507. *Vibrational Spectra of Ionic Forms of Oxides and Oxy-acids of Nitrogen. Part II. Raman Spectra of Solutions in Sulphuric Oleum. The Polysulphuric Acids. Ionisation of Nitric Acid in Oleum.*

By D. J. Millen.

Chédin's observations on the Raman spectra of fuming sulphuric acid of various concentrations are analysed. The frequencies are separated into those belonging to H_2SO_4, $H_2S_2O_7$, $H_2S_3O_{10}$, $H_2S_4O_{13}$ or higher poly-acids, and SO_3. Spectral characteristics suitable for the detection of the different polysulphuric acids are pointed out.

New observations are recorded on the Raman spectra of solutions of sulphates in oleum of concentrations in the range over which disulphuric acid is the most important polysulphuric acid. These spectra are analysed. The frequencies, collectively assigned to disulphuric acid, are separated into those belonging to the molecular, and to each of the anionic, forms, $H_2S_2O_7$, $HS_2O_7^-$, $S_2O_7^{--}$. Their spectral identification is discussed.

Chédin's observations on the Raman spectra of solutions of nitric acid in oleum are supplemented by some new observations. All these results are now chemically interpreted on the basis of the above spectral analyses. The following conclusions are drawn. (1) In a dilute solution of nitric acid in dilute or moderately dilute oleum, the following reaction takes place nearly completely:

$$HNO_3 + 2H_2S_2O_7 = NO_2^+ + HS_2O_7^- + 2H_2SO_4$$

(2) On the addition of sufficient nitric acid to a dilute or moderately dilute oleum, the following reaction occurs nearly completely:

$$HNO_3 + H_2S_2O_7 = NO_2^+ + HSO_4^- + H_2SO_4$$

(3) In more concentrated oleum, and with correspondingly more concentrated nitric acid, the second reaction does not go nearly to completion, because its products tend to revert to those of the first reaction, in consequence of the following balanced process, which shifts towards the right with increasing concentration:

$$2NO_2^+ + 2HSO_4^- = NO_2^+ + HS_2O_7^- + HNO_3$$

All this is in good agreement with the cryoscopic and preparative chemical evidence.

The Raman spectra of mixtures of nitric acid with fuming sulphuric acid have been extensively studied by Chédin. His results are now supplemented, and the interpretation revised. It will be necessary to refer first to the Raman spectra of the sulphuric oleums themselves, and then to the spectra given by sulphates dissolved in oleum of various strengths; only then shall we be in a position to discuss the spectra given by mixtures of nitric acid with fuming sulphuric acid.

(1) *Raman Spectra of Sulphuric Oleums.*

(1.1) *Dependence of the Spectrum on the Strength of the Oleum.*—The "strength" of an oleum will be designated as usual by the content of sulphur trioxide, supposing sulphur trioxide and sulphuric acid to be the sole components of oleum. An $x\%$ oleum is that which could be made by mixing $100 - x$ parts by weight of pure sulphuric acid with x parts of sulphur trioxide.

In an accompanying paper (*J.*, 1950, 2516) Gillespie offers cryoscopic evidence to the effect that fuming sulphuric acid contains, not only disulphuric acid, $H_2S_2O_7$, but also trisulphuric acid, $H_2S_3O_{10}$, and tetrasulphuric acid, $H_2S_4O_{13}$; it may contain still higher polysulphuric acids, as well as free sulphur trioxide. The work now to be described gives support to this view of the constitution of oleum.

The Raman spectra of oleums have been studied by Gopala Pai (*Phil. Mag.*, 1935, **20**, 616) and by Chédin (*Compt. rend.*, 1935, **201**, 724; *Ann. Chim.*, 1937, **8**, 243). Some of Chédin's results are quoted in Table I. It will be convenient to note that a 45%, a 62%, and a 71% oleum have the compositions of di-, tri-, and tetra-sulphuric acid, respectively.

As sulphur trioxide is added progressively to pure sulphuric acid, the Raman lines of molecular sulphuric acid diminish in intensity and finally disappear, the strongest lines vanishing at compositions approximating to 45% oleum, as we should expect from the fact that the freezing-point curve passes through a maximum at this composition.

TABLE I.

Raman frequencies (*cm.*$^{-1}$) *of sulphuric acid* (*after Chédin*).

H_2SO_4.	10% Oleum.	23% Oleum.	36% Oleum.	51% Oleum.	65% Oleum.
—	—	—	—	246 (w)	245 (mw)
—	315 (mw)	305	300 (w)	297 (w)	295 (w)
		327 (m)	325 (m)	331 (m)	330 (m)
395 (ms)	388 (m)	390 (mw)	—	—	—
430 (ms)	427 (m)	427 (mw)	—	—	—
—	—	—	480 (w)	480 (mw)	484 (mw)
—	—	—	525 (w)	535 (mw)	536 (m)
560 (ms)	562 (m)	565 (m)	565 (w)	—	—
—	—	—	—	688 (w)	688 (m)
—	735 (w)	740 (m)	735 (m)	740 (ms)	737 (m)
917 (s)	915 (ms)	915 (m)	904 (mw)	—	—
972 (mw)	970 (mw)	975 (mw)	957 (mw)	960 (mw)	957 (m)
—	—	—	—	1075 (mw)	1075 (s)
1140	1140	1160	1160 (m)	—	—
—	—	1240	1250 (ms)	1250 (ms)	1252 (ms)
1370	1393	1420	1440 (mw)	1450 (m)	1450 (m)

(1.2) *Raman Frequencies of Disulphuric Acid.*—Before the spectrum of sulphuric acid has completely vanished, as the strength of the oleum is increased, a new spectrum makes its appearance. It consists of six frequencies, which can plausibly be assigned to disulphuric acid. Two of them, 325 and 735 cm.$^{-1}$, are prominent and characteristic : they can be used to diagnose the presence of disulphuric acid. Two more, 1240 and 1440 cm.$^{-1}$, are moderately strong, but appear to be the common possession of disulphuric acid, and at least one, possibly several, of the higher polysulphuric acids. A further one, 960 cm.$^{-1}$, is certainly possessed by sulphuric acid, and appears to be common to this acid, to disulphuric acid, and at least one, perhaps several, of the higher polysulphuric acids. The last frequency, 300 cm.$^{-1}$, appears as a satellite of the lowest of those already mentioned; but it is weak, and sometimes remains unresolved in the spectrum. These assignments may here be summarised :

$$H_2S_2O_7\left\{\begin{array}{l}\text{325, 735 cm.}^{-1}\text{ (strong, diagnostic); 300 cm.}^{-1}\text{ (weak)}\\ \text{1240, 1440 cm.}^{-1}\text{ (in common with higher poly-acids)}\\ \text{960 cm.}^{-1}\text{ (in common with }H_2SO_4\text{ and higher acids)}\end{array}\right.$$

(1.3) *Raman Frequencies of Trisulphuric Acid.*—When the strength of the oleum is increased further, two additional lines appear. Their frequencies are 480 and 530 cm.$^{-1}$; and their intensities increase sharply, while those of the lines already assigned as characteristic of disulphuric acid either remain the same or begin to fall. Evidently these new lines mark the incursion of some new substance in the oleum; and, as this is the first incursion of the kind since disulphuric acid made itself manifest in the spectrum, it is natural to identify the new material as trisulphuric acid.

