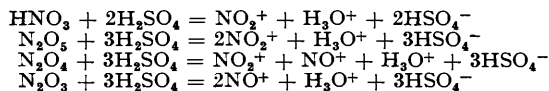


499. *Cryoscopic Measurements in Sulphuric Acid. Part III. The Solutes Nitric Acid, Dinitrogen Pentoxide, Dinitrogen Tetroxide, and Dinitrogen Trioxide. Cryoscopic Proof of the Formation of the Nitronium Ion, NO₂⁺.*

By R. J. GILLESPIE, J. GRAHAM, E. D. HUGHES, C. K. INGOLD, and E. R. A. PEELING.

It is shown by study of the freezing points that the solutes named in the title react with solvent sulphuric acid according to the following equations :



These conversions are quantitative, except that, since water is only a semi-strong base (Part II), the ions formed partly recombine :



For this reason, the ν -factor of nitric acid is less than 4 ; the observed value is 3.77, expressed as a mean over the concentrations used. Similarly, the ν -factors for the three oxides are less than 6 ; the observed mean values are 5.70, 5.69, and 5.69 for the pentoxide, tetroxide, and trioxide, respectively. The deviations from integral values, which are to be expected on account of the incomplete ionisation of water, can be calculated from the basicity constant of water (Part II). The theoretical ν -factors thus computed agree closely with the experimental values.

As is mentioned in Part I, the investigations described in the present paper and in Part V were actually the first to be undertaken of those which are reported in this series. As soon as the kinetic study of aromatic nitration (cf. Hughes, Ingold, and Reed, *J.*, 1950, 2400) had disclosed a rate-determining bond-fission of nitric acid, presumably to form the nitronium ion, it was realised that much of the early work, including all the cryoscopic work, on the condition of nitric acid in solvent sulphuric acid would have to be revised. Such revision in its several aspects was taken in hand ; and the cryoscopic experiments quickly solved the problem to which they were directed, namely, that of ascertaining, simply and unambiguously, the products into which nitric acid is converted in sulphuric acid. Soon afterwards, the same kind of information was obtained in the same way for dinitrogen pentoxide, dinitrogen tetroxide, and dinitrogen trioxide.

This work has already been reported in summary (*Nature*, 1946, 158, 480), but the details have not been published until now for the following reason. At the time of the preliminary report, the cryoscopic results could not be interpreted in a satisfactorily quantitative manner for lack of sufficiently exact information about the general solvent properties of sulphuric acid. The best theory and basic data which were available at that time left differences of several units per cent. between the calculated and observed freezing-point depressions, such differences, although of an order often regarded as negligible, being considerably larger than the experimental error. They could be, and were provisionally, set down to non-ideality ; but they could not be proved to be due to that cause, much less accounted for quantitatively on those lines. It followed that a quantitative investigation of the general solvent properties of sulphuric acid would have to be undertaken before the cryoscopic results of special interest to us could be interpreted satisfactorily. That investigation, which has only recently been completed, is described in three of the accompanying papers (Parts I, II, and IV) ; it provides the required basis for the reduction of our cryoscopic data on nitric acid and the three nitrogen oxides.

(1) *The Solute Nitric Acid.*

(1.1) *Theories of the Condition of Nitric Acid in Sulphuric Acid.*—It has been evident for many years that nitric acid in solution in sulphuric acid exists in an altered form, and that this consists of or contains cations. Saposchnikow's measurements of the partial vapour pressure of nitric acid in water-sulphuric acid mixtures show that, whilst it is large in approximately equimolar solvent mixtures, it becomes relatively small as the solvent composition approaches that of pure sulphuric acid, just as it becomes small when the solvent is nearly pure water (*Z. physikal. Chem.*, 1904, 49, 697; 1905, 51, 607; 53, 225). Hantzsch observed that nitric acid depressed the freezing point of solvent sulphuric acid from two to four times as much as would a solute which dissolved without any form of change (*ibid.*, 1907, 61, 257; 1908, 65, 41). These are clear indications that some change occurs. Both Saposchnikow and Hantzsch observed

that solutions of nitric acid in sulphuric acid have a high electrical conductivity (*loc. cit.*), a result which proves that the change gives rise to ions.

The evidence for an altered form of nitric acid in sulphuric acid has been strengthened by later observations on other physical properties of the solutions. Hantzsch observed that solutions of nitric acid in sulphuric acid show little optical absorption in the near ultra-violet, and, in particular, that they show much less absorption than they would if any substantial proportion of the nitric acid were present either as nitric acid molecules or as nitrate ions (*Ber.*, 1925, 58, 941). Chédin observed that solutions of nitric acid in a sufficient excess of sulphuric acid showed none of the normal Raman spectrum of molecular nitric acid, but instead gave, superposed on the sulphuric acid spectrum, a new and simple spectrum consisting of two strong lines (*Compt. rend.*, 1935, 200, 1397).

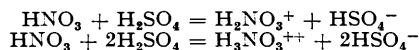
The case for assuming that the altered form of nitric acid in sulphuric acid is cationic rests in part on Hantzsch's proof that nitric acid can, in some conditions, exist in a cationic form. He prepared solid salts from nitric acid and perchloric acid (*Ber.*, 1925, 58, 941). His conclusions about their compositions and constitutions were quite erroneous (cf. *J.*, 1950, paper no. 505); but he and Berger showed that, when these preparations were electrolysed in solution in nitromethane, nitric acid accumulated at the cathode. It was an obviously probable suggestion that similar salts would be present in solutions of nitric acid in sulphuric acid. Attempts to demonstrate that, in the electrolysis of such solutions, nitric acid is transported towards the cathode have met with difficulties; but such transport has recently been demonstrated for solutions of nitric acid in oleum by Bennett, Brand, and Williams (*J.*, 1946, 875).

Many of the above-mentioned observations are revised or extended in this paper and in accompanying papers. The revision allows much more definite conclusions to be drawn. Our special concern here is with the revision of the cryoscopic evidence, by which we unequivocally identify the altered form of nitric acid as the nitronium ion, NO_2^+ .

Throughout the earlier history of the matter, gifted speculation ran ahead of observation and deduction. The three earliest theories about the form assumed by nitric acid in sulphuric acid were all correct or nearly so. Markownikow suggested that it was the mixed anhydride, $\text{NO}_2\cdot\text{O}\cdot\text{SO}_3\text{H}$ (*Ber.*, 1899, 32, 1441); Saposchnikow that it was nitric anhydride, $\text{NO}_2\cdot\text{O}\cdot\text{NO}_2$ (*Z. physikal. Chem.*, 1904, 49, 677); and Euler that it was the nitronium ion, NO_2^+ (*Annalen*, 1903, 330, 280). Each of these ideas has had many adherents. In supporting the nitric anhydride hypothesis, Chédin emphasised that this substance must be present in some modified form. If it is assumed that both of the above anhydrides are ionised, then the three theories become equivalent.

