s_2)m_2 + (\nu_3 - s_3)m_3\}$$

From this, by differentiation, we obtain the result

$$\frac{\mathrm{d}\ln N_1}{\mathrm{d}m_2} = -\frac{\nu_2}{m_1}\left\{1 + \frac{(2s_2 - \nu_2)\nu_2m_2 + (\nu_3s_2 + \nu_2s_3 - \nu_2\nu_3)m_3}{\nu_2m_1}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

provided that we neglect second and higher orders in the small quantities m_2/m_1 and m_3/m_1.

The calculation of the factor $\boldsymbol{R}T^2/\Delta H^f$ involves taking account of the variation of ΔH^f with T. If ΔH_0^f is the molar heat of fusion of pure sulphuric acid, *i.e.*, its latent heat at the temperature T_0, then the latent heat ΔH^f at the temperature T is to be computed by integrating Kirchhoff's equation

$$\delta(\Delta H^f)/\delta T = C_p^l - C_p^s = \Delta C_p$$

where C_p^l and C_p^s are the molar heat capacities of liquid and solid sulphuric acid, respectively, at the freezing point. Disregarding, as we may with sufficient approximation, the temperature dependence of ΔC_p, we find for the integral,

$$\Delta H_0^f - \Delta H^f = \Delta C_p(T_0 - T) = \Delta C_p\theta;$$

and from this, by neglecting second- and higher-order terms in the small quantities $(\Delta H_0^f - \Delta H^f)/\Delta H_0^f$ and θ/T_0, we obtain

$$\frac{\boldsymbol{R}T^2}{\Delta H^f} = \frac{\boldsymbol{R}T_0^2}{\Delta H_0^f}\left\{1 - \frac{2\theta}{T_0} + \frac{\Delta C_p\theta}{\Delta H_0^f}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Substituting from equations (2) and (3) in equation (1) and remembering that $\mathrm{d}T = -\mathrm{d}\theta$, we find

$$\frac{\mathrm{d}\theta}{\mathrm{d}m_2} = \nu_2 \cdot \frac{\boldsymbol{R}T^2}{m_1\Delta H_0^f} \cdot \left\{1 - \left(\frac{2}{T_0} - \frac{\Delta C_p}{\Delta H_0^f}\right)\theta\right\} \cdot \left\{1 + \frac{(2s_2 - \nu_2)\nu_2m_2 + (\nu_3s_2 + \nu_2s_3 - \nu_2\nu_3)m_3}{\nu_2m_1}\right\}$$

The equation for a small but finite change $\Delta\theta$ in the freezing-point depression, caused by a small but finite change Δm_2 in the molality of solute A, is similar, except that, on the left, the ratio $\Delta\theta/\Delta m_2$ will replace the differential coefficient, and, on the right, the mean freezing-point depression $\bar{\theta}$, and the mean molality $\overline{m}_2$ of solute A, over the finite interval, will replace θ and m_2 respectively.

The factor $\boldsymbol{R}T_0^2/m_1\Delta H_0^f$ is a constant of the solvent, *viz.*, the cryoscopic constant k_f. Another constant of the solvent is m_1, which has the value 1000/98·076 = 10·196 g.-mol. kg.$^{-1}$. The factor $(2/T_0) - (\Delta C_p/\Delta H_0^f)$ may be computed to be 0·0035 deg.$^{-1}$ from the following values: $\Delta H_0^f = 2605$ cal. g.-mol.$^{-1}$ (cf. Section 3), $T_0 = 10·36°$ c. = 283·5° K. (cf. Section 4), and $\Delta C_p = 9·2$ cal. g.-mol.$^{-1}$ deg.$^{-1}$ (from Rubin's calorimetric data, cf. Yost and Russell, *op. cit.*). Thus, retaining small quantities in the first order only, we can express the freezing-point equation in the following form:

$$\frac{\Delta\theta}{\Delta m_2} = \nu_2k_f\left[1 - 0{\cdot}0035\bar{\theta} + \left\{\frac{(2s_2 - \nu_2)\nu_2\overline{m}_2 + (\nu_3s_2 + \nu_2s_3 - \nu_2\nu_3)m_3}{\nu_2m_1}\right\}\right] \quad . \quad . \quad (4)$$

In the special case in which the solute B is water in a low concentration, we may assume, with sufficient accuracy for our present purpose, a reaction according to the equation

$$H_2O + 2H_2SO_4 = H_3O^+(H_2SO_4) + HSO_4^-$$

It is shown in Part II that in dilute solution in sulphuric acid water ionises almost completely according to an equation of this general type, one of the formed ions being solvated with approximately one molecule of sulphuric acid. Thus we may substitute $s_3 = 2$ and $\nu_3 = 2$ in equation (4), with the following result :

$$\frac{\Delta\theta}{\Delta m_2} = \nu_2 k_f \left[1 - 0{\cdot}0035\bar{\theta} + \left\{\frac{(2s_2 - \nu_2)\nu_2\bar{m}_2 + 2s_2 m_3}{\nu_2 m_1}\right\}\right] \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This equation gives the change in the freezing-point depression, $\Delta\theta$, caused by a small change Δm_2 in the molality of the experimental solute A, in the presence of a small amount of water of fixed molality m_3. This is the equation which, in this series of papers, has been used for many of the calculations of ν-factors from cryoscopic data, although for some calculations other forms of the general equation (4) have been employed.

Hammett and Deyrup (*loc. cit.*) used equations which, apart from a minor numerical difference, may be regarded as special cases of equation (5). They called the quantity which we term ν_2, the van't Hoff factor i; but it will be evident that, even with the assumption of ideality, the factor ν_2, and the van't Hoff factor i as properly defined, are in general not numerically identical. Two reasons for this appear when we examine equation (5). First, the trinomial [ ] contains ν_2; and for that reason alone the trinomial will not, in general, cancel out when, with the object of computing the true factor i for an electrolytic solute, we calculate the ratio of $\Delta\theta/\Delta m_2$ for the solute ($\nu_2 \neq 1$) to $\Delta\theta/\Delta m_2$ for an ideal, non-solvated, non-electrolyte ($\nu_2 = 1$). Secondly, the expression [ ] also contains s_2; wherefore solvation, even the solvation of a non-electrolyte, will alter i, though it cannot alter ν_2.

(2) *Cryoscopic Constant of Sulphuric Acid.*

(2.1) *Previous Determinations of the Cryoscopic Constant.*—The determination of an accurate value for the cryoscopic constant of sulphuric acid is a matter of some difficulty. There are two ways of obtaining the cryoscopic constant of a solvent : either it can be measured by observation of the depression of freezing point caused by a solute which is believed not to ionise or react in any way with the solvent; or it can be calculated from the calorimetrically determined latent heat of fusion of the solvent. Both methods have been used in the case of sulphuric acid; but it appears that the number of substances which are appreciably soluble in sulphuric acid, but do not react with it, is very small; and, as we shall note later, there seems to be no reliable calorimetric value for the heat of fusion of sulphuric acid.

Previous investigators have employed considerably varying values of the cryoscopic constant of sulphuric acid. Hantzsch used the value 7·00 deg. g.-mol.$^{-1}$ kg., which was an average figure, deduced from freezing-point depressions given by the following solutes : trichloroacetic acid, 2 : 4-dinitromesitylene, 1 : 3 : 5-trinitrobenzene, 2 : 4 : 6-trinitrotoluene, picric acid, phthalic anhydride, oxalic acid, and methyl sulphate. He found that all these substances had little effect on the electrical conductivity of sulphuric acid, and that they all gave about the same molal depression of the freezing point.

Oddo and Scandola adopted the value 6·81 deg. g.-mol.$^{-1}$ kg., which they derived from the freezing-point depressions given by the solutes phosphorus oxychloride and sulphuryl chloride. Later, Oddo changed this figure to 6·9 deg. g.-mol.$^{-1}$ kg. This was an average value, in computing which account was taken of cryoscopic data relating to the solutes trichloroacetic acid, 1 : 3 : 5-trinitrobenzene, and picric acid, solutes which had been used by Hantzsch. Oddo pointed out that the employment of phthalic anhydride, oxalic acid, and methyl sulphate, which had also been used by Hantzsch, led to values of the cryoscopic constant which depended on the concentration of the solute; and that it was therefore to be presumed that these solutes reacted with sulphuric acid.

