The Evidence of Conductivity, Density, and Viscosity on the Reaction of Nitryl Fluoride with Sulphuric Acid. The Conductivity of Solutions of Nitryl Fluoride in Selenic and Phosphoric Acids.

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Nitryl fluoride, in concentrations up to 68 mol.%, reacts exothermally and irreversibly with sulphuric acid to give clear colourless liquids; at 70 mol.% colourless crystals separate and the mother-liquor immediately becomes yellow. Electrical conductivities, densities, viscosities, and Raman spectra of the solutions have been used to interpret the chemistry of the system.

In selenic acid nitryl fluoride behaves similarly and also, at a sufficient concentration, gives colourless crystals. The conductivities of this system have been measured.

In phosphoric acid a different form of conductivity curve is obtained and the chemistry is not the same.

SULPHURIC ACID

NITRYL FLUORIDE boils at −73° to give a colourless vapour which is readily absorbed by concentrated sulphuric acid with the liberation of much heat. Provided the reactants are kept at laboratory temperature during the mixing, there is evidence, up to 68 mol.%, that very little of the nitryl fluoride dissociates to nitrogen peroxide and fluorine. The vapour is so quickly absorbed that bubbles rarely break the surface; more than 2 moles per mole can be taken up. At about 70 mol.%, when the volume of liquid has increased roughly two and a half times, colourless crystals separate and the mother-liquor is coloured yellow by nitrogen peroxide. Analyses suggest the solid is nitronium hydrogen sulphate, NO_2HSO_4, but this needs confirmation and work to that end is in progress.

Let us state what we think happens in the course of absorption up to the separation of the solid and then present the evidence and argument upon which our opinions are based. But first it is emphasised that the reaction differs from that of dinitrogen tetroxide with sulphuric acid by being irreversible and attended by a greater energy change.

The cryoscopic and molar conductivity data applicable to solutions up to 1·0 mol.% indicate respectively *five* particles and *two* ions of high mobility within this concentration limit. These requirements are met by the irreversible reaction (1), followed by the reversible reaction (2):

$$NO_2F + H_2SO_4 \longrightarrow NO_2^+ + HF + HSO_4^- \quad . \; . \; . \; . \; . \; . \quad (1)$$

$$HF + 2H_2SO_4 \rightleftharpoons H_3O^+ + HSO_3F + HSO_4^- \quad . \; . \; . \; . \; . \quad (2)$$

Lange's work (*Z. anorg. Chem.*, 1933, **215**, 321) implies that the equilibrium of (2) is well to the right in the absence of moisture so that when combined with (1) it gives the *five* particles and *two* major conducting ions required. Moisture, according to Lange (*loc. cit.*), caused (2) to move from right to left and this may be the reason for the absence of Raman evidence for fluorosulphonic acid in the more concentrated solutions of nitryl fluoride, though it is possible that the lines are masked. Without more knowledge of the hydrogen fluoride–sulphuric acid system, the authors feel it safer to assume that at higher concentrations much of the hydrogen fluoride remains as such. With these premises, the dissolution of nitryl fluoride in sulphuric acid may be conveniently referred to six stages.

Stage I, to 1·0 mol.%, the irreversible reaction (1), followed by the equilibrium (2).

Stage II, from 1·0 to 9·6 mol.%, the irreversible reaction (1), accompanied by the reversible reaction producing nitronium hydrogen sulphate in solution

$$NO_2^+ + HSO_4^- \rightleftharpoons NO_2HSO_4 \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

Stage III, at about 22 mol.%, the concentration of maximum viscosity, where the increase in viscosity due to NO_2HSO_4 is counterbalanced by the dilution effect of HF.

Stage IV, at 50 mol.%, near the concentration of minimum conductivity (47 mol.%), where all the H_2SO_4 has been used in reaction (1).