The frequency 480 cm.$^{-1}$ appears to be characteristic of trisulphuric acid. The frequency 530 cm.$^{-1}$ seems to be equally diagnostic, provided that the oleum for which it is observed is not too strong. This qualification is necessary because very strong oleum contains free monomeric sulphur trioxide in sufficient amount to produce its own spectrum, and this contains a fairly prominent Raman line near 530 cm.$^{-1}$. Nevertheless the first appearance of the frequency 530 cm.$^{-1}$, when, starting with pure sulphuric acid, the strength of the oleum is gradually increased, cannot be ascribed to free sulphur trioxide, because at that stage of concentration the much stronger sulphur trioxide frequency, 1075 cm.$^{-1}$, is not yet showing.

A study of the intensities of the Raman lines of oleum, as functions of the strength of the oleum, shows that the source of the frequencies 480 and 530 cm.$^{-1}$ also has active frequencies coincident with, or quite close, to some of the active disulphuric acid frequencies; these are 960, 1250, and 1450 cm.$^{-1}$. The following is a summary of the frequencies here assigned to trisulphuric acid :

$$H_2S_3O_{10}\left\{\begin{array}{l}\text{480 cm.}^{-1}\text{ (strong, diagnostic)}\\ \text{530 cm.}^{-1}\text{ (strong, diagnostic except in strong oleum)}\\ \text{960, 1250, 1450 cm.}^{-1}\text{ (in common with other acids)}\end{array}\right.$$

(1.4) *Raman Frequencies of Tetrasulphuric Acid, etc.*—When the strength of the oleum is increased still further, several new lines appear, notably those at 245, 688, and 1075 cm.$^{-1}$. These lines gain considerably in intensity with continued increase in the strength of the oleum; and so also does one of the previously assigned lines, *viz.*, that at 530 cm.$^{-1}$, although all the other lines which are considered to be characteristic of di- and tri-sulphuric acid become weaker or remain of about the same intensity. These new appearances and intensifications clearly mark the intrusion of a new substance, or, possibly, of several new substances in overlapping ranges of concentration. Three compounds, or types of compound, might be considered for assignment to the frequencies concerned, *viz.*, monomeric sulphur trioxide, the polymeric forms of sulphur trioxide, and polysulphuric acids higher than trisulphuric acid. We shall consider these in turn.

Sulphur trioxide, a planar trigonal molecule (Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360), has three fundamental frequencies allowed in the Raman spectrum (cf. Gerding and Lecomte, *Physica*, 1939, **6**, 737). The totally symmetrical frequency, 1075 cm.$^{-1}$, is much the strongest of the three. The next in order of intensity is the bending frequency, 530 cm.$^{-1}$. The third, the degenerate stretching frequency, 1330 cm.$^{-1}$, is weak in the Raman spectrum. In view of the intensity and relative sharpness with which 1075 cm.$^{-1}$ appears in the Raman spectrum of strong oleum, it is almost certainly correct to assign it, as Chédin has done, to sulphur trioxide; and, the presence of sulphur trioxide being admitted, it seems reasonable to attribute to the same substance the observed intensification of the frequency 530 cm.$^{-1}$.

The Raman spectrum of those polymeric forms of sulphur trioxide which are present in the liquid substance near the ordinary temperature has been studied by Bhagavantam (*Indian J. Physics*, 1930, **5**, 48), and by Gerding and his collaborators (*Z. physikal. Chem.*, 1937, **35**, *B*, 193, 216; *Rec. Trav. chim.*, 1937, **56**, 968). A large number of Raman frequencies have been observed, but it is difficult to establish any connexion between them and the oleum frequencies 245 and 688 cm.$^{-1}$, for which we wish now to account. For none of the frequencies of polymeric sulphur trioxide is close to 245 cm.$^{-1}$; and, although two of them are fairly close to 688 cm.$^{-1}$, they are represented by lines of only moderate intensity, and several stronger lines of the polymeric sulphur trioxide spectrum are absent from the oleum spectrum.

On these somewhat negative grounds, one inclines to the view that the frequencies 245 and 688 cm.$^{-1}$ belong to one or more of the polysulphuric acids higher than trisulphuric acid; and as they are amongst the first new frequencies to come into the spectrum, after those which are considered to characterise trisulphuric acid, when the strength of the oleum is increased, it seems natural to assign them to tetrasulphuric acid. A consideration of the intensities of other lines in the spectrum suggests that several of the frequencies of trisulphuric acid, notably 960 and 1250 cm.$^{-1}$, are also possessed by the source of the frequencies 245 and 688 cm.$^{-1}$. These further assignments may be summarised as follows :

$$H_2S_4O_{13},\ \text{etc.}\begin{cases}245,\ 688\ \text{cm.}^{-1}\ \text{(strong, diagnostic)}\\960,\ 1250\ \text{cm.}^{-1}\ \text{(in common with other acids)}\end{cases}$$

It is concluded also that monomeric sulphur trioxide is present in quantity in oleums of strength above 50%; and that it is responsible for the frequency 1075 cm.$^{-1}$, and for part of the intensity of the frequency 530 cm.$^{-1}$. It appears that, in oleums of strengths up to 70%, the polymeric forms of sulphur trioxide are not present in sufficient amount to have a notable influence on the spectrum.