Hantzsch's views developed along different lines. In his experiments on the depression of the freezing point of sulphuric acid by nitric acid, he employed as solute either nitric acid or potassium nitrate, allowing in the latter case for the depression caused by the formed potassium hydrogen sulphate. In one set of experiments by the first method, and three sets by the second, he obtained depressions due to nitric acid, amounting to 2.2–2.5, 1.9–2.6, 3.3–4.0, and 3.8 times the depression to be expected for a non-electrolyte. (The calculations were naturally based on his value for the cryoscopic constant of sulphuric acid; if our value is used, all the figures would be larger by about one-sixth.) His first (1908) conclusions were that ionising complex acids, such as $(\text{OH})_2\text{NO}(\text{SO}_4\text{H})$ and $(\text{OH})\text{NO}(\text{SO}_4\text{H})_2$, are formed, and are extensively ionised.

Later (1925), the general views which Hantzsch had developed to the effect that weaker acids can act as bases towards stronger ones, as well as the special evidence he thought he had secured concerning the compositions of the salts obtained by the interaction of nitric and perchloric acid, led him to abandon the idea that nitric acid in sulphuric acid remains combined in any kind of anion, and to assume instead that it passes into cationic forms. In particular, he assumed univalent and bivalent cations to be furnished by the following reactions :



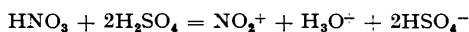
Completed reactions according to these equations would lead to freezing-point depressions respectively equal to twice and thrice the depression to be expected for a non-electrolyte. Hantzsch accepted his previous cryoscopic results as broadly indicative of a three-fold depression, and accordingly assumed that the second reaction is the one that takes place principally in excess of sulphuric acid. He did not attempt to account for his cryoscopic results in detail, or to explain why several experiments had given more than three-fold depressions.

Hantzsch's work on the effect of dissolved nitric acid on the freezing point of sulphuric acid

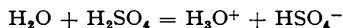
was repeated by Robles and Moles (*Anal. Fis. Quim.*, 1934, **32**, 474). They obtained freezing-point depressions 2.5—3.3 times that to be expected for a non-electrolyte. (This was on the basis of their value of the cryoscopic constant; ours would make the figures about 10% higher.) They regarded their results as confirming Hantzsch's assumption of a three-fold freezing-point depression. It is not necessary to discuss their interpretation.

(1.2) *Cryoscopic Proof of the Conversion of Nitric Acid into the Nitronium Ion.*—The cryoscopic data now reported exclude the idea that either of Hantzsch's cations of nitric acid is present to any appreciable extent in a solution of nitric acid in sulphuric acid. Our figures accord with the view that nitric acid is quantitatively converted into the nitronium ion; and they are not susceptible of any alternative explanation.

The approximate equation for the conversion of nitric acid into the nitronium ion in solvent sulphuric acid is



It indicates a ν -factor of 4 for nitric acid. However, the real ν -factor must be less than 4 on account of the partial recombination of hydroxonium and hydrogen sulphate ions in the balanced reaction



The equilibrium constant of this reaction, *i.e.*, the basicity constant of water in solvent sulphuric acid, has been determined (Part II), and this allows us to calculate exact ν -factors for nitric acid at given concentrations.

Even before we proceed to a careful calculation, the general nature of the result can be appreciated. In Part II it was shown that the figure 1.89 could be taken as an average value for the ν -factor of water over the range of solute concentration which we usually employ in our cryoscopic measurements. Making allowance for the nitronium hydrogen sulphate which is formed from nitric acid, simultaneously with water and its ions, we may set down the figure 3.88 as a closer upper limit than 4.00 to the ν -factor for nitric acid. The real ν -factor will be less even than this, because the presence of the nitronium hydrogen sulphate will tend to repress the ionisation of the water. We should over-estimate this common-ion effect if we were to assume that the second hydrogen sulphate ion will double the association of the ions of water, and hence the figure 3.78 should represent a lower limit to the average ν -factor. Thus, without calculation, we may estimate the average ν -factor for nitric acid over our usual range of solute concentrations as 3.83 ± 0.06 . In our preliminary report (*Nature*, 1946, **158**, 480), we gave the experimental value 3.82, so that there is substantial agreement. Since the date of that report, both the theoretical and experimental figures have been slightly changed as a result of the use of better procedures for calculation. However, the overall effect of these changes is small, and so the substantial agreement remains. Its confirmation by more careful calculations definitely establishes the explanation expressed in the chemical equations given above.

(1.3) *Calculation of Theoretical ν -Factors for Nitric Acid.*—The principal part of the calculation consists in computing the ν -factor for the water formed in the reaction between nitric acid and the sulphuric acid solvent. This ν -factor, which measures the degree of ionisation of the water, depends on the concentration of the formed water, and on the concentrations of other sources, whether pre-existing or simultaneously produced, of hydrogen sulphate ions. There are two such sources, *viz.*, the water, originally added in order to repress the self-ionisation of the solvent, and the nitronium hydrogen sulphate, which is formed along with water from the nitric acid.

Let us first calculate ν -factors for the total water. Suppose that water in molality m_2 has been added in order to repress the ionisation of sulphuric acid, and that nitric acid in molality m_3 has then been introduced, forming extra water in molality m_2' (with $m_2' = m_3$) and nitronium hydrogen sulphate in molality m_3 . Then the basicity constant for water,

$$K_b(\text{H}_2\text{O}) = [\text{H}_3\text{O}^+][\text{HSO}_4^-]/[\text{H}_2\text{O}]$$

the concentrations being in molalities, is easily shown to be given by

$$K_b = \{(m_2 + m_2')(\nu_2 - 1)^2 + m_3(\nu_2 - 1)\}/(2 - \nu_2)$$

In Part II, a value of $K_b(\text{H}_2\text{O})$ was given, 0.72 g.-mol. kg.⁻¹, which is appropriate for calculation by the method here to be used. Employing this figure, ν_2 may be calculated for any given values of m_2 and m_3 . Such calculations of the ν -factors for total water in molality $m_2 + m_2'$ are illustrated in columns 1—3 and 7—9 of Table I.

TABLE I.

Theoretical v-factors for water produced from nitric acid in solvent sulphuric acid already containing water.