Stage V, from 50 to 68 mol.%, the conductivity rises, NO_2F continues to dissolve in the liquid forming more NO_2^+, possibly by reacting with HSO_4^- ions :

$$NO_2F + HSO_4^- \longrightarrow NO_2^+ + HF + SO_4^= \quad . \ . \ . \ . \ . \ . \quad (4)$$

Stage VI, at 70 mol.%, the liquid is saturated with NO_2HSO_4 and crystals (possibly of this composition) separate. Nitrogen peroxide turns the mother-liquor yellow. If the relative absence of secondary reactions is assumed, the molar ratio of species present immediately before the formation of solid should be approximately.

$$NO_2^+ : HF : HSO_4^- : SO_4^= = 3 : 3 : 1 : 1$$

The removal of some HSO_4^- ions by the solid prevents reaction (4) and allows NO_2F to accumulate which can then decompose :

$$2NO_2F \longrightarrow N_2O_4 + F_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

The addition of H_2SO_4 causes the solid to dissolve and the colour disappears because of the reaction

$$N_2O_4 + 3H_2SO_4 \rightleftharpoons NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^- \quad . \ . \ . \ . \quad (6)$$

Electrical Conductivity.—This rises to a maximum with 9·6 mol.% [see Fig. 1 (*a*)], falls to a minimum with 47 mol.%, and then rises again until, at 70 mol.%, the separation of solid prevents further measurement. These changes are to be considered in relation to molar conductivity and cryoscopic measurements in solutions up to 0·5M, to densities of solutions up to 22 mol.%, to viscosities up to 44 mol.%, and to Raman spectra at 15·6 and 23·1 mol.%. The hydrogen fluoride present slowly attacks glass, and more slowly silica, releasing bubbles of silicon tetrafluoride at the surfaces. These, though troublesome in all work at high concentrations, and for spectral observation even at intermediate concentrations, do not prevent a fair degree of accuracy in other measurements.

No previous conductivity measurements have been made on these solutions, and those made on dilute solutions of sulphuric acid in hydrogen fluoride (Fredenhagen and Cadenbach, *Z. phys. Chem.*, 1930, **146**, 245; Fredenhagen, *Z. anorg. Chem.*, 1939, **242**, 23) and interpreted as indicating ionisation of the following kind

$$H_2SO_4 + 2HF \longrightarrow HSO_3F + H_3O^+ + F^-$$

have little bearing on the present work. We have passed fluorine through a solution of dinitrogen tetroxide only to find a negligible amount of it absorbed and little effect on the conductivity. This confirmed us in our rejection of the idea of appreciable decomposition of nitryl fluoride by reaction (5) in these solutions below 70 mol.%, which had been previously made on the grounds that no fluorine is disengaged.

TABLE 1. *Molar conductivities of dilute solutions at* 25°.

Concn. (mole l.$^{-1}$)	NO_2F	Mono-(HSO_4^-) H_2O	Di-(HSO_4^-) HNO_3	Tri-(HSO_4^- N_2O_4	Tetra-(HSO_4^-) hexa-methylenetetramine
0·05	362	—	306	—	454
0·10	225	156	229	296	349
0·15	214	—	197	—	—
0·20	191	115	177	—	—
0·30	161	100	155	—	—
0·40	141	90	138	—	—
0·50	125	—	125	—	—

Molar Conductivities.—Table 1 allows our molar conductivities of nitryl fluoride solutions in sulphuric acid to be compared with those of mono-, di-, tri-, and tetra-hydrogen sulphate ionising compounds (see Gillespie and Wasif, *J.*, 1953, 221). Clearly from this the irreversible reaction with sulphuric acid, at least up to a concentration of 0·5M, belongs to the di-hydrogen sulphate class and should be represented by equations (1) and (2), rather than by (1) alone.