Hammett and Deyrup derived the mean values 6·00, 6·26, and 6·11 deg. g.-mol.$^{-1}$ kg. from cryoscopic measurements with the solutes trichloroacetic acid, 1 : 3 : 5-trinitrobenzene, and picric acid, respectively. Robles and Moles obtained an average value of 6·55 deg. g.-mol.$^{-1}$ kg. from the freezing-point depressions produced by trichloroacetic acid, picric acid, nitrobenzene, and 2 : 4 : 6-trinitrotoluene. They surveyed the values of the cryoscopic constant given by previous workers—values ranging from 6·0 to 7·0 deg. g.-mol.$^{-1}$ kg.—and concluded in favour of a best value of 6·56 deg. g.-mol.$^{-1}$ kg.

The large divergencies between these figures arise in part from errors of experimental method, such as failure to correct for supercooling, failure to control the suppression of the self-ionisation of the solvent, and failure to prevent intrusions of moisture; but, as will be established in Section 2.2 of this paper, and particularly in Part VII, they are due much more to the circumstance that almost all the solutes employed behave as weak bases, becoming ionised in varying degrees, whilst some also react in other ways with the solvent.

As for the second method of determining the cryoscopic constant, the following values of the molar heat of fusion of sulphuric acid are recorded :

Berthelot (*Compt. rend.*, 1874, **78**, 716)	860	cal. g.-mol.$^{-1}$
Pickering (*J.*, 1890, **57**, 365; *Proc. Roy. Soc.*, 1891, **49**, 11)	2355	,,
Knietsch (cf. Hantzsch, *Z. physikal. Chem.*, 1908, **61**, 262)	2236	,,
,, (recalculated by Brönsted, *q.v.*)	1803	,,
Brönsted (*Z. physikal. Chem.*, 1909, **68**, 693)	2550	,,
Rubin (cf. Yost and Russell, *op. cit.*)	2561	,,

Pickering's figure for the latent heat of fusion leads to a value 6·65 deg. g.-mol.$^{-1}$ kg. for the cryoscopic constant. Brönsted's latent heat value gives 6·15 deg. g.-mol.$^{-1}$ kg. This is the figure which Hammett and Deyrup adopted in their work, considering it to be in satisfactory agreement with, and therefore to be the value indicated by, the various determinations which they had made by direct observation of freezing-point depressions. From Rubin's latent heat value one may calculate the figure 6·12 deg. g.-mol.$^{-1}$ kg. for the cryoscopic constant.

Although Rubin's value of the heat of fusion is undoubtedly the most accurate yet obtained, it cannot be correct; for the freezing point of the acid used was only 10·31°, whereas the freezing point of sulphuric acid has been found in this investigation to be 10·36° (Section 4). Small amounts of impurities may lead to quite large errors in calorimetric measurements of the latent heat of fusion, because they cause pre-melting, for which it is difficult to make an accurate correction. It may well be supposed that Rubin's acid contained a small amount of either sulphur trioxide or water, for, as has been mentioned already, it is impossible accurately to control the composition of sulphuric acid by chemical analysis, or to obtain the pure acid by any method other than the adjustment of its freezing point. We may conclude, therefore, that Rubin's latent heat value, although it is the highest yet recorded, is nevertheless too low, and that the cryoscopic constant to which it leads is correspondingly high.

(2.2) *Cryoscopic Evaluation of the Constant* (*First Method*).—In our search for substances which would dissolve unchanged in sulphuric acid, and thus permit a determination of the cryoscopic constant of that solvent by direct observation of their effect on its freezing point, we examined the following solutes : sulphuryl chloride, chlorosulphonic acid, nitromethane, 2 : 4 : 6-trinitrotoluene, phosphorus oxychloride, and methyl sulphate. With each solute a number of experiments were carried out using sulphuric acid solvents of different composition : we used both sulphuric acid having the maximum freezing point, and sulphuric acid of which the freezing point had been reduced by the addition of different small concentrations of water. The results of the experiments on four of the solutes are recorded in Tables I—IV; the figures for the other two solutes are given in an accompanying paper (Part VII).

A selection of these results is here shown as plots of the freezing-point depression against the molality of the solute. The plot for sulphuryl chloride is seen in Fig. 2 ; independently of the water-content of the solvent, all the points lie on one curve. The data for chlorosulphonic acid are exhibited in Fig. 3 : these points lie on a series of divergent curves, whose positions are dependent on the water-content of the solvent. The analogous plots for the other four solutes are not reproduced ; for each of these solutes, the representative points, for sets of readings with solvents having various fixed concentrations of water, lie either on only slightly separated curves, or to a very close approximation on a single curve.

A complete and accurate graphical comparison of the behaviour of all these substances requires a plot on a larger scale than would be suitable for reproduction; but it is a useful preliminary step to make a comparison in the following approximate manner, namely, by reading off from diagrams, such as are shown in Figs. 2 and 3, the depressions of freezing point given by a 0·1 molal solution of each solute. The result of such a comparison is shown in Table V. The concentration 0·1 molal is taken because, as we shall see presently, effects due to non-ideality are negligible up to concentrations at least as high as that. The depression of freezing point caused by a solute in 0·1 molal concentration is, of course, not exactly equal to one-tenth of the value of the cryoscopic constant, k_f, which would be obtained in an application of equation (4) to the experimental data; but the differences between one depression and another for this fixed molality will reflect fairly closely the differences which would be found in values thus calculated for the cryoscopic constant.

TABLE I.

Freezing points of solutions of sulphuryl chloride in sulphuric acid.

Molality of SO_2Cl_2 (Δm_2).	F. p.† (° c.).	k_f.*	Molality of SO_2Cl_2 (Δm_2).	F. p. (° c.).	k_f.*	Molality of SO_2Cl_2 (Δm_2).	F. p. (° c.).	k_f.*
Expt. No. 57. Molality of H_2O (m_3) = 0·005.			Expt. No. 56. Molality of H_2O (m_3) = 0·015.			Expt. No. 42. Molality of H_2O (m_3) = 0·020.		
—	10·342	—	—	10·291	—	—	10·262	—
0·0350	10·131	6·04	0·0256	10·137	6·02	0·0757	9·814	5·94
0·0645	9·961	5·93	0·0608	9·923	6·06	0·0880	9·740	5·96
0·0923	9·798	5·94	0·0909	9·743	6·00	0·1190	9·554	5·99
0·1363	9·546	5·88	0·1181	9·588	5·98	0·1425	9·429	5·91
0·1693	9·364	5·84	0·1517	9·408	5·86	0·1661	9·297	5·86
						0·1896	9·169	5·82
Expt. No. 43. Molality of H_2O (m_3) = 0·025.						Expt. No. 44. Molality of H_2O (m_3) = 0·032.		
—	10·211	—	0·1822	9·161	5·83	—	10·165	—
0·0491	9·818	5·99	0·1989	9·073	5·79	0·0288	9·993	5·93
0·1020	9·619	5·84	0·2302	8·903	5·77	0·0553	9·834	6·00
0·1335	9·442	5·81				0·0754	9·720	5·93

* k_f (in the units deg. g.-mol.$^{-1}$ kg.) is calculated from equation (5) with the substitutions $s_2 = 0$ and $\nu_2 = 1$.

† Throughout these papers, ° c. means degrees Celsius on the international scale of temperature.

TABLE II.

Freezing points of solutions of chlorosulphonic acid in sulphuric acid.

