

501. Cryoscopic Measurements in Sulphuric Acid. Part V. Ionisation of Nitric Acid in Sulphuric Oleum.

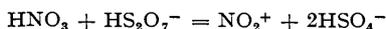
By R. J. GILLESPIE and J. GRAHAM.

When nitric acid is added in increasing quantities to oleum, the freezing point behaves as is shown in Fig. 1, p. 2534. The freezing points of the original oleums lie on the curve limiting the diagram towards the right. The freezing-point curves for added nitric acid run towards the left, rising, passing through maxima, and then falling with increasing gradient.

The main reactions, apart from proton-transfers, are as follows : first, nitric acid desulphates half the disulphuric acid, producing essentially nitronium hydrogen disulphate :



and then, it desulphates the remainder, now present mainly as the hydrogen disulphate ion, to give nitronium hydrogen sulphate :

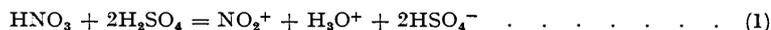


The accompanying proton-transfer processes are as follows. Initially the disulphuric acid is partly ionised as an acid. The first effect of the developing hydrogen disulphate ion is to suppress this ionisation : thus the maximum of the freezing-point curve is reached. Then, as the free disulphuric acid becomes consumed, the hydrogen disulphate ion undergoes some solvolysis : here the freezing point begins to fall. At a later stage, the developing hydrogen sulphate ion partly deprotonates the hydrogen disulphate ion, to form some normal disulphate ion, which is the last form in which disulphuric acid resists desulphation : these processes steepen the fall of the freezing point.

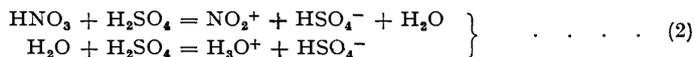
Accompanying this main series of desulphation and deprotonation processes, a minor series must occur, consisting of the desulphation and deprotonation of the small amounts of higher polysulphuric acids originally present in the oleum.

The ν -factors of nitronium hydrogen disulphate and of nitronium hydrogen sulphate are extracted from the results. They agree well with the ν -factors of ammonium hydrogen disulphate and ammonium hydrogen sulphate, respectively. The result for nitronium hydrogen sulphate confirms the analysis, given in Part IV, of the self-dissociation processes of sulphuric acid.

(1) *Preliminary Consideration of the Ionisation of Nitric Acid in Dilute Oleum.*—The work to be reported has reference to the effect of added nitric acid on the freezing points of oleum solvents. It therefore extends the experiments described in Part III (*J.*, 1950, 2504) on the effect of nitric acid on the freezing point of slightly aqueous sulphuric acid. These experiments showed that nitric acid ionises in solvent sulphuric acid according to the following approximate equation :



The same work also showed that a more exact treatment of this process required separate consideration of the following reaction-stages, of which the first proceeds to completion in a large excess of sulphuric acid, whilst the second is appreciably incomplete :



A detailed study of the second of these reactions, in the absence of the complicating presence of the first, was described in Part II (*J.*, 1950, 2493), where the equilibrium constant of the process was determined, which was applied in Part III in a quantitative interpretation of freezing-point measurements on the basis of equations (2).

It was shown in Part II, and in more detail in Part IV (*J.*, 1950, 2516), that dilute oleum can be regarded essentially as a solution, in the sulphuric acid solvent, of disulphuric acid, which is an acid of moderate strength, partly ionising according to the equation

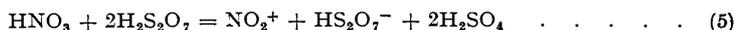


Two of the products of the first of reactions (2) are expected to interact with disulphuric acid : for water will desulphate the acid ; and the hydrogen sulphate ion, which is the strongest base that can exist in quantity in solvent sulphuric acid, will deprotonate it :

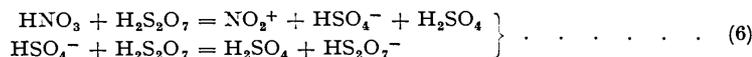


It follows that in oleum solvents the primary ionisation process of nitric acid, represented

by the first of reactions (2), will be succeeded, not by the second of reactions (2), but by the two reactions (4). The over-all effect may be expressed thus :



However, this again is only an approximate expression. The nitronium and hydrogen disulphate ions are quite inert towards each other, as is shown by the formation and stability of solid nitronium hydrogen disulphate (Goddard, Hughes, and Ingold, *J.*, 1950, paper no. 505); and the nitronium ion is quite stable in sulphuric acid (Part III). But the hydrogen disulphate ion is not inert towards sulphuric acid, by which it is reversibly solvolysed, as was shown in Part IV. In other words, of the two reactions (4), the first may be taken as complete, while the second is often a measurably balanced reaction. It is thus convenient to decompose equation (5) into the following two stages, of which the first is complete, whilst the second may be appreciably incomplete :



A study of the reversibility of the second of these reactions, in the absence of complications due to the first, was recorded in Part IV (*loc. cit.*), where an equilibrium constant for the reaction is given, which should be applicable in a quantitative interpretation of relevant freezing-point data on the basis of equations (6).