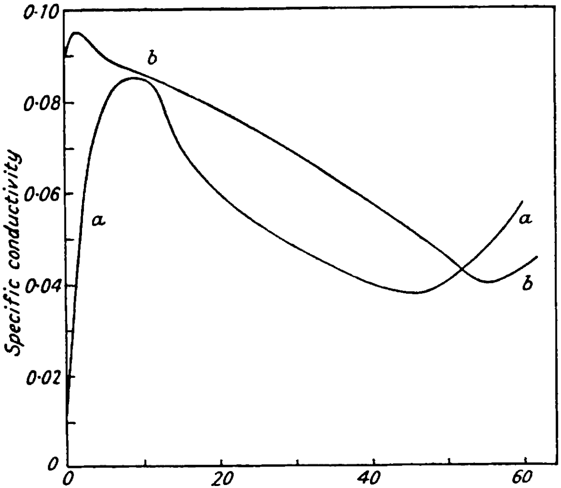
Cryoscopic Evidence.—Equations (1) and (2) imply the formation of five osmotic particles per molecule of solute and their presence is confirmed by the depression of the freezing point of nitryl fluoride in 100% sulphuric acid [Fig. 2 (*b*)] in relation to those of nitric acid (*a*) and dinitrogen tetroxide (*c*) in the same medium, which produce, respectively, four and six particles per molecule of solute :

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

$$N_2O_4 + 3H_2SO_4 \rightleftharpoons NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-$$

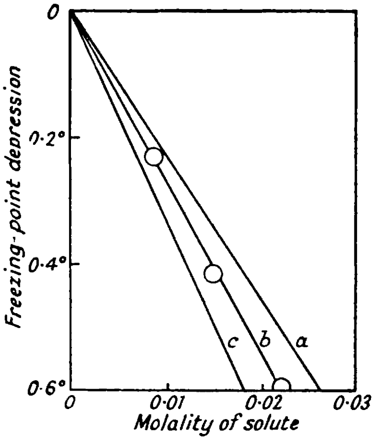
At higher concentrations, following our premise that there is not much fluorosulphonic acid, the main reaction would appear to be (1) which is held to account for the hydrogen sulphate ions; these mainly give rise to the conductivity which has its maximum at 9·6 mol.%.

FIG. 1. *Specific conductivities of solutions of nitryl fluoride in sulphuric and selenic acid.*



(*a*) H_2SO_4, (*b*) H_2SeO_4.

FIG. 2. *Cryoscopic data for nitric acid, nitryl fluoride, and dinitrogen tetroxide in sulphuric acid.*



(*a*) HNO_3, (*b*) $NO_2{\cdot}F$, (*c*) N_2O_4.

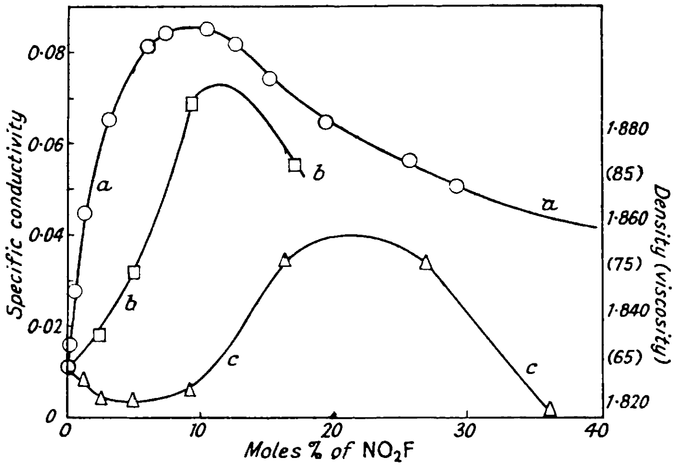
At 50 mol.%, where the conductivity is near a minimum, all the sulphuric acid has been used by reaction (1), and, as the reaction is irreversible, the only species certainly present in quantity are molecular hydrogen fluoride and nitronium hydrogen sulphate, and the ions NO_2^+ and HSO_4^-.