(2) *Raman Spectra of Solutions of Sulphates in Oleum.*

(2.1) *Preliminary Consideration of the Anions in Oleum.*—Before we can expect to be able to interpret the Raman spectra of solutions of nitric acid in oleum, it is necessary to know something of the spectral properties of the anions which are liable to be formed in oleum solutions. In dilute oleum, in which the principal molecular solute is disulphuric acid, the chief anions that can be produced by added substances, acting as bases in such solutions, are the hydrogen sulphate ion and the hydrogen disulphate ion. In the sulphuric acid solvent, disulphuric acid is an " acid " of medium strength, the hydrogen disulphate ion is the anion of a " neutral " salt, and the hydrogen sulphate ion is the strongest " base " that can exist in any considerable quantity in such a solution. These three entities bear the same sort of relation to one another as do acetic acid, the acetate ion, and the hydroxide ion, in solvent water. Thus molecular disulphuric acid and the hydrogen sulphate ion cannot coexist in any considerable concentration, but the hydrogen disulphate ion can coexist with either molecular disulphuric acid or the hydrogen sulphate ion. All this is clear from the work of Gillespie on the freezing points of solutions of sulphates in oleums (*J.*, 1950, 2516).

There are some further matters to be taken into account, which also follow from Gillespie's results. The hydrogen disulphate ion, although called " neutral " as a first approximate description, is actually somewhat basic; for in the absence of free disulphuric acid it undergoes a limited, but appreciable, degree of solvolysis to the hydrogen sulphate ion. In addition, the hydrogen disulphate ion is a very weak acid, such as one might compare, for instance, with the hydrogen phosphate ion of an aqueous solution : in the presence of an excess of basic hydrogen sulphate ions, the hydrogen disulphate ion in a sulphuric acid solution is partly converted into the doubly charged disulphate ion.

In general, polysulphuric acids higher than disulphuric acid are present in oleum. However, the higher polysulphates are not expected to exist in sufficient amount in solutions of bases in weak oleums to have any notable effect on the spectra. On the other hand, a complicated situation could arise in solutions of bases in strong oleum in which the higher polysulphuric acids are present in important quantities.

(2.2) *Description of the Spectra.*—Table II contains a number of Raman frequencies, all measured as the frequency displacements of Stokes lines excited by Hg 4358 A. The figures in column 1 refer to sulphuric acid, which is the solvent throughout ; they are given for comparison. So also are the figures in column 2, which relate to an oleum of the general type of those which were used for the preparation of solutions of sulphates. It is an oleum for which the spectrum of disulphuric acid is developed strongly, but the spectra of the higher polysulphuric acids, and the spectrum of sulphur trioxide, do not appear. The frequencies in the columns headed A—D refer to solutions of sulphates; and they are arranged in order of decreasing acidity and increasing basicity.

TABLE II.

Raman frequencies (*cm.*$^{-1}$) *of solutions of sulphates in sulphuric oleum.*

Pure H_2SO_4.	23% Oleum.	Sulphates in oleum.*			
		A.	B.	C.	D.
—	316 (m)	317 (ms)	323 (m)	322 (m)	326 (vw)
395 (ms)	390 (mw)	386 (mw)	393 (mw)	396 (mw)	407 (m)
430 (ms)	427 (mw)	414 (mw)	423 (mw)	420 (mw)	vis. (m)
560 (ms)	565 (m)	570 (ms)	564 (ms)	561 (ms)	569 (ms)
—	740 (m)	735 (m)	734 (mw)	738 (mw)	vis. (vw)
917 (s)	915 (ms)	908 (s)	909 (s)	896 (s)	892 (s)
972 (mw)	975 (mw)	975 (w)	971 (w)	vis. (w)	—
—	—	—	—	1052 (m)	1042 (s)
—	—	1085 (w)	1081 (ms)	1085 (ms)	1092 (w)
1140	1160	1148	1171	1183	1180
—	1240	1227 (m)	1210 (mw)	bands	bands
1370	1420	1391 (w)	1390 (mw)		

* The entry " vis." means that the Raman line was seen but not measured. The usual reason was that the intensity maximum was too smoothed-off to be accurately located.

Comparing the first two columns, one notices that the spectrum of the oleum exhibits all the stronger Raman frequencies which were shown in Section 1.2 to characterise disulphuric acid, notably the frequencies 325, 735, and 1240 cm.$^{-1}$.

The sulphate solution A is of an " acid " type. It is a moderately dilute solution of potassium hydrogen sulphate in excess of oleum; a quantitative statement of composition will be given later. All that need be noted now is that the composition is such as to leave disulphuric acid in excess, after the added hydrogen sulphate ion has been fully expended in decomposing disulphuric acid by the following proton-transfer process :

$$HSO_4^- + H_2S_2O_7 = H_2SO_4 + HS_2O_7^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

This solution would be denoted by a point well to the right of the " neutral " line (the vertical line) in Gillespie's diagram (*J.*, 1950, 2521), and a little to the left of the sloping line which represents disulphuric acid as the only solute. On passing from the oleum itself to the sulphate solution A, the concentration of disulphuric acid will remain qualitatively similar. The only solute species which (apart from the spectrally non-significant potassium ion) exhibits a sharp relative increase of concentration on passing from the oleum to solution A is the hydrogen disulphate ion It follows that the spectrum of solution A can be understood if it is assumed that the newly appearing frequency 1083 $\pm$ 2 cm.$^{-1}$ (the frequency 1092 cm.$^{-1}$ will be shown to have a different origin) belongs to the hydrogen disulphate ion (cf. also Part IV, *J.*, 1950, paper no. 509).

In Part I (*J.*, 1950, 2576) it was shown that the most characteristic frequency of the hydrogen sulphate ion is about 1050 cm.$^{-1}$, and that, indeed, this anion has no other Raman frequency that can be fully resolved from the frequencies of solvent sulphuric acid. In the spectrum of solution A we do not find the frequency 1050 cm.$^{-1}$, but we do find 1083 cm.$^{-1}$, a clear indication that, in the presence of a large excess of molecular disulphuric acid, the reaction of equation (1) proceeds to completion.

Solution B is " neutral," as this term applies to solutions in sulphuric acid. It is prepared by adding 1 mol. of ammonium sulphate to an oleum whose quantity and composition can be expressed by the statement that it contains 2 mols. of disulphuric acid. Since the reaction

$$SO_4^{--} + 2H_2S_2O_7 = H_2SO_4 + 2HS_2O_7^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

may be assumed, the solution has the composition of a solution of ammonium hydrogen disulphate in sulphuric acid. It would be represented by a point on the neutral line of Gillespie's diagram.