Even this description of the ionisation processes of nitric acid in oleum is not complete, inasmuch as account has still to be taken of the formation and ionisation of the higher polysulphuric acids, which, except in very dilute oleum, are present in appreciable proportion (Part IV). It seems certain that the higher polysulphuric acids are stronger acids than disulphuric acid, especially with respect to the second stage of acid dissociation; and thus the higher acids tend, much more than does disulphuric acid, to enter into a second stage of ionisation. It follows that added bases will tend to deprotonate the higher polysulphuric acids in preference to disulphuric acid, and will begin to produce from the former appreciable proportions of doubly charged higher polysulphate ions, while they are simultaneously producing from disulphuric acid mainly the singly charged hydrogen disulphate ion. Effects on the freezing point, due to the shifting of this system of equilibria, under the influence of added ammonium sulphate caused by base-forming solute, are described in Part IV, and are available for comparison with the analogous effects of the bases which are produced in the ionisation of nitric acid by the reactions already mentioned.

(2) *Effect of Nitric Acid on the Freezing Point of Oleum.*—This has been investigated by the general methods described in previous Parts of this series. The results of two experiments are reported in Table I. They are graphically represented in Fig. 1. In the table and the figure

TABLE I.
Freezing points of solutions of nitric acid in dilute oleum.

Weights (g.).					Weights (g.).				
Added HNO ₃ .	H ₂ S ₂ O ₇ .	H ₂ SO ₄ .	Molality H ₂ S ₂ O ₇ .	F. p. (° c.).	Added HNO ₃ .	H ₂ S ₂ O ₇ .	H ₂ SO ₄ .	Molality H ₂ S ₂ O ₇ .	F. p. (° c.).
Expt. No. 13 G.					Expt. No. 14 G.				
—	2.980	65.85	0.2545	8.633	—	2.660	63.64	0.2350	8.762
0.0943	2.477	66.14	0.2078	8.771	0.1585	1.764	64.13	0.1501	8.981
0.1109	1.820	66.49	0.1538	8.902	0.1809	1.049	64.47	0.0914	9.071
0.2244	0.552	67.19	0.0462	8.994	0.1543	0.277	64.95	0.0240	9.082
			(NO ₂)(HSO ₄).					(NO ₂)(HSO ₄).	
0.3112	0.000	67.49	0.1008	8.543	0.1714	0.000	65.10	0.0597	8.853
0.1596	"	"	0.1759	8.053					
0.0787	"	"	0.2128	7.797					
0.1115	"	"	0.2654	7.328					

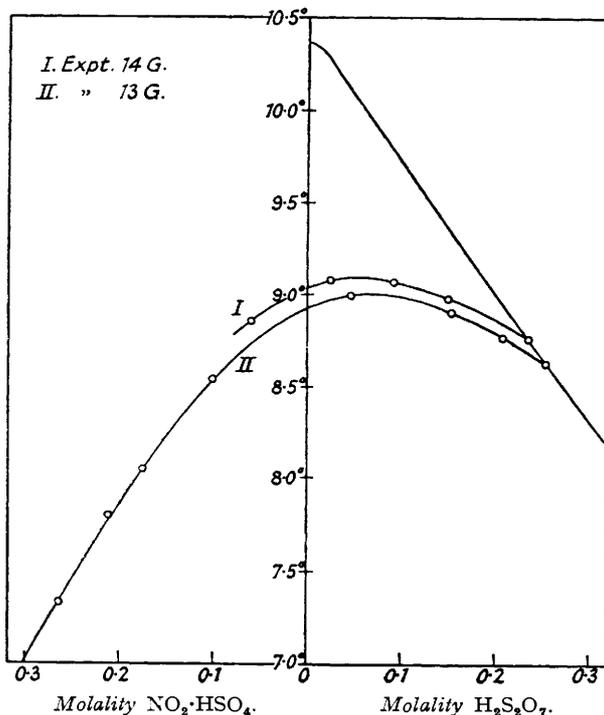
compositions are expressed as follows. The original oleum is regarded as a solution of disulphuric acid in sulphuric acid. Assuming the original presence of 1 mol. of disulphuric acid, solutions formed by the addition of quantities up to 0.5 mol. of nitric acid are treated as solutions of disulphuric acid, and of nitronium hydrogen disulphate formed from nitric acid and disulphuric acid by the completed reaction (5). According to this assumption, when exactly 0.5 mol. of nitric acid has been added, the disulphuric acid will have been destroyed, and the only solute component will be nitronium hydrogen disulphate. Any further quantities of nitric acid, up