Molality of added water			Depression by water			Molality of added water			Depression by water		
(m_2).	(m_3).	v_2 for total water.	total water ($\Delta\theta$).	from HNO ₃ ($\Delta\theta'$).	v_2' for water from HNO ₃ .	(m_2).	(m_3).	v_2 for total water.	total water ($\Delta\theta$).	from HNO ₃ ($\Delta\theta'$).	v_2' for water from HNO ₃ .
0.050	0.00	1.94	0.583°	—	—	0.065	0.00	1.92	0.751°	—	—
„	0.02	1.90	0.798	0.215°	1.78	„	0.02	1.88	0.963	0.212°	1.75
„	0.04	1.86	1.006	0.423	1.75	„	0.04	1.85	1.166	0.415	1.72
„	0.06	1.83	1.211	0.628	1.73	„	0.06	1.82	1.369	0.618	1.70
„	0.08	1.80	1.412	0.829	1.71	„	0.08	1.79	1.566	0.815	1.67
„	0.10	1.77	1.604	1.021	1.68	„	0.10	1.76	1.756	1.005	1.65

The next step towards obtaining v -factors for the water formed from nitric acid consists in calculating that part of the depression of the freezing point of the solvent which can be considered to be due to the total water. This requires the use of the appropriate form of equation (4) of Part I. We insert the determined value of the cryoscopic constant; and, in the nearly-unit correction factor, we write, with sufficient accuracy, the values $s_2 = v_2 = 2$, and $s_3 = v_3 = 0$, thus bringing the equation to the form

$$\Delta\theta = 5.98v_2(m_2 + m_2')\{1 - 0.0035\bar{\theta} + 2(\overline{m_2 + m_2'})/10.20\}$$

It is convenient at this stage, and it does not lead to any appreciable error because of the taking of differences later, to set $s_3 = v_3 = 0$, thus ignoring the presence and solvation of the nitronium hydrogen sulphate. However, the application of the formula requires care on other counts. For, in the first place, the $\Delta\theta$, which it allows one to compute, represents the partial freezing-point depression, due to total water, below what the freezing point of pure sulphuric acid would be if there were no self-ionisation, *i.e.*, below the "extrapolated" freezing point 10.62° c. (cf. Part II). On the other hand, the mean depression $\bar{\theta}$, as one can understand by considering the physical meaning of the term which contains it, relates to actual not to idealised, freezing points. Therefore, in computing depressions of which $\bar{\theta}$ is the mean, we must first allow for the extra depression, approximately $11.96m_2$, caused by the nitronium hydrogen sulphate. Then, having calculated the total depression, due to water plus nitronium hydrogen sulphate, from the extrapolated freezing point, 10.62° c., of the undissociated solvent, we must subtract the temperature corresponding to one-half of this depression from the real freezing point, 10.36° c., of the equilibrium solvent, in order to obtain the mean depression. The numerical work is done by cyclic approximation, a single cycle being sufficient. The computed partial depressions $\Delta\theta$ due to total water are given in the fourth and tenth columns of Table I.

As has been said, these depressions neglect the self-ionisation of the sulphuric acid solvent. However, the water initially introduced in molality m_2 is considered to suppress the solvent dissociation, in conformity with the basis of computation of the employed value of the basicity constant. Therefore, if we subtract the calculated depression, corresponding to the water molality, m_2 , from a calculated depression for a larger water molality $m_2 + m_2'$, where $m_2' = m_3$, the difference will represent the real depression $\Delta\theta'$, due to the extra water in molality m_2' ; that is, it will represent the partial depression due to water formed from nitric acid in molality m_3 . These partial depressions, $\Delta\theta'$, are listed in columns 5 and 11 of Table I.

The corresponding values of v_2' , the v -factors of the water formed from the nitric acid, are given in columns 6 and 12 of Table I. They are readily computed from the depressions, $\Delta\theta'$, by means of the appropriate specialisation

$$\Delta\theta' = 5.98v_2'm_2'\{1 - 0.0035\bar{\theta}' + 2(m_2 + \bar{m}_2')/10.20\}$$

of the previously given formula. Here, the mean freezing-point depression, $\bar{\theta}'$, must be reckoned from the true freezing-point of equilibrium sulphuric acid, and must take into account the depressions caused by the nitronium hydrogen sulphate, just as for the previously considered $\bar{\theta}$. But the intervals over which the means $\bar{\theta}'$ are to be taken are different, having, as one limit, the depression given by the originally introduced water.

The theoretical v -factors for nitric acid itself are now obtained by simply adding 2.00 to each of the figures given in columns 6 and 12 of Table I. This addition is made in respect of the formed nitronium hydrogen sulphate.

(1.4) *Experimental ν -Factors for Nitric Acid and their Comparison with the Theoretical ν -Factors.*—The freezing-point depressions produced by nitric acid were measured in solutions in sulphuric acid containing previously introduced water. The added solute was absolute nitric acid, prepared by methods which are standard in this laboratory (Benford and Ingold, *J.*, 1938, 929; Hughes, Ingold, and Reed, *J.*, 1950, 2400).

Supposing the self-ionisation of the sulphuric acid solvent to have been completely suppressed by the initially added water, the ν -factors for nitric acid may be calculated from the further depressions of freezing point produced by the nitric acid, by the use of an appropriate form of equation (5) of Part I. Now it has been established in Parts I and II that potassium, ammonium, and hydroxonium hydrogen sulphates are solvated in sulphuric acid, and it seems inherently probable that the same will be true of nitronium hydrogen sulphate. Such solvation, as well as the solvation of water and its ions, must be taken into account in choosing our specialised equation, which is derived by substituting a suitable value of s_2 in equation (5) of Part I, s_2 being the total number of solvent molecules which, either by reaction or through solvation, are put out of action as solvent, by one molecule of added nitric acid. If n is the solvation number of nitronium hydrogen sulphate, then $s_2 = n + 3$. The only way we have of estimating n is by choosing it to give consistent ν -factors over a range of concentrations. Using this criterion, not only for solute nitric acid (this paper, and Part V), but also for the other investigated solutes which produce nitronium hydrogen sulphate, *viz.*, dinitrogen pentoxide and dinitrogen tetroxide (this paper), and also nitronium perchlorate (Part VI), it is thus estimated that the solvation number n of nitronium hydrogen sulphate lies between 2 and 3, probably nearer to 2. (The sensitivity of the method is insufficient to enable such values to be determined more closely than to the nearest integer.) In order to illustrate the effect of solvation of the nitronium salt, values of ν for nitric acid have been calculated for the n -values 0, 2, and 3, from the experimental freezing-point depressions. The results of these calculations are shown in Table II.

TABLE II.

Depression of the freezing point of sulphuric acid by added nitric acid. Comparison of the experimental and theoretical ν -factors for nitric acid.