In the Raman spectrum of this solution, the frequency 1083 cm.$^{-1}$ is found to be much intensified. This is intelligible, if, as is suggested, the frequency is characteristic of the hydrogen disulphate ion, which must be the principal solute here present, apart from the ammonium ion. The other significant result is that the frequencies 325, 735, and 1240 cm.$^{-1}$, although they appear more weakly than before, are not absent from the spectrum of this solution. There are two conceivable reasons for this. One is that the hydrogen disulphate ion is solvolysed, as may be represented by reading equation (1) from right to left, with the formation of a certain amount of molecular disulphuric acid, and also the hydrogen sulphate ion. However, it is difficult to believe that this is the main reason for the appearance of the three frequencies, because of the non-appearance of the frequency, 1050 cm.$^{-1}$, of the hydrogen sulphate ion. The alternative hypothesis is that the three frequencies of disulphuric acid are not the exclusive possession of the molecular form of the acid, but are common to the acid and its anion; for we must expect that molecular disulphuric acid and the hydrogen disulphate ion will have a number of nearly coincident frequencies, just as have sulphuric acid and the hydrogen sulphate ion (cf. Part I). A conclusion concerning this matter will be reached in Section 2.3. In further explanation of the observations, it should be mentioned that the highest of the three disulphuric acid frequencies is not satisfactorily measured, because of overlapping by the ammonium ion bands. The ammonium ion has, in theory, a doubly degenerate, and a triply degenerate, bending vibration; but in solution, the degeneracies are split, and the separated frequencies are broadened by hydrogen bonding until they merge into a continuous band, which extends over most of the spectral region 1200—1500 cm.$^{-1}$. Other frequencies in this neighbourhood may therefore be rendered difficult or impossible to measure.

Solution C is " basic." It is prepared by using twice the preceding proportion of ammonium sulphate. Since the reaction

$$SO_4^{--} + H_2S_2O_7 = HSO_4^- + HS_2O_7^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

may be assumed, the solution may be described as containing an equimolecular mixture of the neutral solute, ammonium hydrogen disulphate, with the basic solute, ammonium hydrogen sulphate. The composition would be represented by a point on the left of the neutral line on Gillespie's diagram (*J.*, 1950, 2521), and close to a line (not drawn) which would pass through the freezing-point maxima in this region. Indeed, the composition is so chosen that it corresponds approximately to the end-point of the water-titration of oleum solutions (Gillespie, *loc. cit.*), and to the freezing-point maximum which is obtained by adding water to a solution of sulphates in oleum.

In the spectrum of this solution, we find side by side the diagnostic frequencies of the hydrogen sulphate and hydrogen disulphate ions, 1050 cm.$^{-1}$ and 1083 cm.$^{-1}$, the latter in rather greater spectral strength than the former. We also observe, though with a further slight diminution of intensity as compared with solution B, the two disulphuric acid frequencies 325 and 735 cm.$^{-1}$. The third of the disulphuric acid frequencies discussed above is obscured by the ammonium ion bands in this spectrum.

Solution D may be classified as strongly " basic." It would be represented by a point well down the descending branch of a freezing-point curve such as those which appear on the left of Gillespie's diagram. Four times the preceding proportion of ammonium sulphate was employed for the preparation of this solution. Assuming the reaction

$$4SO_4^{--} + H_2S_2O_7 + 3H_2SO_4 = 7HSO_4^- + HS_2O_7^- \quad . \quad . \quad . \quad . \quad (4)$$

one could describe the solute as consisting of a mixture of 7 mols. of ammonium hydrogen sulphate with 1 mol. of ammonium hydrogen disulphate.

In the spectrum of solution D, the characteristic frequency of the hydrogen sulphate ion is strongly developed. The spectrum also contains a somewhat weak frequency 1092 cm.$^{-1}$. This value occurs so regularly when an excess of hydrogen sulphate ions is present, that one naturally connects it with the expected balanced reaction

$$HSO_4^- + HS_2O_7^- = H_2SO_4 + S_2O_7^{--} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and assigns the frequency to the doubly charged disulphate ion (cf. also Part IV, *J.*, 1950, 2516).

Microphotometer records of parts of the Raman spectra of the four sulphate solutions are reproduced in Fig. 1.

(2.3) *Frequencies of the Molecular and Anionic Forms of Disulphuric Acid.*—It is helpful to make some approximate calculations of the concentrations of the various entities which are present in the solutions whose Raman frequencies are recorded in Table II. The solution A was prepared from 8 parts by weight of potassium hydrogen sulphate and 100 parts of 30% oleum. Solutions B, C, and D were prepared from 33%, 25%, and 10% oleum, respectively, together with ammonium sulphate in the proportions stated already.

In these calculations, two equilibrium constants, due to Gillespie, are utilised, *viz.*, the first acidity constant of disulphuric acid, and the solvolysis constant for the hydrogen disulphate ion (cf. *J.*, 1950, 2516). We are now concerned with solutions which are considerably more concentrated than those for which the equilibrium constants were determined, but it may be hoped that one can arrive at the correct orders of magnitude of the quantities in which we are interested by the use of these constants. Because the mol.-fraction of total solute is not now small in comparison with that of the solvent, it is convenient to re-express the equilibrium constants in forms which show the solvent concentration explicitly :

$$[H_3SO_4^+][HS_2O_7^-]/[H_2S_2O_7][H_2SO_4] = 0{\cdot}0020$$
$$[H_2S_2O_7][HSO_4^-]/[HS_2O_7^-][H_2SO_4] = 0{\cdot}00080$$

These constants are independent of the units of concentration, provided that they are molecular units.

Table III contains the calculated compositions of the different solutions. They are expressed as the number of molecules or ions of each species which are present in as much of a solution as would contain 100 atoms of sulphur—this being an amount which cannot be changed, as the total number of molecules and ions can be changed, by a shifting of some of the equilibria. For lack of knowledge of the second acidity constant of disulphuric acid, we cannot calculate the concentrations of normal disulphate ions, or take account of the other consequences of the balanced reaction (5). It is probable that a small proportion of what are calculated as hydrogen disulphate ions in solution C, actually exist as normal disulphate ions; and that a large proportion of what are entered as hydrogen disulphate ions in solution D really consist of normal disulphate ions.

TABLE III.