to a second 0.5 mol., are now assumed, for the purpose of expressing compositions, to react according to the following equation with the hydrogen disulphate ion which was formed from the first 0.5 mol. :



This means that, during the addition of the second 0.5 mol. of nitric acid, composition is given in terms of the two solutes, nitronium hydrogen disulphate and nitronium hydrogen sulphate; and that when the second 0.5 mol. has been fully added, the solution contains only the one solute component, *viz.*, nitronium hydrogen sulphate. In the figure, the central vertical line (neutral line) represents compositions expressible in terms of nitronium hydrogen disulphate as the only solute. If we start with 1 mol. of disulphuric acid at some point on the nearly linear curve which slopes downward on the right-hand side of the diagram, then the addition

FIG. 1.
Freezing points of solutions of nitric acid in oleum solvents.



of 0.5 mol. of nitric acid, producing 0.5 mol. of nitronium hydrogen disulphate, carries us leftward to the neutral line, whilst the addition of another 0.5 mol. of nitric acid converts this nitronium hydrogen disulphate into 1 mol. of nitronium hydrogen sulphate, thereby taking us an equal distance to the left of the neutral line.

(3) *Qualitative Interpretation of the Freezing-point Curves.*—As will be seen from Fig. 1, the first effect of added nitric acid on the freezing point of oleum is to raise it. Now if the total solute in the original oleum were undissociated disulphuric acid, and if equation (5) were accurately to represent the stoichiometry of the reactions undergone by nitric acid, then the freezing point would not be changed; for according to equation (5), two original solute molecules become replaced by two ions. The evident reason why the freezing point is raised by nitric acid is that the original disulphuric acid is considerably ionised according to equation (3), so that the loss of two stoichiometric molecules of disulphuric acid involves the loss of more than two solute particles. There can be no doubt about the applicability of equation (5) in this region of composition; for disulphuric acid is still in large excess, and hence there can be no appreciable solvolysis of the hydrogen disulphate ion. When solvolysis does occur, each anion solvolysed produces one extra solute particle; and thus solvolysis tends to lower the freezing point.

As the addition of nitric acid is continued, but before the composition has been shifted quite as far as corresponds to the neutral line of Fig. 1, the freezing point approaches a somewhat flat maximum. The reason is that, in this region of composition, the large amount of hydrogen disulphate ion now present suppresses the ionisation of the small amount of disulphuric acid still remaining; this residue of substantially non-ionised disulphuric acid undergoes conversion, as we have seen, without change of freezing point.

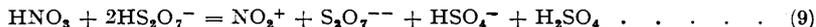
The maximum is attained, and passed, a little before the neutral line, *i.e.*, a little before the solute composition is exactly that of nitronium hydrogen disulphate, because, when only a very small amount of free disulphuric acid remains, the solvolysis of the hydrogen disulphate ion begins to become appreciable; and the effect of that process, as has been noted, is to lower the freezing point.

At the neutral line, the composition of the solute can be expressed in terms of nitronium hydrogen disulphate as the only component; but owing to the solvolysis of this anion some nitronium hydrogen sulphate is present, and some free disulphuric acid still survives. The effect of added nitric acid on the freezing point is therefore a mixture of two effects, *viz.*, a decomposition of practically undissociated disulphuric acid, according to equation (5), without change in the number of solute particles, and a decomposition of the hydrogen disulphate ion, according to equation (7), with an increase in the number of solute particles. Therefore the freezing-point curve for added nitric acid in this region of composition slopes downward with only a moderate gradient.