Expt. no.	Molality of		F. p. ($^{\circ}$ C.).	ν (exptl.).			ν (theor.)
	H ₂ O (m_2).	HNO ₃ (Δm_2).		$n = 0$.	$n = 2$.	$n = 3$.	
2 G *	0.066	—	9.799	—	—	—	—
	"	0.01463	9.460	3.84	3.79	3.79	3.76
	"	0.02960	9.109	3.86	3.80	3.79	3.74
	"	0.04461	8.763	3.84	3.77	3.75	3.72
	"	0.05946	8.407	3.86	3.78	3.76	3.70
84	0.055	—	9.926	—	—	—	—
	"	0.00890	9.721	3.84	3.80	3.79	3.78
	"	0.02213	9.418	3.82	3.77	3.76	3.77
	"	0.03805	9.061	3.77	3.72	3.70	3.74
	"	0.06769	8.364	3.82	3.75	3.71	3.72
	"	0.08231	8.007	3.85	3.77	3.73	3.70

* One of an early series (1942).

The ν -factors computed with allowance for solvation are to be compared with the theoretical ν -factors entered in the last column of the Table. These theoretical factors are calculated from the chemical equations representing the decomposition of nitric acid in sulphuric acid, and the ionisation constant of water, as is illustrated in Section 1.3.

(1.5) *Calculation of a Theoretical Curve for the Freezing-point Depression due to Nitric Acid.*—A theoretical curve for the depression of the freezing point of sulphuric acid by added nitric acid may be calculated by an application of the principles outlined in Sections 1.3 and 1.4. The results of such a calculation are given in Table III. They relate to two cases in which the sulphuric acid solvent has been pre-treated by the addition of water in 0.05 and 0.065 molal concentrations.

Col. 3 in this Table gives the partial depression, calculated for the partly ionised water formed from the nitric acid. These figures are copied from Table I. Col. 4 contains the partial depressions calculated for the binary electrolyte (NO₂⁺)(HSO₄⁻) into which the nitric acid is assumed to be completely converted, in the presence of the simultaneously formed, and previously added water. These figures contain no allowance for the solvation of the nitronium salt; and since, on this basis, one molecule of sulphuric acid is required for the production of one

molecule of the binary electrolyte, equation (5) of Part I is used with the substitutions $s_2 = 1$ and $\nu_2 = 2$, so that it reduces to

$$\Delta\theta/\Delta m_2 = 11.96(1 - 0.0035\bar{\theta} + m_3/10.20)$$

where m_3 is the total molality of water present. Cols. 5 and 6 give the corresponding partial depressions, as calculated by those special forms of equation (5) of Part I, which take into account the solvation of the nitronium salt with the solvation numbers 2 and 3, so that s_2 becomes 3 and 4, respectively. In all these calculations allowance is made for the presence of the other set of solutes, *viz.*, water and its ions, when computing the mean depression $\bar{\theta}$. The figures in the last three columns of Table III are obtained by addition of the appropriate partial depressions.

TABLE III.
Calculated depressions of the freezing point of sulphuric acid by nitric acid.

Molality of		Freezing-point depressions (° C.):						
added water (m_3).	added HNO ₃ (Δm_2).	H ₂ O and its ions.	(NO ₂) ⁺ (HSO ₄) ⁻ .			HNO ₃ .		
			$n = 0.$	$n = 2.$	$n = 3.$	$n = 0.$	$n = 2.$	$n = 3.$
0.050	0.02	0.215	0.240	0.245	0.247	0.455	0.460	0.462
"	0.04	0.423	0.481	0.494	0.500	0.904	0.917	0.923
"	0.06	0.628	0.723	0.747	0.760	1.351	1.375	1.388
"	0.08	0.829	0.965	1.005	1.026	1.794	1.834	1.855
"	0.10	1.021	1.208	1.267	1.297	2.229	2.288	2.319
0.065	0.02	0.212	0.241	0.246	0.248	0.453	0.458	0.460
"	0.04	0.415	0.482	0.496	0.504	0.897	0.911	0.919
"	0.06	0.618	0.724	0.751	0.764	1.342	1.369	1.384
"	0.08	0.815	0.966	1.010	1.031	1.781	1.825	1.846
"	0.10	1.005	1.209	1.273	1.306	2.214	2.278	2.311

The difference between the depressions for the two different initial water concentrations is very small; and a theoretical freezing-point curve has been constructed from the data for an initial water concentration of 0.05 molal, with a solvation number of 2 for the nitronium hydrogen sulphate. In Fig. 1 (p. 2513), this curve is shown, in comparison with observational points representing the data of Table II. Evidently our theory that nitric acid is converted in sulphuric acid into fully dissociated nitronium hydrogen sulphate and partly ionised water, according to the equations already given, is in satisfactory agreement with experiment.

(2) *The Solute Dinitrogen Pentoxide.*

(2.1) *Theories of the Condition of Dinitrogen Pentoxide in Sulphuric Acid.*—It was noticed by Klemenc and Schöller (*Z. anorg. Chem.*, 1924, **141**, 231) that solutions of dinitrogen pentoxide in sulphuric acid possess nitrating properties very similar to those of nitric acid in sulphuric acid: not only was nitration by dinitrogen pentoxide a reaction of the second order, like nitration by nitric acid, in solvent sulphuric acid, but also the rates of nitration with these two reagents were practically identical, provided that, in calculating the concentrations, one molecule of dinitrogen pentoxide was taken as the equivalent of two molecules of nitric acid. This would mean, if dinitrogen pentoxide were to dissolve unchanged in sulphuric acid, that the nitric acid is converted into dinitrogen pentoxide, an interpretation which has been suggested or supported more than once. Alternatively, it could mean, if dinitrogen pentoxide is in any way changed in sulphuric acid, that nitric acid is dehydrated and converted into the products of the change.

It was emphasised by Chédin particularly that dinitrogen pentoxide is changed in sulphuric acid. He showed that nitric acid and dinitrogen pentoxide, in solution in sulphuric acid, gave the same Raman spectrum, which was neither that of nitric acid, nor that of dinitrogen pentoxide as this substance exists in non-ionising solvents (in which it had been proved to have a normal molecular weight), but was almost exactly similar to that of the Raman spectrum of solid dinitrogen pentoxide (*Compt. rend.*, 1935, **200**, 1397; **201**, 724; 1936, **203**, 722). Therefore Chédin concluded that the substance which was formed from nitric acid, and from dinitrogen pentoxide, in solvent sulphuric acid was a special form of dinitrogen pentoxide, but was not the molecule of the gaseous substance, or of its solutions in non-ionising solvents.