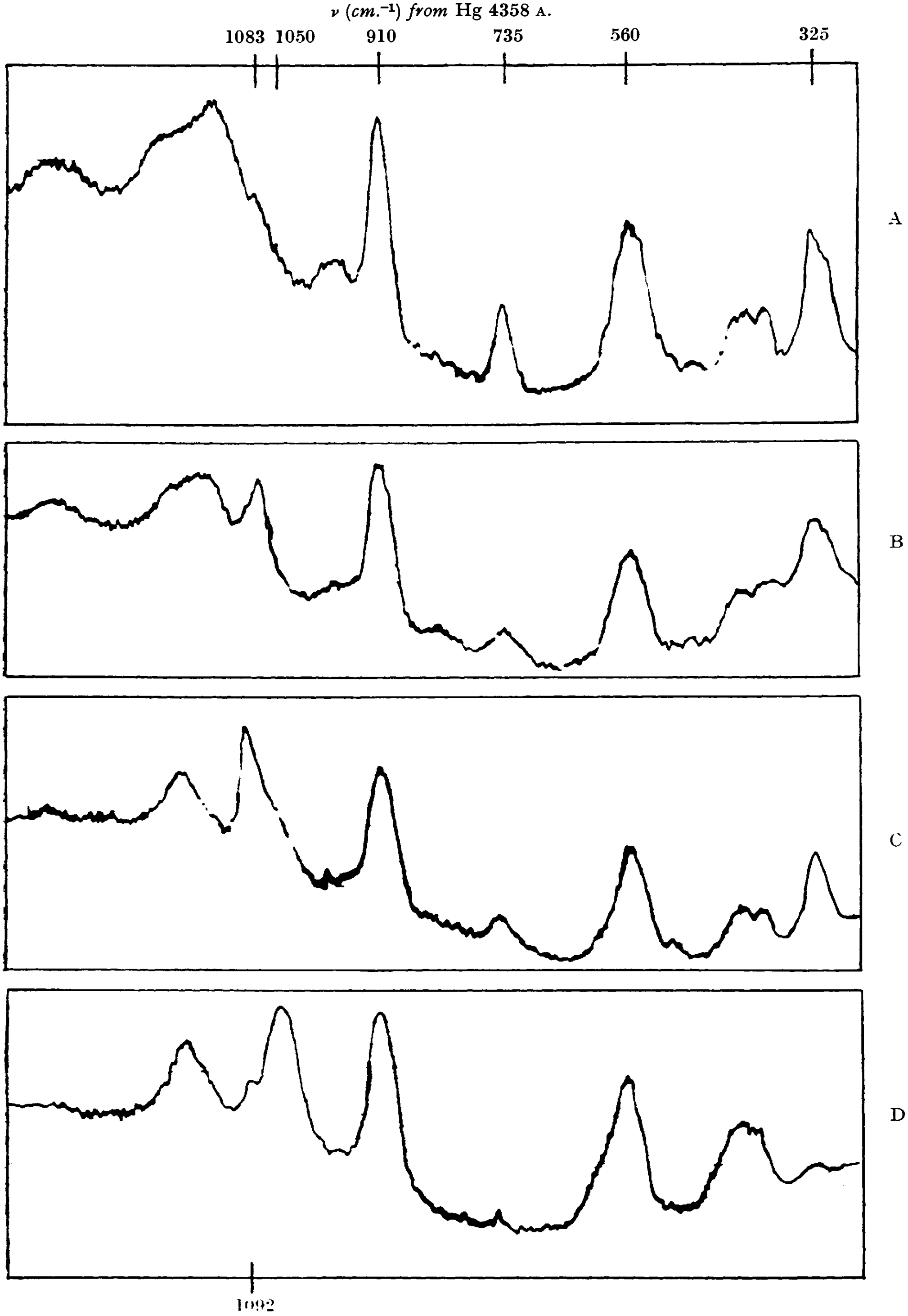
Calculated molecular compositions of the solutions of Table II.

	100% H_2SO_4.	23% Oleum.	Sulphate solutions.			
			A.	B.	C.	D.
$H_3SO_4^+$	0·1	1·6	0·3	0·0	0·0	0·0
H_2SO_4	99·7	45·0	32·8	35·4	32·5	27·1
HSO_4^-	0·1	0·0	0·0	0·9	22·5	56·8
$H_2S_2O_7$	0·0	25·1	28·2	0·9	0·0	0·0
$HS_2O_7^-$	0·1	1·6	5·2	30·5	22·5	8·1

Let us consider, in the light of these figures, the variations of intensity, from one solution to another, of the different Raman lines representing the various solutes. We commence with the lines in the frequency region 1050—1090 cm.$^{-1}$, which are essentially characteristic of the anions. Taking account of the variations, from one solution to another, of the calculated concentration of the hydrogen disulphate ion, as given in Table III, it is intelligible that the frequency 1083 cm.$^{-1}$, which is assigned to, and considered to be diagnostic for, this ion, should not appear in the spectrum of sulphuric acid, or of the oleum, and should appear weakly in the spectrum of solution A, strongly in the spectra of solutions B and C, and again weakly in the spectrum of solution D. In the last-mentioned spectrum, the line occurs at the displaced frequency 1092 cm.$^{-1}$, and this, as has been noted already, may mean that its source in this spectrum is the normal disulphate ion. Again, a glance at the calculated concentrations of the

FIG. 1.

Microphotometer records of parts of the Raman spectra (*Stokes lines excited by nitrite-filtered* Hg 4358 A.) *of solutions of sulphates in oleum. As to the compositions of solutions* A, B, C, *and* D, *see the text. The frequencies* 560 *and* 910 *cm.*$^{-1}$ *belong to the solvent sulphuric acid, whilst* 1050 *cm.*$^{-1}$ *is assigned to the hydrogen sulphate ion,* 1083 *cm.*$^{-1}$ *to the hydrogen disulphate ion, and* 1092 *cm.*$^{-1}$ *to the normal disulphate ion; and* 735 *and* 325 *cm.*$^{-1}$ *are considered as common to the disulphuric acid molecule and the hydrogen disulphate ion, but with differences of intensity* (*see text*).



hydrogen sulphate ion, as given in Table III, renders it intelligible that the characteristic frequency 1050 cm.$^{-1}$, of this ion, should not be visible in the spectra of sulphuric acid, the oleum, and the sulphate solutions A and B, but should be prominent in the spectrum of solution C, and very strong in that of solution D.