Densities.—These [Fig. 3(*b*)] rise to a maximum at about 11 mol.% and then fall with increasing concentration. In spite of the maximum's occurring at a composition near that giving the greatest conductivity [Fig. 3(*a*)] and of a parallelism between the two curves, we believe there is little connection between density and conductivity. As with dinitrogen tetroxide (see Hetherington, Nichols, and Robinson, *J.*, 1955, 3141,) the increase in density is ascribed to solvation of the nitronium ion, and the subsequent decrease to dilution. For nitryl fluoride the dilution effect comes earlier because all the diluent, hydrogen fluoride, remains intact; whereas of the nitrogen peroxide added, some reacts, even up to a high concentration, with the sulphuric acid.

Viscosities.—On the other hand the viscosities (again as with dinitrogen tetroxide), seem to be closely associated with the conductivities and, up to a concentration of 47 mol.% largely to control them. The curve, Fig. 3(*c*), falls to a minimum at a concentration just a little below that responsible for the maximum conductivity and rises steeply after that point is passed. By the reasoning adopted in the case of dinitrogen tetroxide, the initial fall in viscosity is ascribed to the formation of the nitronium ion and the subsequent rise to compound formation; then the compound was nitrosonium hydrogen sulphate, now it is probably nitronium hydrogen sulphate. The second decline in viscosity is due to dilution with hydrogen fluoride which, when this decline becomes apparent, is present to the extent of about 22 mol.%.

The final rise in conductivity from about 47 mol.% must be related to the fact that at 50 mol.%, although all the sulphuric acid has been used, nitryl fluoride continues to be freely absorbed. Some of it must go to increase the concentration of nitronium ion if, as we believe, a nitronium salt eventually comes out of solution. This increase may be caused by the nitryl fluoride's reacting with the hydrogen sulphate ion according to equation (4). Such a reaction would at once account for the increase in conductivity observed by allowing the substitution of a $SO_4^=$ for a HSO_4^- ion, and for the rise in concentration of the nitronium ion which forces precipitation. That nitrogen peroxide appears in the solution immediately the solid begins to separate betokens a decomposition of the sort shown in (5). This may be brought about by a dearth of HSO_4^- ions with which the additional nitryl fluoride can react (4), or may be due to the formation of a soluble molecular compound between nitryl fluoride and the nitronium salt at high concentrations, which leads to the release of the former when the latter is precipitated. Either need occur only to a slight degree to account for the phenomena observed.

FIG. 3. *Conductivities, densities, and viscosities of solutions of nitryl fluoride in sulphuric acid.*



(*a*) Specific conductivity (ohm^{-1} cm.$^{-1}$); (*b*) density (g. c.c.$^{-1}$); (*c*) viscosity (arbitrary units).

Raman Spectra.—Through the courtesy of Dr. F. M. Brewer, we prepared nitryl fluoride and two solutions of it in sulphuric acid in the Inorganic Chemistry Laboratory, Oxford, where Dr. L. A. Woodward and Mr. J. A. Rolfe kindly examined their Raman spectra. The results obtained for nitryl fluoride itself will be published shortly. The concentrations of the two solutions were 15·6 and 23·1 mol.%, the first a little beyond the conductivity maximum and the second near the viscosity maximum. Neither showed any sign of the spectrum of nitryl fluoride. This is in harmony with the view that its reaction with sulphuric acid is not reversible—Ruff, Menzel, and Neumann (*Z. anorg. Chem.*, 1932, **208**, 293) found the reaction of nitrosyl fluoride with sulphuric acid to be irreversible. Nor were any Raman lines observed which could be attributed to fluorosulphonic acid or the fluorosulphonate ion. Apart from slight shifts of the frequencies of the solvent the only characteristic features shown by the solutions were the frequencies 1034, 1397, and 2290 cm.$^{-1}$. There is little doubt that the first of these is due to HSO_4^- and the second to the nitronium ion NO_2^+ (cf. Ingold, Millen, and Poole, *J.*, 1950, 2576), and the presence of these ions is completely in keeping with the picture of the system given above. The third frequency, 2290 cm.$^{-1}$, is close to that of the nitrosonium ion NO^+ (Millen, *J.*, 1950, 2600) to which it presumably must be ascribed. This evidence for the presence of nitrosonium ions in appreciable concentration in these solutions is surprising unless it happens to be due to the fact that they were prepared by diluting solutions of or near 63·5 mol.% with sulphuric acid. At this concentration the decomposition (5) could operate and, once formed, the nitrosonium ions would remain in the liquid. In sulphuric acid solutions of dinitrogen tetroxide, where nitrosonium and nitronium ions occur in equal concentrations, only a nitrosonium salt is precipitated. With nitryl fluoride we have found no sign of nitrosonium salt in the solid and this would indicate that the concentration of the ion in these solutions is probably not high.