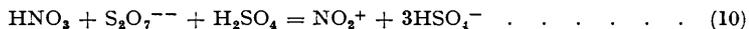
As the addition of nitric acid is continued further, the last of the free disulphuric acid disappears, and the freezing-point curve falls more rapidly. The rough reason for this is that each added molecule of nitric acid is now producing two solute particles in accordance with equation (7). However, this is an inadequate description. Even when the free disulphuric acid has disappeared, the freezing point does not immediately begin to fall as rapidly as equation (7) would suggest. This is because, during the stage in which a good deal of hydrogen disulphate ion has not yet been desulphated by reaction (7), but a considerable concentration of hydrogen sulphate ion has nevertheless been built up, these two ions interact reversibly as follows:



the basic hydrogen sulphate ion inducing a second stage of ionisation of the very weakly acidic hydrogen disulphate ion. The effect of this equilibrium is that, over the first region of composition that is traversed after the free disulphuric acid is destroyed, each added molecule of nitric acid will produce between one and two extra solute particles. The total reaction can be represented as a mixture of reaction (9), which produces one extra solute particle, and reaction (7) which produces two:



In the next region of composition, when a large proportion of the hydrogen disulphate ion has been destroyed by processes (7) and (9), but most of the doubly charged disulphate ion has not yet been desulphated, the freezing-point curve will fall more rapidly than equation (7) would require. This is because desulphation of the normal disulphate ion sets in. Each molecule of added nitric acid then produces between two and three additional solute particles. The total reaction can be represented as a mixture of process (10), which gives three extra solute particles, and process (7) which produces two:



Thus, as we pass towards the left from the neutral line in Fig. 1, by the progressive addition of nitric acid, the descending freezing-point curve steepens in a continuous manner.

When the amount of added nitric acid is sufficient to displace the solute composition just as far to the left of the neutral line as it started in the original oleum to the right of the neutral line, then disulphuric acid, in its molecular form and both its anionic forms, will have been fully destroyed (except for the very small amounts arising by self-dissociation of the sulphuric acid solvent). The solute composition will now be that of nitronium hydrogen sulphate; and furthermore, this salt will be substantially the only solute actually present in the dilute solution.

If still further amounts of nitric acid are added, the freezing-point curve continues to descend. We expect this, even though there can be no reaction between the solute nitronium hydrogen sulphate and the newly added nitric acid. We also expect the slope of the freezing-point curve to be somewhat steeper than before. For each added molecule of nitric acid will

now ionise by reaction with the sulphuric acid solvent, and will therefore produce an average of nearly four extra solute particles, as is described in detail in Part III.

Part of the above description becomes quantitatively changed when we take into account the presence, ionisation, and desulphation of the higher polysulphuric acids (Part IV). In comparison with disulphuric acid, these higher acids are more easily ionised, and their ionisation tends more to proceed to a second stage; and they are also more easily desulphated than is disulphuric acid. Both the ionisations and the desulphations will be promoted by the basic materials which arise from the decompositions of the added nitric acid. These processes will have some effect, for instance, on the position of the freezing-point maximum, and on the position of the point at which the freezing-point curve cuts the neutral line. However, owing to the large tendency of the higher acids to desulphation, all these disturbances will diminish as one passes towards the left in Fig. 1. Furthermore, since the total destruction of the higher acids must precede that of disulphuric acid, the said disturbances must completely vanish well before that composition is reached at which even disulphuric acid, in all its forms, is practically completely absent, *i.e.*, the point at which the solute is nitronium hydrogen sulphate.

(4) *The ν -Factors of Nitronium Hydrogen Disulphate.*—We proceed to check this interpretation quantitatively for certain specific compositions, first taking compositions represented by points on the neutral line, on which the total solute can be referred to the single component, nitronium hydrogen disulphate.

If no solute were present except nitronium hydrogen disulphate, the ν -factor at this composition would be 2. However, two disturbances combine to render the value not exactly equal to 2. First, some solvolysis of the hydrogen disulphate ion tends to raise the figure. Secondly, the formation of a certain quantity of doubly charged higher polysulphate ions tends to lower the figure. This second effect becomes more important in more concentrated solutions, and hence the ν -factor, although it is greater than 2 in dilute solution, will fall as the concentration is increased.

The combined effect of these disturbances was analysed in some detail in Part IV, in connexion with the ν -factors of ammonium hydrogen disulphate; and the solvolysis constant of the hydrogen disulphate ion, as well as an equilibrium constant connected with the formation of higher polysulphates, were extracted from the results. This case parallels the present example so closely that we may expect the freezing point of a solution of nitronium hydrogen disulphate to be practically the same as that of an equimolar solution of ammonium hydrogen disulphate; for the disturbances mentioned are both independent of the cation. Therefore one of the simplest tests that we

can make of the preceding interpretation is to ascertain whether the freezing points of solutions of nitronium hydrogen disulphate, as given by the intersections of our freezing-point curves with the neutral line of Fig. 1, lie on a smooth curve drawn through the freezing points of solutions of ammonium hydrogen disulphate, as determined in Part IV. This test is shown in Fig. 2. The data required for it are given in columns 3 and 4 of Table II.