Molality of $Cl{\cdot}SO_3H$ (Δm_2).	F. p. (° c.).	k_f.*	Molality of $Cl{\cdot}SO_3H$ (Δm_2).	F. p. (° c.).	Molality of $Cl{\cdot}SO_3H$ (Δm_2).	F. p. (° c.).
Expt. No. 47. Molality of H_2O (m_3) = 0·003.			Expt. No. 48. Molality of H_2O (m_3) = 0·034.		Expt. No. 46. Molality of H_2O (m_3) = 0·081.	
—	10·347	—	—	10·131	—	9·631
—	10·135	—	0·0556	9·746	0·0664	9·368
0·0440	9·874	5·97	0·0982	9·608	0·0998	9·242
0·0995	9·544	6·00	0·1312	9·434	0·1501	9·008
0·1438	9·280	6·02	0·1704	9·225	0·1926	8·805
0·1996	8·963	5·98				

* Calculated from equation (5) with the substitutions $s_2 = 0$ and $\nu_2 = 1$ (units as in Table I).

TABLE III.

Freezing points of solutions of phosphorus oxychloride in sulphuric acid.

Expt. No. 51. Freezing point of solvent = 10·354°. Molality H_2O = 0·00.				Expt. No. 49. Freezing point of solvent = 10·150°. Molality H_2O = 0·035.			
Molality $POCl_3$.	F. p. (° c.).	Molality $POCl_3$.	F. p. (° c.).	Molality $POCl_3$.	F. p. (° c.).	Molality $POCl_3$.	F. p. (° c.).
0·0168	10·249	0·0924	9·777	0·0219	10·002	0·0878	9·559
0·0594	9·996	0·1360	9·471	0·0586	9·767	0·1178	9·252

TABLE IV.

Freezing point of solutions of methyl sulphate in sulphuric acid.

Expt. No. 55. Freezing point of solvent = 10·348°. Molality H_2O = 0·00.				Expt. No. 53. Freezing point of solvent = 10·186°. Molality H_2O = 0·031.			
Molality $(CH_3)_2SO_4$.	F. p. (° c.).	Molality $(CH_3)_2SO_4$.	F. p. (° c.).	Molality $(CH_3)_2SO_4$.	F. p. (° c.).	Molality $(CH_3)_2SO_4$.	F. p. (° c.).
0·0161	10·244	0·0735	9·866	0·0333	9·974	0·1399	9·252
0·0466	10·054	0·1017	9·671	0·0724	9·710	0·1645	9·061
				0·1053	9·487		

It will be clear from Table V, and from such graphs as are reproduced here, that the differences between the freezing-point depressions given by the various solutes in identical concentration are much larger than could be attributed to experimental error. The same inference can, indeed, be derived from a comparison of the results obtained by earlier workers : notwithstanding the larger experimental error, it is impossible to avoid the conclusion that the differences of behaviour between the different substances are real. This being so, we cannot be content to take an average from such results when computing the cryoscopic constant, or to adopt any other procedure for obtaining it which leaves the discrepancies unexplained.

FIG. 2.

Depression of the freezing point of sulphuric acid by sulphuryl chloride.

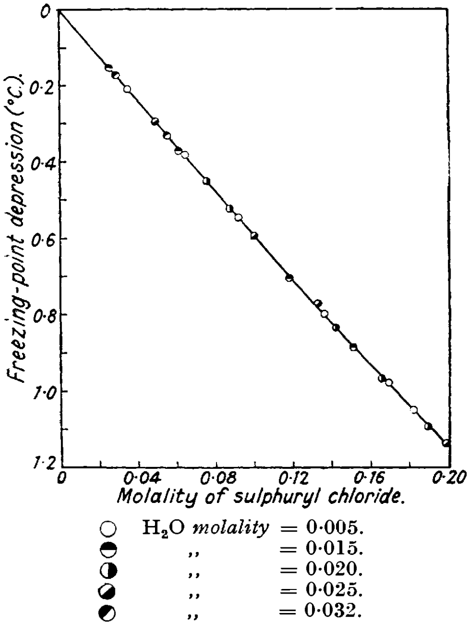


FIG. 3.

Depression of the freezing point of sulphuric acid by chlorosulphonic acid.

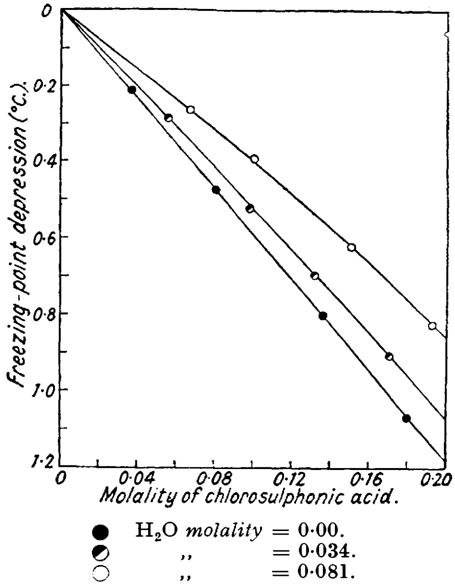


TABLE V.

Depression of the freezing point of sulphuric acid by solutes in 0·1 *molal concentration.*

Solute.	Expt.	Molality H_2O.	Depression (m = 0·1).
Sulphuryl chloride	all	0·00—0·03	0·590°
Chlorosulphonic acid	47	0·00	0·590
Nitromethane	32	0·04	0·625
2 : 4 : 6-Trinitrotoluene	39	0·07	0·655
Methyl sulphate	55, 53	0·00—0·03	0·660
Phosphorus oxychloride	51	0·00	0·675

Two of our solutes, sulphuryl chloride and chlorosulphonic acid, but the latter only in sulphuric acid of maximal freezing point, gave the same freezing-point depression at the concentration 0·1 molal; and it is significant that, of all the substances examined, these two gave the smallest depressions. As none of our solutes is likely to be associated in dilute solution in sulphuric acid, the most obvious conclusion is that sulphuryl chloride and chlorosulphonic acid dissolve unchanged, whereas all the other solutes ionise or react with the solvent in some other way.

From the freezing-point depressions given by sulphuryl chloride in pure and in slightly aqueous sulphuric acid, and by chlorosulphonic acid in pure sulphuric acid, we have calculated the cryoscopic constants of sulphuric acid, using equation (5) with the substitutions $s_2 = 0$ and $\nu_2 = 1$. The results of these calculations are given in the last columns of Tables I and II.

It is necessary to consider the limits of concentration within which the solutions, from whose freezing points we compute the cryoscopic constant, can be considered ideal. The curve

(Fig. 2) for the depression of freezing point given by sulphuryl chloride agrees very closely indeed up to a concentration of 0·12 molal with the almost linear form of curve required by equation (4) for an ideal solute; and, accordingly, we may conclude that over this range of concentration the solutions are accurately ideal. Above this limit the curve swings away slightly from the theoretical form; and this we interpret as an indication of non-ideality in these more concentrated solutions. The direction of the effect is such as might indicate a slight tendency to association of the solute; alternatively, it might point to a slight reduction in the ionising power of the medium as a whole, with consequent diminution in the extent of the ionisation of its constituents, sulphuric acid and water. We need not here discuss the very exact ideality of the dilute solution—*i.e.*, the apparent insignificance in sulphuric acid of the long-range forces between solute particles, which often produce appreciable non-ideality in dilute solution—because we shall presently encounter the same phenomenon in the much more remarkable case of ionic solutes. For chlorosulphonic acid, the range of ideality seems to extend at least to 0·20 molal.

We may then accept for consideration those calculated values of the cryoscopic constant which are based on measurements with solutions of sulphuryl chloride and chlorosulphonic acid having concentrations within the indicated ranges of ideality. These values are assembled in Table VI. They indicate a figure, 5·98 deg. g.-mol.$^{-1}$ kg., for the constant, a value which we shall confirm in other ways.

TABLE VI.

Determination of the cryoscopic constant (k_f) *of sulphuric acid.*

(Method 1.)