SELENIC ACID

Selenic acid absorbs more than 2 moles of nitryl fluoride per mole of selenic acid. The conductivities of the solutions are shown in Fig. 1(*b*). There is some doubt about the value for the acid itself, which may be much lower than we found (see below). The curve, except for its initial portion, resembles that of the sulphuric acid solutions and the phenomena displayed are the same, including the absence of colour up to 68 mol.% and the separation of a solid at 70 mol.% followed by an immediate colouring of the solution with nitrogen peroxide. Preliminary examination suggests the solid is nitronium hydrogen selenate, and this is being further investigated. The evidence points to a series of stages as nitryl fluoride is absorbed, similar in most respects to those already postulated for the solutions in sulphuric acid. Where the stages differ is in the concentrations at which the maximum (1·40 mol.%) and minimum (58·6 mol.%) conductivities are found. Equations (1) to (5), with the substitution of Se for S are applicable to this system.

PHOSPHORIC ACID

The amount of nitryl fluoride absorbed by phosphoric acid is also considerable, 1·7 moles per mole. The curve of conductivities against concentration (Fig. 4) is however entirely different as, indeed, are the phenomena observed. But even in this case there is a small initial maximum at 1 mol.% at which point the solution becomes coloured with nitrogen peroxide. Beyond this the curve slowly rises to a second very blunt maximum and, at a concentration of approximately 60 mol.%, a colourless solid begins to separate. Neither the solid nor the system has been fully investigated.

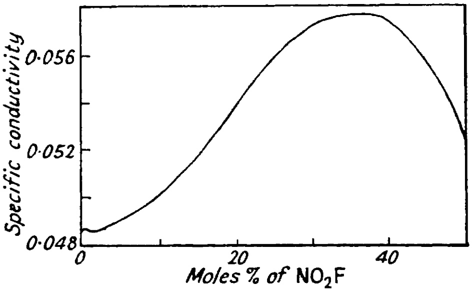


FIG. 4. *Specific conductivities of solutions of nitryl fluoride in phosphoric acid.*

EXPERIMENTAL

Materials.—Sulphuric acid of minimum conductivity at 25·00 ± 0·01° was prepared in the manner described by Hetherington, Hub, Nichols, and Robinson (*J.*, 1955, 3300), using a cell similar to that of Gillespie and Wasif (*J.*, 1953, 204) but with its electrode chamber disposed vertically instead of horizontally. Electrical measurements were to ±0·00002 ohm^{-1} cm.$^{-1}$.

As supplied in sealed ampoules (B.D.H. pure) selenic acid is extremely hygroscopic and its conductivity is markedly increased by the slighest exposure to the atmosphere. Although the individual specimens varied little in specific conductivity the figure found, 0·09105 ohm^{-1} cm.$^{-1}$ at 25°, is probably high; that for the absolute acid might be expected to be more of the order of the 0·01045 ohm^{-1} cm.$^{-1}$ recorded for sulphuric acid.

Also from ampoules (B.D.H. 100%), phosphoric acid was used as supplied, and again our figure 0·04858 ohm^{-1} cm.$^{-1}$ could be high. Since with selenic and phosphoric acid we were more interested in the form of the conductivity curves of the nitryl fluoride solutions than in the accuracy of particular points, we contented ourselves with these materials.