(2.2) *Cryoscopic Proof of the Conversion of Dinitrogen Pentoxide into the Nitronium Ion.*—In view of the conclusion (Section 1.2) that nitric acid is converted in solvent sulphuric acid into fully dissociated nitronium hydrogen sulphate and partly ionised water, the substantial equivalence, by both chemical and Raman-spectroscopic tests, of solutions of nitric acid and of

dinitrogen pentoxide in sulphuric acid, leads to the inference that dinitrogen pentoxide also is converted into nitronium hydrogen sulphate and partly ionised water, though, naturally, with a diminished proportion of water. The approximate equation is as follows :



This is the equation which would represent the change if the dinitrogen pentoxide were to dissolve in its ionised form, $(\text{NO}_2^+)(\text{NO}_3^-)$, and then the nitrate ion were to become converted, as it is bound to be by sulphuric acid, into nitric acid, and thence into a second nitronium ion, in accordance with the equation given on p.

The above equation requires a ν -factor of 6 for dinitrogen pentoxide. However, this estimate must be too high because the ions of water, the hydroxonium and hydrogen sulphate ions, will partly recombine (cf. Part II). This effect in principle renders the ν -factor dependent on the concentration. A closer estimate of the ν -factors applying to our concentrations can be obtained by using the determined average ν -factor for water in a similar range of concentrations, and making a rough allowance for the common-ion effects of the simultaneously formed nitronium hydrogen sulphate, just as was done in the case of the solute nitric acid (Section 1.2). This procedure indicates that one should expect ν -factors in the range 5.78 ± 0.11 . In our preliminary report on the cryoscopic behaviour of dinitrogen pentoxide in sulphuric acid (*Nature*, 1946, 158, 480), we gave the value 5.85, as the experimentally determined ν -factor for this solute. However, this value becomes a little changed as a result of improved constants and better procedures for calculation. The result is to improve the agreement, which definitely establishes the form of ionisation postulated.

(2.3) *Calculation of Theoretical ν -Factors for Dinitrogen Pentoxide.*—This calculation is made by the same method as that illustrated in Section 1.3, though some of the details of the procedure are a little different, because of the altered ratio in which nitronium hydrogen sulphate and water are formed from dinitrogen pentoxide, as compared with the ratio in which they are produced from nitric acid.

It is necessary first to compute ν -factors for total water in molality $m_2 + m_2'$, assuming that water in molality m_2 has first been added in order to repress the self-ionisation of the sulphuric acid, and that dinitrogen pentoxide in molality m_3 has then been introduced, producing extra water in molality m_2' (with $m_2' = m_3$), and nitronium hydrogen sulphate in molality $2m_3$. The formula for the basicity constant of water then becomes

$$K_b = \{(m_2 + m_2')(\nu_2 - 1)^2 + 2m_3(\nu_2 - 1)\} / (2 - \nu_2)$$

Thus using the value $K_b = 0.72 \text{ g.-mol. kg.}^{-1}$ (cf. Part II), one obtains ν -factors for total water, such as are listed in Table IV. From these, one may proceed to compute the partial depression $\Delta\theta$ of the freezing point due to total water, using the formula

$$\Delta\theta = 5.98\nu_2(m_2 + m_2') \{1 - 0.0035\bar{\theta} + 2(\overline{m_2 + m_2'})/10.20\}$$

By subtracting the partial depressions, calculated for total water in molality $m_2 + m_2'$, from the depression calculated for the water originally added in molality m_2 , one obtains the partial depression, called $\Delta\theta'$, corresponding to the water produced from the dinitrogen pentoxide. From these partial depressions, one can now calculate the ν -factors, which we term ν_2' , for the water formed from the dinitrogen pentoxide. The equation used is

$$\Delta\theta' = 5.98\nu_2'm_2'\{1 - 0.0035\bar{\theta}' + 2(m_2 + m_2')/10.20\}$$

The whole calculation up to this stage is illustrated by the figures in Table IV. The headings of the Table anticipate what will be pointed out later, *viz.*, that just the same figures hold if the added solute is dinitrogen tetroxide or dinitrogen trioxide.

The final step in the calculation of theoretical ν -factors for dinitrogen pentoxide, tetroxide, or trioxide consists in adding 4.00 to each of the ν' values given in the last column of Table IV. The addition is made in respect of the two molecules of fully dissociated nitronium or nitrosonium hydrogen sulphate which are assumed to be formed from any of these oxides simultaneously with the one molecule of partly ionised water.

(2.4) *Experimental ν -Factors for Dinitrogen Pentoxide and their Comparison with Theoretical ν -Factors.*—Since our first report (*Nature*, 1946, 158, 480), some new cryoscopic measurements in solvent sulphuric acid, leading to a ν -factor for dinitrogen pentoxide, as well as to one for nitric acid, have been reported by Kuhn (*J. Amer. Chem. Soc.*, 1947, 69, 1974). For the pentoxide he obtained $\nu = 5.50$, a value which, according to our work, is low, and would be even

lower if recalculated by our methods. For nitric acid he records $\nu = 3.97$, a result which is high, and would not be much improved if recalculated.

TABLE IV.

Theoretical ν -factors for water produced from dinitrogen pentoxide, dinitrogen tetroxide, or dinitrogen trioxide, in solvent sulphuric acid containing water.

Depression by					Depression by				
Molality of added N_2O_{3-5} (m_3)	ν_2 for total water.	total water ($\Delta\theta$).	water from N_2O_{3-5} ($\Delta\theta'$).	ν_2' for water from N_2O_{3-5} .	Molality of added N_2O_{3-5} (m_3)	ν_2 for total water.	total water ($\Delta\theta$).	water from N_2O_{3-5} ($\Delta\theta'$).	ν_2' for water from N_2O_{3-5} .
Molality of added water (m_2) = 0.050.					Molality of added water (m_2) = 0.070.				
0.00	1.94	0.583°	—	—	0.00	1.92	0.806°	—	—
0.01	1.91	0.688	0.105°	1.74	0.01	1.89	0.909	0.103°	1.70
0.02	1.88	0.790	0.207	1.71	0.02	1.86	1.007	0.201	1.66
0.03	1.85	0.890	0.307	1.69	0.03	1.83	1.104	0.298	1.64
0.04	1.82	0.986	0.403	1.67	0.04	1.81	1.199	0.393	1.62
0.05	1.80	1.083	0.500	1.65	0.05	1.79	1.293	0.487	1.61

Our measurements were made with dinitrogen pentoxide prepared from nitric acid and phosphoric oxide. It was sublimed from excess of phosphoric oxide, and purified by being twice resublimed through phosphoric oxide in ozonised oxygen between room temperature and -80° . A series of cryoscopic results is recorded in Table V.

TABLE V.

Depression of the freezing point of sulphuric acid by added dinitrogen pentoxide. Comparison of experimental and theoretical ν -factors (Expt. 98).