Solute (and range of its molality).	Expt. no.	Molality of water.	k_f (deg. g.-mol.$^{-1}$ kg.).	Mean k.
Sulphuryl chloride ($0 < m < 0{\cdot}12$)	57	0·005	5·97	5·98
	56	0·015	6·02	
	42	0·020	5·96	
	43	0·025	5·99	
	44	0·032	5·95	
Chlorosulphonic acid ($0 < m < 0{\cdot}20$)	47	0·003	5·99	5·99
			Mean	5·98

The behaviour of the other investigated solutes requires comment. The nature of the influence of water on the freezing-point depression produced by chlorosulphonic acid has not yet been unequivocally elucidated. There are two conceivable reactions between chlorosulphonic acid and water; and the first of them is almost certainly in operation, whilst the second might be. The first is an acid-to-base proton transfer :

$$\mathrm{Cl{\cdot}SO_3H + H_2O = Cl{\cdot}SO_3^- + H_3O^+}$$

Since water is largely ionised as a binary electrolyte (cf. Part II), this process, if complete, would simply replace one binary electrolyte by another; and hence no change of freezing point would result when chlorosulphonic acid is added, until the amount of it began to exceed that of the originally present water. The second possible reaction with water involves hydrolytic separation of chlorine from the chlorosulphonic acid molecule :

$$\mathrm{Cl{\cdot}SO_3H + H_2O = HCl + H_2SO_4}$$

The cryoscopic behaviour of hydrogen chloride has not yet been determined, but under any hypothesis, the above hydrolysis, if complete, would cause the addition of chlorosulphonic acid to a sulphuric acid solution, already containing water, to produce either no change of freezing point, or a rise of freezing point, until the concentration of the added chlorosulphonic acid begins to exceed that of the water. The fact that, in the presence of water, we observe a depression, though a reduced one, from the commencement of the addition of the chlorosulphonic acid, must be interpreted to mean that the above reactions at best proceed only partly in the forward direction.

As the desirability of adding water to the sulphuric acid solvents employed for cryoscopic measurements is often emphasised, it may be noted here that the need for this precaution does not apply to measurements on non-ionising solutes. If a solute does not ionise, and does not react in any way with either the sulphuric acid or the water, then the presence of water in small amount cannot make any difference to the cryoscopic behaviour of the solute. This is illustrated in the example of sulphuryl chloride. If a solute does not ionise, and does not react in any way with the sulphuric acid, but does react with the water, then we cannot hope to get correct cryoscopic results unless the water is omitted. This is the situation with chlorosulphonic acid, for instance. The object of adding water has significance in the case of basic solutes, and ionising salts, because they generate the hydrogen sulphate ion, which is one of the ions produced by the self-ionisation of sulphuric acid. As the hydrogen sulphate ion, generated by a basic solute or an ionising salt, would repress the self-ionisation of the solvent, thereby disturbing the change of freezing point due to the solute, it is better largely to repress the self-ionisation initially, by the addition of a base, such as water, so that the solute under investigation can itself have little further effect in that direction. This type of case is exemplified by the nitro-compounds mentioned below; and there are some further illustrations in Sections 2.3 and 2.4. Of course, the originally added base need not be water: any strong base, such as benzoic acid or acetophenone, and, still more simply, any ionised sulphate or hydrogen sulphate will do what is necessary.

The choice of an agent for so modifying the solvent that errors caused by changes in its self-ionisation on addition of the experimental solute are avoided is really a more complicated matter than would appear from the explanation given above. It will be shown in Part IV that sulphuric acid suffers two forms of self-dissociation; water has an advantage over other possible agents in that it suppresses both. It will be shown in Part II, however, that water does not behave as an infinitely strong base in sulphuric acid; therefore water suffers from the disadvantage that its own degree of ionisation may be altered by the experimental solute. When this solute produces a liberal supply of one or more of the dissociation products of the solvent, then the self-dissociation of the latter can be suppressed or stabilised by the use of some of the experimental solute for this purpose.

We return to the discussion of the data in the preceding Tables. Of the other substances investigated, all of which gave greater depressions of the freezing point than did sulphuryl chloride or chlorosulphonic acid, two, namely, nitromethane and 2 : 4 : 6-trinitrotoluene, will be considered in detail in Part VII. It will there be shown that these and other nitro-compounds, including those used by all the earlier workers in their attempts to determine the cryoscopic constant, behave as weak bases in sulphuric acid, ionising to varying extents according to the general equation

$$R\cdot NO_2 + H_2SO_4 = R\cdot NO_2H^+ + HSO_4^-$$

Phosphorus oxychloride gave a freezing-point depression, which not only varied quite appreciably with the water content of the solvent, but also increased with the time. The readings of the freezing point which are here recorded as given by phosphorus oxychloride, were actually the steady values attained in each case several hours after the addition of the solute. It is clear from this alone that phosphorus oxychloride undergoes some form of solvolysis; and, of course, it may behave as a weak base, or its solvolysis products may behave as weak bases, in addition.

Oddo and Scandola first suggested (*Gazzetta*, 1910, **40**, ii, 163) that methyl sulphate undergoes reaction with sulphuric acid, and the present results give support to that idea. Here one suspects reversible solvolysis to methyl hydrogen sulphate. Methyl sulphate may act as a weak base in addition (cf. Part VII).

Of the other substances which were used by the earlier workers for the purpose of determining the cryoscopic constant, trichloroacetic acid and phthalic anhydride almost certainly behave as weak bases. They will be discussed in a later Part of this series. Presumably oxalic acid also behaves as a base, as do almost all carboxylic acids; but in any case oxalic acid decomposes in sulphuric acid.

The measurements of electrical conductivity on which Hantzsch relied in deriving his conclusion that the solutes he used were non-electrolytes have little significance. Pure sulphuric acid is considerably self-ionised, and therefore has a substantial electrical conductivity. The addition of a weak base, which, besides providing a limited number of new ions, suppresses the ionisation of the solvent, is not expected to increase the conductivity very greatly. Actually, small increases, such as might be expected, were observed by Hantzsch in several cases.

It would, of course, be desirable to have measurements of the depression of the freezing point of sulphuric acid by other non-reacting, non-ionising substances; but nearly all such substances are insoluble. It appears that liquid sulphuric acid possesses a very considerable amount of structure (as is indicated by its low vapour pressure and high viscosity), the molecules being held together in large groups by strong hydrogen bonds; and that such groups cannot in general be broken into by a molecule unable to exert the strong forces of reaction or ionisation. It seems significant that the only soluble, non-reacting, non-ionising compounds that we have discovered have molecules which are similar in their general framework to the molecule of sulphuric acid, and are capable of participating in hydrogen bonds: such molecules may, perhaps, be pictured as replacing a sulphuric acid molecule in liquid sulphuric acid without producing more than a slight local fault in the structure.

(2.3) *Cryoscopic Evaluation of the Constant* (*Second Method*).—It is not customary to employ salts as solutes for the purpose of evaluating a cryoscopic constant, because ionic interactions extend over considerable distances, and thus tend to produce non-ideality in quite dilute solutions. However, it transpires that in solvent sulphuric acid these electrostatic non-ideality effects are extremely small over ranges of concentration amply sufficient to permit good cryoscopic measurement; this peculiarity of sulphuric acid renders the use of salts entirely feasible.

We have used two salts, *viz.*, potassium sulphate and ammonium sulphate. We assume that, when dissolved in sulphuric acid, they are completely converted into the corresponding hydrogen sulphates. The chemical equation for the conversion being, *e.g.*,

$$K_2SO_4 + H_2SO_4 = 2K^+ + 2HSO_4^-$$

we must expect, if we disregard certain disturbances noted below, to calculate the cryoscopic constant k_f from our results by means of equation (5) with the substitutions $s_2 = 1$ and $\nu_2 = 4$.

Since we are relying in part upon hydrogen sulphate ions to produce the measured depression of the freezing point, it is necessary, as has been mentioned above, to control the self-ionisation of the sulphuric acid. This has been done in two ways. We first give the results of experiments in which added water was employed for the purpose. They are contained in Tables VII and VIII, and are shown graphically in Figs. 4 and 5.

TABLE VII.

Freezing points of solutions of potassium sulphate in aqueous sulphuric acid.