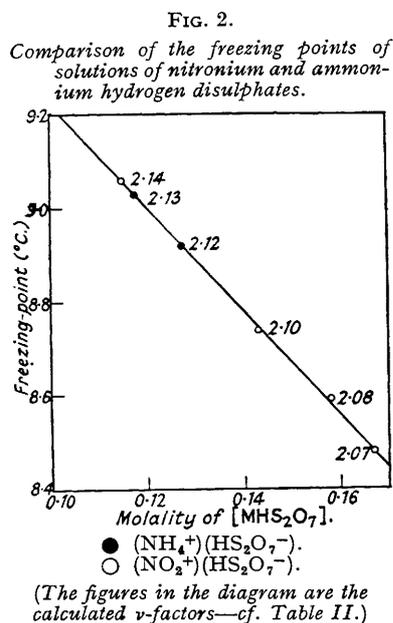


TABLE II.

*Freezing-point depressions and ν -factors for nitronium hydrogen disulphate. Comparison with similar values for ammonium hydrogen disulphate.**

Expt.	Cation.	Molality.	F. p. ($^{\circ}$ c.).	$\Delta\theta'$.	$\Delta\theta''$.	ν' .	ν'' .
106	NH_4^+	0.115	9.06	1.56 $^{\circ}$	1.48 $^{\circ}$	2.27	2.14
14 G	NO_2^+	0.117	9.03	1.59	1.51	2.23	2.13
13 G	NO_2^+	0.127	8.92	1.70	1.63	2.21	2.12
106	NH_4^+	0.143	8.74	1.88	1.81	2.19	2.10
105	NH_4^+	0.158	8.59	2.03	1.97	2.15	2.08
104	NH_4^+	0.167	8.48	2.14	2.08	2.14	2.07

* The values for the ammonium salts are taken from Table II of Part IV.

The last four columns in Table II are concerned with the calculation and comparison of ν -factors. Freezing-point depressions $\Delta\theta'$ are given, which are reckoned from the theoretical freezing point, 10.62° , of undissociated sulphuric acid. Some self-dissociation of the solvent contributes to these depressions. A correction for this effect having been applied, as described in Part IV, the corrected depressions $\Delta\theta''$ are listed.

The ν -factors which are calculated from the uncorrected depressions are given as ν' , whilst those which are computed from the corrected depressions are termed ν'' . In these calculations it has been assumed that the solvation number of nitronium hydrogen disulphate is the same as that of nitronium hydrogen sulphate, *viz.*, 2 to the nearest unit, as given in Part III, just as the solvation number of ammonium hydrogen disulphate was taken in Part IV to be the same as that of ammonium hydrogen sulphate, *viz.*, 1, as found in Part I. It will be noted that the ν -factors of nitronium hydrogen disulphate interpolate themselves quite smoothly amongst the corresponding values of ammonium hydrogen disulphate.

The quantitative success of these tests shows that we were correct, not only in regarding equation (5) as a good approximate expression of the ionisation of nitric acid in oleum, but also in suggesting that more detailed specification of the process which involved assuming the first of equations (6) to be complete, and the second to lack completeness only on account of causes which have nothing to do necessarily with nitric acid, and only to extents which can be quantitatively estimated from independent studies of the equilibria involved.

(5) *The ν -Factor of Nitronium Hydrogen Sulphate.*—When 1 mol. of nitric acid has been added for each 1 mol. of disulphuric acid in the original oleum, the only solute present should be nitronium hydrogen sulphate. The ν -factor should therefore be 2.00. All such disturbances as are discussed in the preceding Section are absent.

From the graph of Expt. 13 G (cf. Fig. 1) it can be read that the freezing point of a 0.2545 molal solution of nitronium hydrogen sulphate in sulphuric acid is 7.42° . We have to consider to what extent the self-dissociation of the solvent is involved in this result. The ionic self-dehydration will not have been affected, and therefore the solvent freezing point from which the freezing-point depression due to the added solute should be computed is 10.52° , as was shown in Parts I and IV. The autoprotolysis of the solvent is not quite completely repressed, and 0.01° must be subtracted from the observed depression in order to allow for this. From the corrected depression, we may calculate the ν -factor of nitronium hydrogen sulphate, exactly as described for the ν -factor of ammonium hydrogen sulphate in Part IV, except that in the present case the solvation number 2 is used, in accordance with the decision reached in Part III concerning the solvation of the nitronium ion. The computed ν -factor for the nitronium salt is 1.99, in good agreement with expectation, again confirming the estimated freezing point, 10.52° , of the non-autoprotolysed solvent.

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