Molality of added water (m_3) = 0.064.											
Molality N_2O_5 (Δm_2).	F. p. ($^\circ$ c.).	ν (exptl.).			ν (theor.).	Molality N_2O_5 (Δm_2).	F. p. ($^\circ$ c.).	ν (exptl.).			ν (theor.).
		$n = 0$.	$n = 2$.	$n = 3$.				$n = 0$.	$n = 2$.	$n = 3$.	
—	9.827	—	—	—	—	—	—	—	—	—	—
0.00614	9.615	5.74	5.67	5.65	5.72	0.02111	9.086	5.82	5.73	5.69	5.66
0.01247	9.395	5.76	5.68	5.65	5.69	0.02755	8.858	5.83	5.73	5.68	5.64
						0.03452	8.614	5.82	5.70	5.65	5.63

We have calculated the ν -factors both neglecting the effect of solvation of the nitronium salt and also taking this into account, the solvation numbers of 2 and 3 being assumed. In these calculations it is a sufficient approximation to substitute $s_2 = 4$ and $\nu_2 = 6$ in the nearly-unit correction factor of equation (5) of Part I, when solvation is being neglected, and, since $s_2 = 2n + 4$, to write $s_2 = 8$ and $\nu_2 = 6$, and $s_2 = 10$ and $\nu_2 = 6$, where the solvation number n of the nitronium salt is being taken to be 2 and 3, respectively. The sets of ν -factors, calculated from the cryoscopic results with inclusion of the corrections for solvation of the nitronium salt, are to be compared with the theoretical ν -factors given in the last column. These theoretical ν -factors are calculated, as illustrated in Section 2.3, from the already given chemical interpretation of the reactions which take place on dissolving dinitrogen pentoxide in sulphuric acid.

(2.5) *Calculation of a Theoretical Curve for the Freezing-point Depression due to Dinitrogen Pentoxide.*—This calculation is made by the general method already illustrated in Section 1.5 for solute nitric acid. The results of such a calculation for solute dinitrogen pentoxide are given in Table VI, the headings of which anticipate the point, which will be required later, that exactly the same figures apply to the solutes dinitrogen tetroxide and dinitrogen trioxide. The calculation is made for the case in which the sulphuric acid solvent has been pre-treated by the addition of water in 0.07 molal concentration.

Col. 3 of the Table contains the partial depression of freezing point due to the single molecule of water, which is formed from each molecule of dinitrogen pentoxide, and to the pairs of ions into which this water is partly converted in the sulphuric acid solvent. These figures are taken over from Table IV. The next three columns of Table VI contain partial depressions of freezing point calculated as for a quaternary electrolyte, giving the two nitronium and the two hydrogen sulphate ions, which each molecule of dinitrogen pentoxide is assumed to furnish, in addition to the single molecule of water which becomes partly ionised. The depressions given in col. 4 (headed $n = 0$) were calculated by assuming the solvation number n of the nitronium salt to be zero, equation (5) of Part I being employed with the substitutions $s_2 = 2$ and $\nu_2 = 4$, since the formation of one molecule of the quaternary electrolyte needs two molecules of solvent sulphuric

acid. The depressions in cols. 5 and 6 were calculated by assuming the solvation number n of nitronium hydrogen sulphate to be 2 and 3, respectively, the appropriate forms of equation (5) of Part I being employed ($s_2 = 2n + 2$). The values in the last three columns of Table VI are total depressions, obtained by addition of the relevant partial depressions.

TABLE VI.

Calculated depressions of the freezing-point of sulphuric acid by dinitrogen pentoxide, dinitrogen tetroxide, or dinitrogen trioxide.

Molality of added water (m_3).	Molality of added N_2O_{3-5} (Δm_2).	Freezing-point depressions ($^{\circ}C$).						
		Formed H_2O and its ions.	$2(NO_2)^+(HSO_4)^-$.			N_2O_{3-5} .		
			$n = 0.$	$n = 2.$	$n = 3.$	$n = 0.$	$n = 2.$	$n = 3.$
0.070	0.01	0.103	0.240	0.245	0.248	0.343	0.348	0.351
"	0.02	0.201	0.481	0.494	0.500	0.682	0.695	0.701
"	0.03	0.298	0.722	0.745	0.756	1.020	1.043	1.054
"	0.04	0.393	0.963	1.000	1.015	1.356	1.393	1.408
"	0.05	0.487	1.204	1.257	1.283	1.691	1.744	1.770

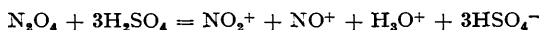
The curve for the figures in the penultimate column, corresponding to the solvation number $n = 2$, is shown in Fig. 1 on p. 2513, in association with points representing the observations. It will be seen that there is a close agreement.

(3) The Solute Dinitrogen Tetroxide.

(3.1) *Theory of the Condition of Dinitrogen Tetroxide in Sulphuric Acid.*—It was shown, though in a somewhat qualitative manner, by Pinck (*J. Amer. Chem. Soc.*, 1927, **49**, 2536), and has been confirmed in this laboratory, that many aromatic compounds, provided that they are not too easily nitrosated, may be smoothly nitrated by solutions of dinitrogen tetroxide in sulphuric acid, but that, in this process, only one of the two nitrogen atoms of the dinitrogen tetroxide becomes introduced as a nitro-group into the aromatic molecule. Even deactivated aromatic compounds, such as nitrobenzene, may be readily nitrated in this way.

This is a significant result, but no well-supported view about the nature of the solutions of dinitrogen tetroxide in sulphuric acid seems to have been advanced before our preliminary publication (*Nature*, 1946, **158**, 480), in which it was suggested that dinitrogen tetroxide undergoes an ionisation, generally similar to that of dinitrogen pentoxide, but differing from the latter in that the tetroxide gives one nitronium ion and one nitrosonium ion in place of the two nitronium ions given by the pentoxide. We recorded at that time that Dr. D. J. Millen had detected in such solutions of dinitrogen tetroxide both the nitronium ion and the nitrosonium ion, as well as the hydrogen sulphate ion, by the method of Raman spectroscopy; and we submitted cryoscopic evidence that ionisation in the form suggested was substantially complete.

(3.2) *Cryoscopic Proof of the Conversion of Dinitrogen Tetroxide into the Nitronium and Nitrosonium Ions.*—The approximate equation for the postulated ionisation is as follows :



Apart from the regeneration of a small proportion of water from its ions, this equation would represent the total change if the dinitrogen tetroxide were to dissolve in either of its possible ionic forms $(NO)^+(NO_3)^-$ or $(NO_2)^+(NO_2)^-$; for, in the first case, the nitrate ion would be converted by the sulphuric acid solvent into nitric acid, and thence into the nitronium ion, whilst in the second, the nitrite ion would yield nitrous acid, and thence a nitrosonium ion.