K_2SO_4 (Δm_2).	$\Delta\theta$. (uncorr.).	$\Delta\theta$ (corr.).				k_f (deg. g.-mol.$^{-1}$ kg.).			
		$n = 0$.	$n = 1$.	$n = 2$.	$n = 3$.	$n = 0$.	$n = 1$.	$n = 2$.	$n = 3$.
Expt. 86 (molality H_2O, $m_3 = 0{\cdot}048$. F. p. of treated solvent, 9·990° c.):									
0·0085	0·204°	0·210°	0·208°	0·207°	0·207°	6·14	6·05	6·00	5·95
0·0169	0·405	0·416	0·413	0·411	0·410	6·15	6·04	5·97	5·89
0·0239	0·563	0·577	0·574	0·571	0·569	6·06	5·97	5·88	5·77
0·0444	1·069	1·093	1·088	1·083	1·079	6·18	6·07	5·96	5·81
0·0585	1·408	1·439	1·433	1·426	1·420	6·19	6·09	5·94	5·78
0·0667	1·612	1·647	1·640	1·633	1·626	6·22	6·09	5·95	5·77
0·0844	2·051	2·096	2·087	2·077	2·068	6·27	6·12	5·96	5·75
Expt. 63 (molality H_2O, $m_3 = 0{\cdot}056$. F. p. of treated solvent, 9·901° c.):									
0·0182	0·438	0·450	0·447	0·445	0·443	6·19	6·09	6·01	5·94
0·0286	0·680	0·697	0·694	0·692	0·689	6·11	6·02	5·92	5·83
0·0394	0·948	0·972	0·967	0·962	0·957	6·20	6·08	5·97	5·85
0·0527	1·266	1·296	1·290	1·284	1·277	6·19	6·06	5·93	5·82
Expt. 85 (molality H_2O, $m_3 = 0{\cdot}045$. F. p. of treated solvent, 10·022° c.):									
0·0499	1·198	1·225	1·220	1·214	1·208	6·17	6·06	5·95	5·84
0·0590	1·429	1·461	1·454	1·448	1·441	6·24	6·10	5·98	5·85
0·0700	1·701	1·738	1·730	1·723	1·715	6·26	6·11	5·97	5·85
0·0803	1·960	2·003	1·994	1·985	1·976	6·30	6·14	5·97	5·85

TABLE VIII.

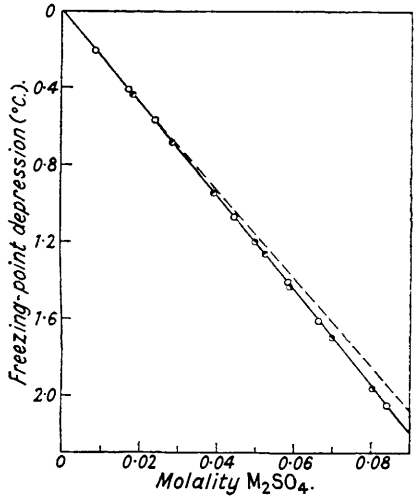
Freezing points of solutions of ammonium sulphate in aqueous sulphuric acid.

Am_2SO_4 (Δm_2).	$\Delta\theta$ (uncorr.).	$\Delta\theta$ (corr.).			k_f (deg. g.-mol.$^{-1}$ kg.).		
		$n = 0$.	$n = 1$.	$n = 2$.	$n = 0$.	$n = 1$.	$n = 2$.
Expt. 123 (molality water, $m_3 = 0{\cdot}058$. F. p. of treated solvent, 9·837° c.):							
0·01413	0·331°	0·342°	0·339°	0·337°	6·06	5·98	5·87
0·02850	0·669	0·688	0·684	0·678	6·05	5·95	5·83
0·04231	1·000	1·027	1·021	1·015	6·10	5·98	5·86
0·07391	1·762	1·808	1·799	1·790	6·18	6·01	5·87
0·08450	2·023	2·075	2·062	2·052	6·21	6·04	5·88
0·1083	2·598	2·665	2·647	2·635	6·24	6·03	5·85

The calculation of accurate ν-factors involves taking account of the already noted fact that water does not behave as an infinitely strong base in sulphuric acid, with the result that the water used to suppress the self-dissociation of the solvent has its own degree of ionisation altered by the added inorganic sulphate. Thus the depression of freezing point which follows the addition of the sulphate is smaller than it would have been if the effect of the pre-treatment water on the freezing point had remained constant. In order to correct for this, it is necessary to know the basicity constant for water $K_b(H_2O) = [H_3O^+][HSO_4^-]/[H_2O]$.

FIG. 4.

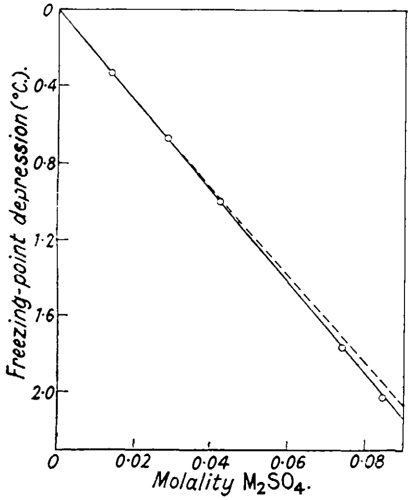
Depression of the freezing point of water-treated sulphuric acid by potassium sulphate.



○ *Expt.* 86. ◐ *Expt.* 63. ◑ *Expt.* 85.
---- *Calc. for* k_f = 5·98 *deg. g.-mol.*$^{-1}$ *kg., neglecting solvation* (n = 0).
——— *Ditto, allowing for solvation* (n = 2).

FIG. 5.

Depression of the freezing point of water-treated sulphuric acid by ammonium sulphate.



○ *Expt.* 123.
---- *Calc. for* k_f = 5·98 *deg. g.-mol.*$^{-1}$ *kg., neglecting solvation* (n = 0).
——— *Ditto, allowing for solvation* (n = 1).

In Part II, the effect of added water on the freezing point of sulphuric acid is studied, and some values of K_b are deduced. They are not very accurate, depending as they do on the manner in which corrections are applied for residual, unrepressed self-dissociation, and for solvation of the ionic dissociation products. But a value deduced by a given procedure will accurately reproduce the experimental results, if it is applied in association with the same procedure. In the case now under discussion, the most convenient way of computing the part played by the water in modifying the freezing-point depression arising from the addition of the ionising sulphates is to use the value $K_b(H_2O) = 0{\cdot}72$ g.-mol. kg.$^{-1}$. This requires that we omit any explicit correction for residual self-dissociation, but allow for solvation of the hydroxonium ion with solvation number unity.

Employing the formula $0{\cdot}72 = \{(\nu - 1)^2 m_2 + (\nu - 1)m'\}/(2 - \nu)$, we first compute a ν-factor for water in molality m_2, in the presence of a molality m' of hydrogen sulphate ions derived from the added potassium or ammonium sulphate. Then, from the ν-factor, we calculate the freezing-point depression due to the water, by means of the appropriate form of equation (4), in applying which water is regarded as the experimental solute A, whilst the potassium or ammonium sulphate is taken as the solute B. We substitute $s_2 = 2$ and $\nu_2 = 2$, for the reason explained in connexion with the derivation of equation (5); and, assuming each formed ion-pair, potassium hydrogen sulphate or ammonium hydrogen sulphate, to be solvated with n molecules of sulphuric acid, according to equations of some such form as

$$K_2SO_4 + (2n + 1)H_2SO_4 = 2K(H_2SO_4)_n^+ + 2HSO_4^-$$

we make the further substitutions $s_3 = 2n + 1$ and $\nu_3 = 4$, thus obtaining the specialised equation

$$\Delta\theta = 5{\cdot}98\nu m_2[1 - 0{\cdot}0035\bar{\theta} + \{2\bar{m}_2 + (2n + 1)m_3/10{\cdot}20\}]$$