Nitryl fluoride, prepared and purified by the method developed in this laboratory (*J.*, 1954, 1119), was kept in the Pyrex break-seal vessels as short a time as possible before use.

The fluorine for saturation of the dinitrogen tetroxide and nitryl fluoride solutions in sulphuric acid was prepared electrolytically and purified by passage over dry sodium fluoride and through a trap cooled to −180°.

Manipulation and Measurement.—The solutions were prepared in an all-Pyrex glass apparatus at 0° and transferred to the conductivity cell without contact with the air of the room. The cell was similar in design to the small one used by Gillespie and Wasif (*J.*, 1953, 204). As it was constructed of Pyrex glass, the stout electrode leads were fitted snugly into vertical tubes and the joints rendered vacuum-tight by a lining and capping of " Polythene." The cell provided for a resistance greater than 1000 ohms, and its constants were determined by the use of potassium chloride solutions of accurately known strength, the specific conductivities of Jones and Bradshaw (*J. Amer. Chem. Soc.*, 1933, **55**, 1780) for these solutions being employed. The temperature of the liquids during measurements was kept at 25·00° ± 0·01° by means of a thermostat. Only at high concentrations of nitryl fluoride was difficulty experienced from the formation of bubbles of silicon tetrafluoride and this could be overcome by tilting the cell just before making the final adjustment and allowing the bubbles to escape from the electrode chamber into the upper part of the cell. The circuit used for measuring the resistances will be described in detail later.

The densities were determined by weighing a known volume of liquid under conditions which protected it from atmospheric moisture. The viscosities, being for comparison only, are in arbitrary units. The range of composition over which these two properties could be measured was limited by the appearance of gaseous silicon tetrafluoride beyond a certain concentration.

The specific conductivities of nitryl fluoride in the three solvents at 25·00°, κ (ohm^{-1} cm.$^{-1}$), are set out below :

Mol.%	100κ	Mol.%	100κ	Mol.%	100κ
		Sulphuric acid.			
63·69	5·619	19·34	6·442	3·046	6·496
58·26	4·643	15·22	7·413	1·412	4·447
50·08	3·904	12·66	8·175	0·626	2·714
44·29	3·895	10·56	8·497	0·240	1·586
29·20	5·064	7·287	8·408	0·000	1·045
25·73	5·569	6·026	8·148		
		Phosphoric acid.			
57·54	4·621	15·73	5·227	1·032	4·860
39·36	5·762	12·09	5·094	0·550	4·856
34·35	5·766	8·823	4·992	0·255	4·863
30·75	5·741	6·045	4·927	0·119	4·858
25·00	5·597	3·581	4·886	0·052	4·858
20·30	5·394	1·983	4·869	0·000	4·858

Mol.%	100κ	Mol.%	100κ	Mol.%	100κ
		Selenic acid.			
Expt. 1.					
67·84	4·204	30·17	6·694	9·402	8·703
56·73	4·029	18·81	7·830	4·463	8·972
46·48	5·089	13·48	8·470	0·000	9·105
39·08	5·920				
Expt. 2.					
64·44	4·635	18·68	7·827	0·922	9·542
56·85	4·378	11·33	8·492	0·478	9·479
50·62	4·814	5·481	8·949	0·202	9·429
39·29	6·194	2·661	9·405	0·000	9·105
29·70	6·900	1·675	9·492		
Expt. 3.					
19·36	8·015	4·340	8·969	0·795	9·490
8·282	8·709	1·626	9·535	0·000	9·105

The effect on the specific conductivity of dinitrogen tetroxide solutions in sulphuric acid of passing through them appreciable quantities of fluorine is evidently small (see Table).

N_2O_4, mole%	42·66	20·24	6·11	2·08
100κ (ohm^{-1} cm.$^{-1}$), before passing F_2	3·25	7·25	10·15	7·22
after ,,	3·36	6·88	10·34	7·16
Fluorine passed (g.)	2·0	2·0	5·2	2·0

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