New conclusions can be derived by applying this method of examination to the three frequencies 325, 735, and 1240 cm.$^{-1}$, which in Section 1.2 were assigned to disulphuric acid. Consider first the frequency 325 cm.$^{-1}$. Table III shows that molecular disulphuric acid is present in very considerable concentration in the oleum and in the sulphate solution A, but is completely, or almost completely, absent from the solutions B, C, and D. Table II and Fig. 1 show, however, that the frequency 325 cm.$^{-1}$ appears fairly strongly in the spectrum of the oleum, and in that of solution A, and suffers only a small loss of intensity, in comparison with the sulphuric acid frequencies, in the spectra of solutions B and C. Since the molecular disulphuric acid which is present in the oleum and in solution A becomes largely replaced in solutions B and C by the hydrogen disulphate ion, it must be from this anion that, in the spectra of solutions B and C, the Raman line at 325 cm.$^{-1}$ is deriving its intensity. We must conclude that the frequency 325 cm.$^{-1}$ is common to molecular disulphuric acid and the hydrogen disulphate ion, and that it has intensities of the same order of magnitude in the spectra of both these sources. The same frequency appears much more weakly in the spectrum of solution D, as might be expected on the basis of the calculated figures in Table III : for these figures show that the concentration of hydrogen disulphate ion is much reduced in solution D, as compared with solutions B and C. However, the same result could be understood along the lines of the suggestion that, in solution D, the hydrogen disulphate ion is largely converted into the normal disulphate ion, provided that one assumes, as is by no means unlikely, that this ion also has a Raman frequency in the neighbourhood of 325 cm.$^{-1}$.

The frequency 735 cm.$^{-1}$ appears fairly strongly in the spectrum of the oleum, and in that of solution A, but only weakly in the spectra of solutions B and C, and very weakly in that of solution D. However, it does not vanish in the spectra of solutions B or C, or even D, although, as Table III shows, molecular disulphuric acid is completely, or almost completely, absent from these solutions. This proves that the frequency 735 cm.$^{-1}$ belongs to the hydrogen disulphate ion, as well as to the disulphuric acid molecule; and it also shows that, whilst 735 cm.$^{-1}$ is a fairly strong Raman frequency of the molecule, it is only a somewhat weak frequency of the anion. The intensities of the line at 735 cm.$^{-1}$ in the different spectra can be made intelligible on the basis that in the spectrum of oleum, and in that of solution A, practically the whole of the observed intensity comes from the disulphuric acid molecule, whereas, in the spectra of solutions B and C, the observed intensities of the line are derived almost entirely from the hydrogen disulphate ion. As to the very weak appearance of the frequency in the spectrum of solution D, it might be held that this frequency is common to the hydrogen disulphate ion and the normal disulphate ion; but it is difficult to be sure that such a weak line does not arise from a small amount of unconverted hydrogen disulphate ion.

The observations on the frequency 1240 cm.$^{-1}$ are less complete. This frequency appears, as it should, in the spectrum of the oleum, and in that of solution A, where, without doubt, it arises from molecular disulphuric acid. In the spectra of solutions B, C, and D, the line, or the position of the line, is overlapped by the ammonium ion bands. However, the line is present, though with the somewhat displaced frequency 1210 cm.$^{-1}$, in the spectrum of solution B, which contains scarcely any molecular disulphuric acid, but a large amount of hydrogen disulphate ion. It therefore seems certain that this appearance of the line is due to the hydrogen disulphate ion.

The following is a list of frequency assignments (cm.$^{-1}$), which summarise the results of these considerations concerning the Raman-spectral characteristics of disulphuric acid in its molecular and anionic forms :

$H_2S_2O_7$	325 (ms)	735 (ms)	—	1240 (m)
$HS_2O_7^-$	325 (ms)	735 (mw)	1083 (s)	1210 (mw)
$S_2O_7^{--}$	325 (m)	735 ?	1092 (s)	?

It is not surprising that the three entities have a number of identical or nearly identical frequencies, because the mechanical coupling between the more remote parts of such structures must be very weak. Thus the frequencies 1083 and 1092 cm.$^{-1}$ (like the frequency 1050 cm.$^{-1}$ of the hydrogen sulphate ion) are obviously breathing frequencies of the group OSO_3^-; and it can matter little to the vibration of such a group, in an anion of disulphuric acid, whether the other end of the anion contains one proton more or less.

With regard to the problem of the spectroscopic detection of the forms of disulphuric acid, the anions can evidently be recognised by means of their characteristic frequencies 1083 and 1092 cm.$^{-1}$. When these are absent, the neutral molecule can be detected by means of the frequencies 325 and 735 cm.$^{-1}$. When the frequency 1092 cm.$^{-1}$ is present, the molecule may be assumed absent. When the frequency 1083 cm.$^{-1}$ is present, then the presence of the molecule has to be judged from the relative intensities of the frequencies 325 and 735 cm.$^{-1}$.

(3) *Raman Spectra of Solutions of Nitric Acid in Oleum.*

(3.1) *Identification of the Nitronium and Hydrogen Disulphate Ions.*—In Table IV the Raman frequencies are given which have been measured in the spectrum of a solution of 5 parts by weight of anhydrous nitric acid in 100 parts of 20% oleum (solution N). The lines measured were Stokes lines excited by nitrite-filtered Hg 4358 A. In the Table, the frequencies of these lines are compared with those of a solution of potassium hydrogen sulphate in oleum (solution A). An assignment of all these frequencies to their sources is given in the Table. The assignment is based to a considerable extent on the conclusions of Section 2.3.

TABLE IV.

Raman frequencies (cm.$^{-1}$) of a solution of nitric acid, and of a solution of potassium hydrogen sulphate, in oleum ; and an assignment.