Here $\Delta\theta$ is the depression of freezing point due to the water, m_2 is the molality of the water, and m_3 is that of the potassium or ammonium sulphate. Since at this stage a correction term only is being calculated, it is sufficient to insert, as has been done, the provisional value of the cryoscopic constant, 5·98 deg. g.-mol.$^{-1}$ kg., which was derived in Section 2.2. The determination of the solvation number n is discussed below. By employing this equation, first with an experimental value of the sulphate molality m_3, and then with m_3 set equal to zero, one obtains two values of $\Delta\theta$, the difference between which is the correction sought. This has to be added to the observed depression of freezing point due to the sulphate, in order to correct for the changed behaviour of the pre-treatment water. Having thus obtained corrected depressions of freezing point due to the sulphate, one may now compute values of k_f by means of equation (5), in which $\Delta\theta$, $\bar{\theta}$, Δm_2, and $\bar{m}_2$ all now refer to potassium or ammonium sulphate, and m_3 refers to the pre-treatment water. Therefore we have to insert $s_2 = 2n + 1$ and $\nu_2 = 4$, thus obtaining the following specialised form :

$$\Delta\theta/\Delta m_2 = 4k_f[1 - 0{\cdot}0035\bar{\theta} + \{4(2n - 1)\bar{m}_2 + (2n + 1)m_3\}/20{\cdot}40]$$

We may direct attention first to the results of calculations in which solvation of the inorganic sulphate is neglected, so that n is set equal to zero. In Table VII one sees (cf. especially Expt. 86, in which Δm_2 is varied over a 10-fold range) that the calculated values under the heading $k_f(n = 0)$ are fairly steady at the lower values of Δm_2, but rise markedly at the higher values (the same is shown by Expts. 63 and 85, taken together). The direction of this non-ideality in the more concentrated solutions is not that which might indicate an effect of inter-ionic attraction. It is the direction which points to solvation of one or both of the formed ions as the source of the disturbance; and we shall try in this way to account for the effect. In principle this is easily done : we have only to insert the appropriate value of the solvation number n into the equations already given. The best criterion for n is the constancy of k_f over a range of concentrations of the solute. As Table VII shows, the condition of constancy is best satisfied by the value $n = 2$. Hence we conclude that the solvation number for potassium hydrogen sulphate is approximately 2, and that the mean value of k_f, calculated with this solvation number, is the result which we should accept as the value of the cryoscopic constant given by this group of experiments. It appears that the solvation number of ammonium hydrogen sulphate is appreciably less than that of the potassium salt. This is confirmed in the experiments next to be mentioned; and a survey of all our results has led to the conclusion that, for the ammonium salt, the nearest integral value is $n = 1$.

In our second procedure for dealing with sulphates, sulphuric acid of maximal freezing point was taken as solvent, and the first added portions of the experimental solutes were trusted to generate hydrogen sulphate ions in sufficient quantity largely to suppress their production from sulphuric acid. In this case, the residual, unrepressed production of hydrogen sulphate ions from the solvent was computed, and the appropriate allowances were made. It was assumed that dissociation processes which do not involve hydrogen sulphate ions remain unaltered by the added solute. Some results, obtained by this method for the solutes potassium and ammonium sulphate, are recorded in Tables IX and X.

TABLE IX.

Freezing points of solutions of potassium sulphate in anhydrous sulphuric acid.

K_2SO_4 (Δm_2).	F. p. (° c.).	Depressions.		k_f (deg. g.-mol.$^{-1}$ kg.).		
		$\Delta\theta_1$.	$\Delta\theta_2$.	$n = 0$.	$n = 1$.	$n = 2$.
Expt. 122 (F. p. of solvent, 10·357° c.) :						
0·00579	10·278	0·242°	—	—	—	—
0·01205	10·165	0·355	0·287°	5·96	5·95	5·94
0·03653	9·620	0·900	0·872	5·99	5·96	5·93
0·05618	9·154	1·366	1·348	6·04	5·99	5·94
0·07080	8·795	1·725	1·711	6·09	6·02	5·95
0·08243	8·504	2·016	2·004	6·13	6·05	5·97
0·1268	7·374	3·146	3·137	6·24	6·11	5·98
Expt. 121 (F. p. of solvent, 10·352° c.) :						
0·01548	10·091	0·429°	0·372°	6·02	6·00	5·98
0·02509	9·882	0·638	0·600	6·00	5·97	5·94
0·04779	9·354	1·166	1·145	6·03	5·98	5·93
0·06224	9·003	1·517	1·501	6·08	6·01	5·94
0·07967	8·576	1·944	1·932	6·13	6·03	5·93

TABLE X.

Freezing points of solutions of ammonium sulphate in anhydrous sulphuric acid.

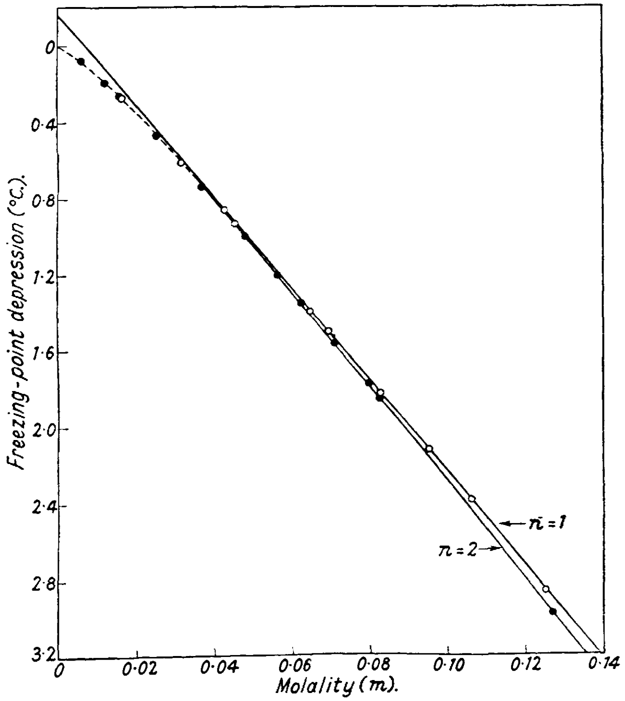
Am_2SO_4 (Δm_2).	F. p. (° c.).	Depressions. $\Delta\theta_1$.	Depressions. $\Delta\theta_2$.	k_f.* $n = 0$.	k_f.* $n = 1$.
Expt. 110 (F. p. of solvent, 10·353° c.) :					
0·04240	9·492	1·028°	1·004°	5·95	5·92
0·06931	8·851	1·669	1·654	6·01	5·95
0·08266	8·530	1·990	1·978	6·04	5·95
0·09490	8·229	2·291	2·281	6·09	5·97
0·1058	7·963	2·557	2·547	6·10	5·97
0·1259	7·489	3·031	3·023	6·14	5·98
Expt. 111 (F. p. of solvent, 10·350° c.) :					
0·01625	10·077	0·436°	0·382°	5·98	5·96
0·03140	9·739	0·776	0·746	6·00	5·97
0·04516	9·420	1·095	1·073	6·00	5·95
0·06465	8·933	1·562	1·547	6·06	5·98

* In deg. g.-mol.$^{-1}$ kg.

In calculating the results of these experiments, one has not to deal with the variable degree of ionisation of water, and this permits some simplification of procedure. After enough salt has been added largely to suppress the production from sulphuric acid of hydrogen sulphate ions, the freezing-point curve runs very nearly linearly over a wide range of solute concentrations. So slight is the curvature that the graph may be produced back, as is shown in Fig. 6, to locate with considerable precision, on the axis of zero solute concentration, a point which represents what the freezing point of sulphuric acid would be in the absence of that form of dissociation which generates hydrogen sulphate ions. The extrapolation can equally be made with the help of theoretical equations for freezing-point depression. The extrapolated freezing point lies at 10·52° c.* The depressions tabulated under the heading $\Delta\theta_1$ are reckoned from this

FIG. 6.

Depression of the freezing point of anhydrous sulphuric acid by potassium sulphate and by ammonium sulphate.