The above equation represents dinitrogen tetroxide as having a ν -factor of 6; but, as was discussed in connexion with the solute dinitrogen pentoxide, we should expect ν -factors of about 5.78 ± 0.11 on account of the balanced reaction between water and the ions which it forms in solvent sulphuric acid. In our preliminary report (*loc. cit.*) we quoted the cryoscopically determined ν -factor of dinitrogen tetroxide as 5.84. The agreement is tolerable; and it is improved in the more refined treatment now to be described. It is diagnostic of the form of ionisation postulated, and shows that the conversion of dinitrogen tetroxide into the nitronium and nitrosonium ions is quantitative in sulphuric acid.

(3.3) *Experimental ν -Factors for Dinitrogen Tetroxide and their Comparison with Theoretical ν -Factors.*—The dinitrogen tetroxide employed in the present experiments was prepared from 70% nitric acid and solid sodium nitrite, the evolved gas being carried in a stream of oxygen through a condenser arranged to retain nitric acid and water, and into a receiver kept at -80° .

Purified by redistillation in oxygen through phosphoric oxide, the tetroxide was collected at -80° as colourless crystals. A concentrated solution of dinitrogen tetroxide in sulphuric acid was made up for convenience in the addition of the tetroxide to the sulphuric acid in the freezing-point cell (cf. Section 1.3 of Part I). The cryoscopic observations, and the relevant calculations, are reported in Table VII.

TABLE VII.

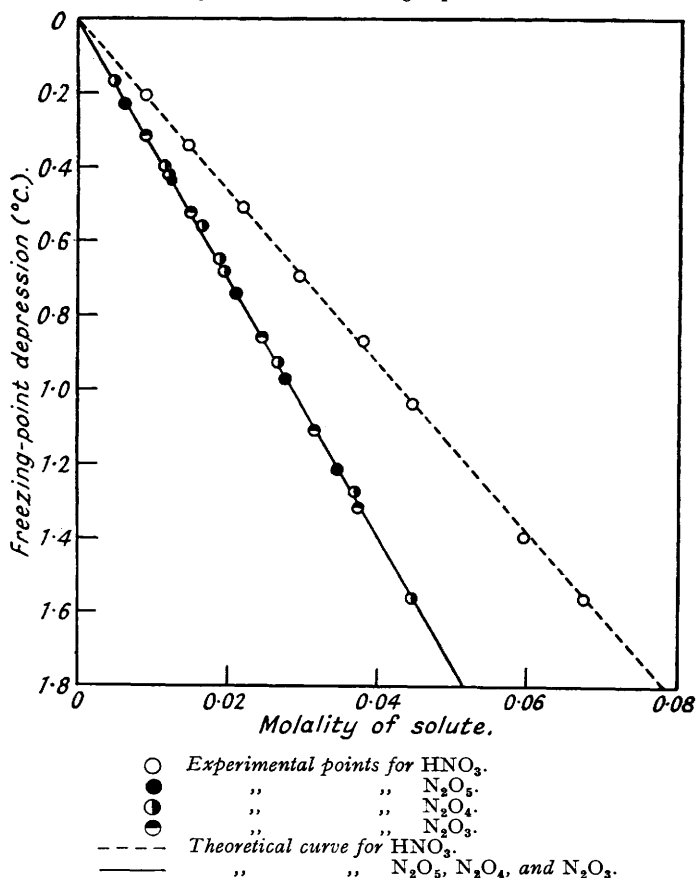
Depression of the freezing point of sulphuric acid by dinitrogen tetroxide. Comparison of experimental and theoretical ν -factors.

Molality of N_2O_4 (Δm_2).	F. p. ($^{\circ}C.$).	ν (exptl.).			ν (theor.).	Molality of N_2O_4 (Δm_2).	F. p. ($^{\circ}C.$).	ν (exptl.).			ν (theor.).
		$n = 0.$	$n = 2.$	$n = 3.$				$n = 0.$	$n = 2.$	$n = 3.$	
—	9.691	—	—	—	—	9.775	—	—	—	—	
0.00481	9.524	5.82	5.76	5.73	5.72	0.01144	9.381	5.72	5.64	5.60	5.69
0.01189	9.273	5.82	5.74	5.70	5.69	0.01868	9.130	5.73	5.64	5.59	5.66
0.01637	9.113	5.86	5.76	5.71	5.67	0.02646	8.856	5.76	5.65	5.61	5.64
0.01933	9.012	5.82	5.72	5.68	5.66	0.03677	8.501	5.75	5.61	5.56	5.62
—	—	—	—	—	—	0.04454	8.217	5.80	5.65	5.57	5.61

The calculations of ν -factors from the experimental results are made exactly as in the case of dinitrogen pentoxide, although, for the purpose of computing the correction for solvation, an estimate had to be made of the solvation number of the nitronium ion. We have already

FIG. 1.

Observed depressions of the freezing point of sulphuric acid, and theoretical freezing-point depression curves, for solute nitric acid, and for the solutes dinitrogen pentoxide, tetroxide, and trioxide.



estimated that of the nitronium ion to be close to 2. Taking account not only of the cryoscopic data for dinitrogen tetroxide, but also of those for dinitrogen trioxide which are reported below, we estimate the solvation number of the nitrosonium ion also as approximately 2. The corrected experimental values of ν are given in col. 4 of Table VII. These are to be compared with the theoretical ν -factors entered in the last column of the Table. As is noted in Section 3.2, the theoretical ν -factors for dinitrogen tetroxide, *i.e.*, those required by the postulated form of ionisation of this substance, may be calculated in the same way as for dinitrogen pentoxide.

Another form of comparison between theory and experiment is illustrated in Fig. 1 (p. 2513). As was noted in Section 2.5, a theoretical curve for the depression of freezing point produced by dinitrogen tetroxide may be calculated exactly as for dinitrogen pentoxide; it is, in fact, the same curve. This curve appears in the figure, as also do the points which represent the observed depressions given in Table VII. The agreement is evidently satisfactory.

(4) *The Solute Dinitrogen Trioxide.*

(4.1) *Theory of the Condition of Dinitrogen Trioxide in Sulphuric Acid.*—It was first suggested by Hantzsch and Berger (*Z. anorg. Chem.*, 1930, **190**, 321) that the substance long known as nitrosylsulphuric acid, or "chamber crystals," has the ionic constitution of nitrosonium hydrogen sulphate, $(\text{NO}^+)(\text{HSO}_4^-)$. Their evidence for this structure was derived from the cryoscopically determined molecular weight in sulphuric acid solution, from comparisons with other nitrosonium salts, such as the perchlorate, and from the fact that solutions of the substance in sulphuric acid nitrosate, but do not nitrate, suitable aromatic compounds, such as dimethylaniline. The fundamental Raman frequency of the nitrosonium ion was found by Angus and Leckie in solid nitrosonium hydrogen sulphate, and also in nitrosonium perchlorate; and they found it again in solutions of chamber crystals in sulphuric acid (*Proc. Roy. Soc.*, 1935, *A*, **149**, 327; *A*, **150**, 615).