HNO_3 (Soln. N).	$KHSO_4$ (Soln. A).	Assignment.	HNO_3 (Soln. N).	$KHSO_4$ (Soln. A).	Assignment.
321 (mw)	317 (ms)	$H_2S_2O_7$ and $HS_2O_7^-$	983 (w)	975 (w)	H_2SO_4
387 (mw)	386 (mw)	H_2SO_4	1083 (w)	1085 (w)	$HS_2O_7^-$
419 (mw)	414 (mw)	,,	1158	1148	H_2SO_4
567 (ms)	570 (ms)	,,	1220 (mw)	1227 (m)	$H_2S_2O_7$ and $HS_2O_7^-$
735 (w)	735 (m)	$H_2S_2O_7$ (mainly)	Present	1391 (w)	H_2SO_4
914 (s)	908 (s)	H_2SO_4	1402 (m)	—	NO_2^+

It is notable that, in the spectrum of solution N, even the strongest lines of nitric acid do not appear. On the other hand, the presence of the sharp line at 1400 cm.$^{-1}$ shows that the solution contains nitronium ion. As to anions, neither the nitric acid solution nor the potassium hydrogen sulphate solution gives the Raman frequency 1050 cm.$^{-1}$, which is characteristic of the hydrogen sulphate ion; but both give the frequency 1083 cm.$^{-1}$, by which the hydrogen disulphate ion can be recognised. The reaction undergone by nitric acid is therefore essentially as follows :

$$HNO_3 + 2H_2S_2O_7 = NO_2^+ + HS_2O_7^- + 2H_2SO_4 \quad . \; . \; . \; . \; . \quad (6)$$

These conclusions may be confirmed by comparing the spectra with the calculated compositions of the solutions. Such compositions are given in Table V. They are calculated in the same way, and are expressed in the same form, as the compositions in Table III. It is assumed that nitric acid is quantitatively decomposed according to equation (6), and that then sulphuric and disulphuric acids come into equilibrium with each other, and with their ions, in the ways already described.

TABLE V.

Calculated molecular compositions of the solutions of Table IV.

	NO_2^+.	$H_3SO_4^+$.	H_2SO_4.	HSO_4^-.	$H_2S_2O_7$.	$HS_2O_7^-$.
Soln. N	7·9	0·2	66·7	0·0	8·4	7·6
Soln. A	0·0	0·3	32·8	0·0	28·2	5·2

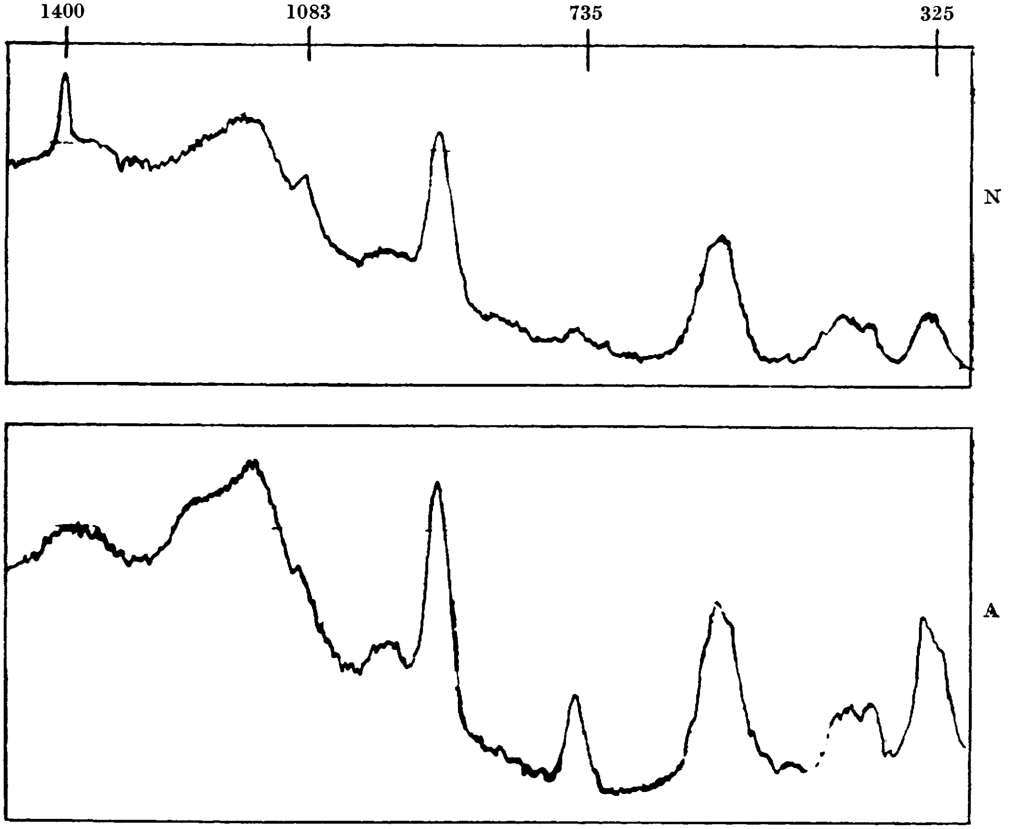
As can be seen from the microphotometer records of the spectra reproduced in Fig. 2, the hydrogen disulphate ion frequency, 1083 cm.$^{-1}$, is appreciably stronger in the spectrum of solution N than in that of solution A. On the other hand, the frequencies 325 and 735 cm.$^{-1}$ are markedly weaker in the spectrum of solution N than in that of solution A, the difference being more marked in the case of the frequency 735 cm.$^{-1}$. All these differences can be understood on the basis of the figures in Table V.

(3.2) *Stability of Nitronium Hydrogen Sulphate.*—A comprehensive study of the Raman spectra of mixtures of nitric acid with oleum of various strengths has been reported by Chédin (*Compt. rend.*, 1936, **292**, 220; *Ann. Chim.*, 1937, **8**, 243). It has not previously been possible to give a satisfactory interpretation of these spectra for lack of sufficient knowledge about the characteristic frequencies of the ions in such solutions. An interpretation is now offered, which is based on the conclusions of Section 2.3.

A condensed survey of Chédin's results (already partly interpreted as an aid to summarisation) is given in Table VI. The data relate to various mixtures of anhydrous nitric acid with oleum of each of three different strengths. The " experimental " proportions of nitric acid, given in column 2, are the proportions which refer to the tabulated spectral particulars. The significance of the " calculated critical " proportions, in column 1, will be explained later. The observed frequencies are assigned either collectively, as in the case of the sulphuric acid frequencies, or individually, as with most of the ionic frequencies. Thus the Table shows which species are present at the different concentrations of added nitric acid, and the direction in which the concentration of each species changes as the proportion of added nitric acid is varied. In the spectra of mixtures with larger proportions of added nitric acid than those indicated in the Table, the stronger Raman lines of molecular nitric acid appear.

FIG. 2.

Microphotometer records of parts of the Raman spectra (Stokes lines excited by nitrite-filtered Hg 4358 A.) *of solutions of nitric acid* (N) *and potassium hydrogen sulphate* (A) *in oleum. As to compositions, see text. The frequency* 1400 *cm.*$^{-1}$ *belongs to the nitronium ion, whilst* 1083 *cm.*$^{-1}$ *arises from the hydrogen disulphate ion. Molecular disulphuric acid is the main source of the frequency* 735 *cm.*$^{-1}$*, whilst both disulphuric acid and the hydrogen disulphate ion contribute to the intensity of the line at* 325 *cm.*$^{-1}$.