● *Experimental points for potassium sulphate (Expts.* 121, 122).
○ ,, ,, *ammonium* ,, *(Expts.* 110, 111).
——— *Theoretical curves, allowing for solvation of the solutes.*
- - - - *Curve showing the disturbance of solvent ionisation.*

---

* In Parts IV and V the temperature 10·52° c. is obtained again in several different ways : it seems to be closely located. It must not be confused with the temperature 10·62° c. deduced in Part II for the freezing point of sulphuric acid in the absence of *all* forms of dissociation.

temperature. In general, a part of this depression will be caused by the products of that form of solvent dissociation which gives hydrogen sulphate ions, *viz.*, the autoprotolytic reaction

$$2H_2SO_4 = H_3SO_4^+ + HSO_4^-$$

Much of this dissociation process may have been suppressed by the introduced hydrogen sulphate ions, but a part will survive. How much survives can be calculated with the help of the ionic product

$$K_{ap} = [H_3SO_4^+][HSO_4^-] = 1{\cdot}7 \times 10^{-4} \text{ g.-mol.}^2 \text{ kg.}^{-2}$$

the determination of which is described in Part IV. From the concentration of added hydrogen sulphate ions, the concentration of surviving sulphuric acidium ions can thus be deduced; and from this, the partial depression of freezing point caused by un-repressed autoprotolysis may be derived by means of the formula $\delta\theta = 11{\cdot}96[H_3SO_4^+]$. By subtraction, $\Delta\theta_2 = \Delta\theta_1 - \delta\theta$, we obtain the corrected depressions, θ_2, due to the added solute only. From θ_2, we have now to compute k_f by means of the appropriate specialisation of equation (5), *viz.*,

$$\Delta\theta'/\Delta m_2 = 4k_f\{1 - 0{\cdot}0035\bar{\theta} + (4n - 2)\bar{m}_2/10{\cdot}20\}$$

where θ is the difference between the real freezing point, 10·36°, of sulphuric acid and the mean between the extrapolated freezing point, 10·52°, and the observed freezing point of the solution.

In the above formula, n represents, as before, the solvation number of potassium or ammonium hydrogen sulphate. We have already concluded that the solvation numbers of potassium and ammonium hydrogen sulphate are approximately 2 and 1, respectively: these values are now confirmed, using the criterion of the constancy of the derived k_f values. The latter we take to be the values, which are indicated by the present group of experiments, for the cryoscopic constant of sulphuric acid.

We summarise in Table XI the values of the cryoscopic constant (k_f, in units deg. g.-mol.$^{-1}$ kg.) which follow from these experiments on the depression of the freezing point of water-treated, and of anhydrous, sulphuric acid by the solutes potassium and ammonium sulphate. Theoretical curves of freezing-point depression, calculated from the equations already given, with the use therein of the cryoscopic constant 5·97 deg. g.-mol.$^{-1}$ kg., are shown in Figs. 4, 5, and 6. Evidently, they well represent the observational data.

TABLE XI.

Determination of the cryoscopic constant k_f (*deg. g.-mol.*$^{-1}$ *kg.*) *of sulphuric acid.*

(Method 2.)

Solute.	Expt. no.	Solute. molality.	Water molality.	k_f.	Solute.	Expt. no.	Solute molality.	Water molality.	k_f.
K_2SO_4	88	0·01—0·08	0·047	5·97	Am_2SO_4	123	0·02—0·11	0·058	6·00
	86	0·02—0·05	0·048	5·96		110	0·04—0·03	0·001	5·96
	89	0·05—0·08	0·056	5·96		111	0·04—0·06	0·002	5·97
	122	0·06—0·13	0·000	5·95					
	121	0·05—0·08	0·001	5·95					
				Mean	5·97				

(2.4) *Cryoscopic Evaluation of the Constant* (*Third Method*).—The conclusion that electrostatic activity effects are negligible in dilute solution in sulphuric acid allows us, subject to certain limitations, to employ organic bases for the determination of the cryoscopic constant. The limitations are that the bases shall be completely ionised according to the general equation

$$B + H_2SO_4 = BH^+ + HSO_4^-,$$

that they shall have no basic centre other than the one responsible for this reaction, and that they shall not react with the solvent in any other way than as bases. We have found a number of quite differently constituted organic bases which fulfil these conditions. They all give essentially the same final result, as we shall here illustrate with the solutes acetone and acetic acid, leaving the other cases for record, and for discussion on different lines, in later parts of the series.

The experimental results are given in Tables XII and XIII. The observed depressions of freezing point are represented graphically in Fig. 7, from which it will be seen that the depressions given by the two solutes define a common curve.

According to the chemical equation given above, the measured depressions of freezing point will be due in part to hydrogen sulphate ions; and therefore we have to employ sulphuric acid solvents in which the self-dissociation of the sulphuric acid has been suppressed. The suppression was secured by pre-treatment with water. This necessitated correcting the observed depressions of freezing point, just as is described in Section 2.3, for that change in the degree of ionisation of the water which results from the generation of hydrogen sulphate ions by the added organic base. From the corrected depressions, the cryoscopic constant, k_f, was calculated by means of equation (5), with the substitutions, $s_2 = 1$ and $\nu_2 = 2$, as required by the above-written chemical equation. These calculations were made at first without regard to possible solvation of the ions of the organic oxonium hydrogen sulphate.

TABLE XII.

Freezing points of solutions of acetone in sulphuric acid.

Me_2CO (Δm_2).	$\Delta\theta$. (uncorr.).	$\Delta\theta$ (corr.).			k_f (deg. g.-mol.$^{-1}$ kg.).		
		$n = 0$.	$n = 1$.	$n = 2$.	$n = 0$.	$n = 1$.	$n = 2$.
Expt. 92 (molality H_2O, $m_3 = 0·045$. F. p. of treated solvent, 10·016° c.) :							
0·0169	0·200°	0·205°	0·204°	0·203°	6·05	5·98	5·92
0·0282	0·337	0·346	0·343	0·342	6·12	6·02	5·95
0·0476	0·565	0·578	0·575	0·572	6·05	5·97	5·88
0·0671	0·799	0·816	0·812	0·808	6·07	5·97	5·87
0·0864	1·028	1·050	1·045	1·040	6·08	5·97	5·84
0·1158	1·383	1·411	1·405	1·398	6·09	5·96	5·84

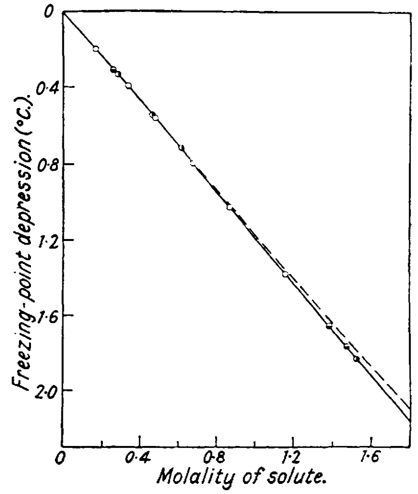
TABLE XIII.

Freezing points of solutions of acetic acid in sulphuric acid.

$Me·CO_2H$ (Δm_2).	$\Delta\theta$ (uncorr.).	$\Delta\theta$ (corr.).			k_f (deg. g.-mol.$^{-1}$ kg.).		
		$n = 0$.	$n = 1$.	$n = 2$.	$n = 0$.	$n = 1$.	$n = 2$.
Expt. 89 (molality H_2O, $m_3 = 0·050$. F. p. of treated solvent, 9·977° c.) :							
0·0332	0·397°	0·407°	0·404°	0·402°	6·09	6·01	5·93
0·0462	0·553	0·566	0·563	0·560	6·11	6·02	5·93
0·0609	0·721	0·737	0·733	0·730	6·03	5·94	5·83
0·1166	1·388	1·416	0·410	1·403	6·06	5·94	5·81
0·1533	1·828	1·864	1·856	1·847	6·09	5·94	5·79
Expt. 88 (molality H_2O, $m_3 = 0·063$. F. p. of treated solvent, 9·851° c.) :							
0·0261	0·311	0·320	0·318	0·317	6·10	6·01	5·94
0·0731	0·872	0·895	0·890	0·885	6·11	5·99	5·87
0·1142	1·346	1·380	1·372	1·364	6·08	5·94	5·79
0·1390	1·652	1·692	1·683	1·673	6·10	5·94	5·78
0·1479	1·762	1·804	1·794	1·784	6·11	5·95	5·78

FIG. 7.