Dinitrogen trioxide, although itself a deep blue, forms a colourless solution in sulphuric acid. Such solutions are closely similar in all their more obvious chemical and physical properties, for instance, in their power of nitrosating aromatic compounds, and, as is shown in detail in an accompanying paper (*J.*, 1950, paper no. 508), in their Raman spectrum, to solutions of nitrosonium hydrogen sulphate in sulphuric acid; and thus the suggestion becomes almost inevitable that solutions of dinitrogen trioxide in sulphuric acid contain nitrosonium ions and hydrogen sulphate ions as the characteristic and essential solutes. In our preliminary account of this work (*Nature*, 1946, **158**, 480), we put forward this hypothesis, supposing that the dinitrogen trioxide undergoes in sulphuric acid a quantitative ionisation quite similar to that of dinitrogen pentoxide or dinitrogen tetroxide, except, naturally, that the trioxide will produce two nitrosonium ions instead of two nitronium ions or one cation of each kind. We recorded at that time that Dr. D. J. Millen had found the characteristic Raman frequencies of the nitrosonium and hydrogen sulphate ions in solutions of dinitrogen trioxide in sulphuric acid; and we ourselves presented cryoscopic evidence in favour of the ionisation suggested.

(4.2) *Cryoscopic Proof of the Conversion of Dinitrogen Trioxide into the Nitrosonium Ion.*—The approximate equation for the assumed ionisation is



Apart from the neglected partial regeneration of water from its ions, this equation expresses what would be the total change if the dinitrogen trioxide were to dissolve in its ionic form $(\text{NO}^+)(\text{NO}_2^-)$, and the nitrite ion were then to be converted, as it would be in the sulphuric acid solvent, into nitrous acid, and thence into a second nitrosonium ion.

The above equation gives to dinitrogen trioxide a ν -factor of 6; but, just as for dinitrogen pentoxide and dinitrogen tetroxide, we have to expect somewhat smaller ν -factors, owing to the balanced reaction between water and its ions. As in the previously discussed cases, we may, in advance of detailed calculation, set down the ν -factors theoretically to be expected as lying in the range 5.78 ± 0.11 . In our preliminary report we gave 5.85 as the cryoscopically estimated ν -factor. The agreement even at this stage is tolerable, but a more refined treatment establishes with precision the ionisation postulated.

(4.3) *Experimental ν -Factors for Dinitrogen Trioxide and their Comparison with the Theoretical ν -Factors.*—The dinitrogen trioxide employed in the present work was prepared by the interaction of solid sodium nitrite with 70% nitric acid. The evolved gases were carried in a stream of nitrogen through a reflux condenser arranged to retain nitric acid and water, and were then condensed at -80° . The liquid condensate was distilled at as low a temperature as possible,

in a fairly rapid stream of dry nitric oxide, through phosphoric oxide; and it was again condensed at -80° . Dry nitric oxide was passed for some hours through the condensate, which was preserved at -80° in an atmosphere of nitric oxide.

Owing to the tendency of dinitrogen trioxide to decompose when allowed to become warm, some difficulty was experienced in the preparation of those concentrated solutions of known composition of dinitrogen trioxide in sulphuric acid which were required as a means for the addition of accurately weighed amounts of dinitrogen trioxide to the sulphuric acid in the freezing-point cell (cf. Section 1.3, Part I). Our attempts to prepare such solutions by direct addition, *i.e.*, by the addition of liquid dinitrogen trioxide at -80° to solid sulphuric acid, the whole being then allowed to warm to above the eutectic temperature in a closed tube until the liquid contents of the tube became homogeneous, always produced small residues of unabsorbed nitric oxide. This meant that a little of the dissolved material was dinitrogen tetroxide, and that therefore a measurement of the increase in weight of the solution above that of the originally used solvent would not give accurately the molecular composition of the solution. Dr. Millen was usually able to find in the Raman spectra of solutions prepared by this method a faint but distinct record of the characteristic frequency of the nitronium ion, besides, of course, a strong record of the fundamental frequency of the nitrosonium ion. The effect of the disturbance was also easily detectable in our cryoscopic measurements with these solutions, which gave non-reproducible ν -factors always from 1% to 5% too low.

Correct results were obtained when the dinitrogen trioxide was carried into the sulphuric acid by distillation in a stream of dry nitric oxide at the lowest convenient temperatures. The solution in the sulphuric acid absorbs a little of the nitric oxide with the formation of a pale violet colour; but this nitric oxide is at once evolved with discharge of the colour when, after the transference, the nitric oxide atmosphere above the sulphuric acid is replaced, first by nitrogen, and then by dry air, in preparation for the final weighing. Some cryoscopic results obtained by this method are recorded in Table VIII.

TABLE VIII.

Depression of the freezing point of sulphuric acid by dinitrogen trioxide. Comparison of experimental and theoretical ν -factors (Expt. 101).

Molality of added water (m_3) = 0.070.

Molality of N_2O_3 (Δm_2).	F. p. ($^{\circ}C.$).	ν (exptl.).			ν (theor.).	Molality of N_2O_3 (Δm_2).	F. p. ($^{\circ}C.$).	ν (exptl.)			ν (theor.).
		$n = 0.$	$n = 2.$	$n = 3.$				$n = 0.$	$n = 2.$	$n = 3.$	
—	9.758	—	—	—	—	0.02448	8.904	5.79	5.68	5.63	5.65
0.00901	9.446	5.75	5.68	5.64	5.70	0.03140	8.651	5.86	5.73	5.68	5.63
0.01498	9.237	5.77	5.68	5.64	5.68	0.03754	8.441	5.83	5.69	5.63	5.62

The calculations of the ν -factor are made exactly as for dinitrogen pentoxide and dinitrogen tetroxide. The ν -factors calculated with the solvation number $n = 2$ for nitrosonium hydrogen sulphate are in columns 4 and 8 of the Table; and they are to be compared with the theoretical ν -factors. These are calculated from the postulated chemical changes, as described in Section 2.3.

The comparison between theory and experiment is shown again in Fig. 1. As was noted in Section 2.5, the theoretical curves for the depression of the freezing point of sulphuric acid by dinitrogen pentoxide, tetroxide, and trioxide are identical. The diagram shows that the observational points for dinitrogen trioxide, no less than those for the tetroxide and the pentoxide, lie well on this common curve.

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WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

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