The proportions of nitric acid which are marked with an asterisk in column 1 of Table VI are those proportions which are calculated to be stoicheiometrically necessary for a complete decomposition of all solutes in the sulphuric acid solvent according to the equation

$$HNO_3 + 2SO_3 = NO_2^+ + HS_2O_7^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In this equation, oleum is taken as a system (in the thermodynamic sense) of the two components, sulphur trioxide and sulphuric acid, its detailed chemical constitution being irrelevant. With reagents in the calculated proportions, a complete reaction according to equation (7) should produce a solution of nothing but nitronium hydrogen disulphate in sulphuric acid. The spectrum of such a solution should show the presence of the nitronium ion, of the hydrogen disulphate ion, and of the sulphuric acid molecule; and it should indicate the absence of the hydrogen sulphate ion, of the disulphuric acid molecule, and of the nitric acid molecule. It seems from Chédin's data that, the correct quantities of the reagents being supplied, this situation would very approximately be realised with mixtures made from oleum of all the strengths he investigated. It must be concluded that, in very concentrated, as well as in more dilute, solution in sulphuric acid, the group of reactions summarised in equation (7) tends to proceed nearly to completion.

TABLE VI.

Survey and interpretation of Chédin's Raman frequencies (cm.$^{-1}$) for mixtures of nitric acid with fuming sulphuric acid.

Wt. % HNO_3.							
Calc. crit.	Exptl.	NO_2^+ (~1400).	$HS_2O_7^-$ and $S_2O_7^{--}$ (~1090).	HSO_4^- (~1050).	$H_2S_2O_7$ and $HS_2O_7^-$ (~325).	$H_2S_2O_7$ mainly (~735).	H_2SO_4 lines.
Mixtures of HNO_3 *with* 60% *oleum :*							
19 *	10	1400	~1080	absent	330	735	absent
	20	,,	1080	,,	,,	v. weak	appear
33 †	30	,,	1094	1044	,,	absent	,,
	40 ‡	,,	1094	,,	,,	,,	,,
	—	strengthening	weakening	strengthening	weakening	,,	strengthening
Mixtures of HNO_3 *with* 45% *oleum :*							
15 *	10	1400	1086	absent	325	735	appear
26 †	20	,,	1091	,,	,,	absent	,,
	30	,,	absent	1040	,,	,,	,,
	—	strengthening	,,	strengthening	weakening	,,	strengthening
Mixtures of HNO_3 *with* 35% *oleum :*							
12 *	10	1401	1084	absent	323	737	appear
21 †	20	,,	absent	1040	absent	absent	,,
	30 ‡	,,	,,	,,	,,	,,	,,
	—	strengthening	,,	strengthening	,,	,,	strengthening

* Theoretical quantity for the production of $(NO_2^+)(HS_2O_7^-)$ as the only solute.
† ,, ,, ,, ,, $(NO_2^+)(HSO_4^-)$,, ,,
‡ Molecular HNO_3 lines were present in the spectra of these mixtures.

The proportions of nitric acid which are marked with a dagger on the left of Table VI are the proportions which would stoicheiometrically permit a complete decomposition of all solutes in the sulphuric acid solvent according to the equation

$$HNO_3 + SO_3 = NO_2^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Here again, oleum is taken as a system of the components, sulphur trioxide and sulphuric acid, the manner of their combination being irrelevant. With reagents in the correct proportions, a complete reaction of this kind should produce a solution of nothing but nitronium hydrogen sulphate in sulphuric acid. Its spectrum should reveal the presence of the nitronium ion, of the hydrogen sulphate ion, and of the sulphuric acid molecule; and it should indicate the absence of the hydrogen disulphate or disulphate ion, of the disulphuric acid molecule, and of the nitric acid molecule. This would seem to be approximately the situation in a mixture involving the most dilute of Chédin's oleums. It might not be quite true, but it could not be very far from a correct description, in the intermediate case. But it would definitely not be true for a mixture made from the most concentrated of the oleums. In this case, as Chédin's results show, anions of disulphuric acid are present in quantity, side by side with the hydrogen sulphate ion, and even with the nitric acid molecule after more than enough nitric acid has been supplied to convert all forms of disulphuric acid into the hydrogen sulphate ion. (Incidentally, it is consistent with the results and discussion given in Sections 2.2 and 2.3 that, when an anion of disulphuric acid coexists with the hydrogen sulphate ion in these solutions, the former exhibits the higher frequency, 1092 cm.$^{-1}$, which is assumed to be indicative of the normal disulphate ion.) The general conclusion is that, in dilute solution in sulphuric acid, the group of reactions summarised in equation (8) tends to proceed nearly to completion; but that, in concentrated solution, no such nearly complete conversion takes place, the products of reaction (8) tending to revert to those of reaction (7) in the following balanced reaction :

$$2NO_2^+ + 2HSO_4^- = NO_2^+ + HS_2O_7^- + HNO_3 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

These conclusions fall well into line with contemporaneously reported evidence of other kinds. The cryoscopic data of Gillespie, Graham, Hughes, Ingold, and Peeling (*J.*, 1950, 2504) show that nitronium hydrogen sulphate is perfectly stable in dilute solution in sulphuric acid; and those of Gillespie and Graham (*J.*, 1950, 2532) prove the same for nitronium hydrogen disulphate in dilute solution. But there is a very distinct difference in the stability of the two salts in concentrated forms. As is shown by Goddard, Hughes, and Ingold (*J.*, 1950, 2559), nitronium hydrogen sulphate cannot be isolated in a pure condition, because, in the concentrated state, it loses nitric acid, yielding the easily isolated, much more stable salt, nitronium hydrogen disulphate. The last-named authors explained these observations on the basis of equation (9), describing the reaction as a dehydration of the anion of nitronium hydrogen sulphate by its own cation, or, more generally, as the extraction from the feebly nucleophilic anion of a more strongly nucleophilic portion (OH^-) by the very strongly electrophilic nitronium ion. Thermodynamically, it is axiomatic that a balanced reaction of the form represented in equation (9) must move towards the right as concentration is increased.

The author is indebted to Professor C. K. Ingold for invaluable help and advice.

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

[*Received, December* 17*th*, 1949.