Depression of the freezing point of sulphuric acid by acetone and by acetic acid.



○ *Acetone* (*Expt.* 92). ◑ *Acetic acid* (*Expt.* 89). ◒ *Acetic acid* (*Expt.* 88).

- - - - *Calc. for* k_f = 5·98 *deg. g.-mol.*$^{-1}$ *kg., neglecting solvation of the solute* (n = 0).

——— *Ditto, allowing for solvation* (n = 1).

The more general treatment of the data takes account of the possibility that either or both of the ions of the organic oxonium hydrogen sulphate may be solvated with a total of n molecules of solvent. The chemical equation for the ionisation of the organic base then takes some such form as the following:

$$B + (n + 1)H_2SO_4 = BH(H_2SO_4)_n^+ + HSO_4^-$$

Accordingly we have to employ equation (5) with the substitutions $s = n + 1$ and $\nu_2 = 2$, where n is not necessarily zero. These calculations have been made for a number of values of n, and the results are given in Tables XII and XIII. Using the criterion of the constancy of k_f, it follows that the investigated range of n-values, 0—2, contains the true solvation number, the best round value of which is 1. The mean k_f values, obtained on this basis from the results of the different experiments, are summarised in Table XIV.

TABLE XIV.

Determination of the cryoscopic constant (k_f) *of sulphuric acid.*

Method 3.

Solute (and range of its molality).	Expt. no.	Molality of water.	k (deg. g.-mol.$^{-1}$ kg.).
Acetone ($0<m<0{\cdot}12$)	92	0·045	5·98
Acetic acid ($0<m<0{\cdot}16$)	89	0·050	5·96
	88	0·063	5·96
		Mean	5·97

Employing the mean value $k_f = 5{\cdot}97$ deg. g.-mol.$^{-1}$ kg., theoretical curves of freezing-point depressions for basic solutes, such as acetone and acetic acid, have been computed assuming the solvation numbers 0 and 1. These are shown in Fig. 7, together with the experimental points for acetone and acetic acid.

(2.5) *Values of the Cryoscopic Constant.*—In the preceding sections, three groups of experiments have been reported, through which we have sought to determine the cryoscopic constant of sulphuric acid. They give closely concordant results, which are noted in Table XV.

TABLE XV.

Cryoscopically determined values of the cryoscopic constant of sulphuric acid.

Method.	Section.	Types of solute.	Examples.	k_f (deg. g.-mol.$^{-1}$ kg.).
(1)	2.2	Non-electrolytes	SO_2Cl_2, $Cl{\cdot}SO_3H$	5·98
(2)	2.3	Salts	K_2SO_4, $(NH_4)_2SO_4$	5·97
(3)	2.4	Bases	Me_2CO, $Me{\cdot}CO_2H$	5·97

Because of the more direct nature of the procedure involved in applying method (1), we weight its result more highly than those of the other two methods; but the latter furnish useful confirmation. Accordingly, we have adopted the value

$$k_f = 5{\cdot}98 \text{ deg. g.-mol.}^{-1} \text{ kg.}$$

as the uniform basis of the calculations reported in the accompanying papers of this series.

(3) *The Heat of Fusion of Sulphuric Acid.*

It is considered that the figure $k_f = 5{\cdot}98$ deg. g.-mol.$^{-1}$ kg. is more nearly correct than any previously derived value for the cryoscopic constant of sulphuric acid. Therefore we have used this figure for the purpose of computing a value for the heat of fusion of sulphuric acid, hoping that the value so derived will be more nearly correct than any of the values which have been determined calorimetrically. Employing the formula $\Delta H_0^f = \boldsymbol{R}T_0^2/k_fm_1$, and the numerical data $\boldsymbol{R} = 1{\cdot}9866$ cal. deg.$^{-1}$ g.-mol.$^{-1}$, $T_0 = 10{\cdot}36°$ c. $= 283{\cdot}5°$ K., $k_f = 5{\cdot}98$ deg. g.-mol.$^{-1}$ kg., and $m_1 = 10{\cdot}196$ g.-mol. kg.$^{-1}$, we obtain for the molar heat of fusion $\Delta H_0^f = 2605$ cal. g.-mol.$^{-1}$.

(4) *The Freezing Point of Sulphuric Acid.*

It has been mentioned that the only practicable way of preparing sulphuric acid free from an excess of either sulphur trioxide or water is to adjust its composition, by the addition of one or other of these solutes, until the freezing point reaches a maximum. This has been done on numerous occasions with many samples of sulphuric acid; and always the freezing-point maximum has been found to lie between 10·35° and 10·36°. The readings have usually lain in the range 10·356° ± 0·002°, but the standardisation of our temperatures on the international scale of temperature cannot be guaranteed to the last of these figures, and our value for the freezing point is therefore quoted as 10·36° ± 0·01° c.

This result seems very surprising, because most of the previously recorded values lie higher. The following freezing points of sulphuric acid have been recorded :

Marignac (*Ann. Chim. Phys.*, 1853, **39**, 184)	10·6° c.
Pickering (*Proc. Roy. Soc.*, 1891, **49**, 11)	10·35
Pictet (*Compt. rend.*, 1894, **119**, 642)	10·5
Knietsch (*Ber.*, 1901, **34**, 4100)	10·0
Bredig (*Z. Elektrochem.*, 1906, **12**, 460)	10·43
Hantzsch (*Z. physikal. Chem.*, 1907, **61**, 257)	10·46
Oddo and Scandola (*Gazzetta*, 1908, **38**, i, 603)	10·43
Lichty (*J. Amer. Chem. Soc.*, 1908, **70**, 1934)	10·43
Brönsted (*loc. cit.*)	10·49
Robles and Moles (*loc. cit.*)	10·52
Rubin (cf. Yost and Russell, *op. cit.*)	10·31
This investigation	10·36

We made many attempts to raise our value of the maximal freezing point. Our usual method of preparing sulphuric acid for cryoscopic experiments consisted of distilling a small excess of sulphur trioxide from oleum into 98% " AnalaR " sulphuric acid, at room temperature and at low pressure, in all-glass apparatus, and then adjusting the freezing point of the resulting acid by successive small additions of distilled water. The analytically determinable impurities in the " AnalaR " acid can have had no detectable effect upon the observed freezing points. We tried to improve the treatment of this acid in several ways. One way was separately to condense the sulphur trioxide obtained from the oleum, and to redistil it, before passing it into the 98% acid. In case any small amount of sulphur dioxide present in the oleum had passed through into the sulphuric acid, this was heated at 200° at a low pressure until practically all the excess of sulphur trioxide had been removed. In another attempt to eliminate any disturbance due to sulphur dioxide, potassium perdisulphate was added to the oleum from which the sulphur trioxide was distilled. None of these modifications of procedure made any difference to the observed maximal freezing points. Therefore, finally, the sulphuric acid was subject to repeated fractional freezing, the bulk of retained material being thus reduced to less than one-tenth of the original bulk. Even this treatment failed to yield an acid with a higher maximal freezing point, and therefore we cannot help concluding that the freezing point of sulphuric acid is 10·36°.

It is difficult to account adequately for the differences between this result and those given in the literature. No doubt the temperatures recorded by the early workers were on the mercury-thermometer scale, and therefore require correction to bring them to the international temperature scale. At 10° c. the correction amounts to −0·05°, and thus accounts for a part of the discrepancy. The remainder must be assumed to be due to general thermometric errors. These remarks do not, one imagines, apply to the recent determination by Rubin ; here our assumption is that thermometry was accurate, but that his acid contained an excess of either sulphur trioxide or water.

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