The Electrical Conductivity of Dinitrogen Tetroxide Solutions in Sulphuric, Selenic, and Phosphoric Acids.

By G. HETHERINGTON, M. J. NICHOLS, and P. L. ROBINSON.

[Reprint Order No. 6286.]

The conductivities of solutions of dinitrogen tetroxide in sulphuric acid have been measured at concentrations previously unexplored. The conductivity reaches a fairly sharp maximum at a concentration of 6 mol. % and, thereafter, falls regularly to about one-fifth of that value at approximately 48 mol. %. Here nitrosyl hydrogen sulphate, $NOHSO_4$, is formed, followed, at a slightly higher concentration, by the separation of dinitrogen tetroxide as an immiscible layer.

Dinitrogen tetroxide in selenic and phosphoric acids gives similar conductivity–concentration curves, except that their maxima appear at a much lower concentration. Furthermore, the conductivities at the limit of homogeneity are well below that of the solvent. At a sufficient concentration, nitrosyl hydrogen selenate, $NOHSeO_4$, separates from selenic acid, but no solid is formed with phosphoric acid.

The significance of these facts is discussed in the light of viscosity and density measurements made in connection with this work, and the cryoscopic, Raman, and other examinations which have been made of parts of the dinitrogen tetroxide–sulphuric acid system by earlier investigators.

So far as we know the electrical conductivities of solutions of dinitrogen tetroxide in anhydrous sulphuric acid have not been measured beyond a concentration of 0·663 mol. % (Gillespie and Wasif, *J.*, 1953, 209), although homogeneous solutions of 45 mol. % are easily prepared. Nothing has been found in the literature about its solutions in selenic and phosphoric acids; there is but one mention of the conductivity of anhydrous phosphoric (Mason and Culvern, *J. Amer. Chem. Soc.*, 1949, **71**, 2387), and none of anhydrous selenic acid. Yet both dissolve the oxide in considerable proportions: selenic acid about 40 mol. %, and phosphoric acid about 10 mol. %. This paper provides the missing conductivities, and also some information on the densities and viscosities of the solutions in sulphuric acid. These data are discussed in relation to conclusions reached by other workers, from physicochemical studies on certain parts of the dinitrogen tetroxide–sulphuric acid system.

As dinitrogen tetroxide is added to the acids at room temperature, they change, at a concentration characteristic of each, from colourless to yellow. The yellow solutions become colourless on cooling; this suggests the colour is due, in part at least, to the presence of molecular dinitrogen tetroxide. With a further increase in concentration the yellow becomes darker, and, eventually, separation into two layers takes place; the less dense one is liquid dinitrogen tetroxide which, incidentally, we find to be completely free from the acid in question. It did, however, contain nitric acid which was not present in the original liquid. Somewhat below the concentrations at which the systems display immiscibility, colourless crystals of nitrosyl hydrogen sulphate and nitrosyl hydrogen selenate are formed in the respective solutions. Precipitation does not occur with phosphoric acid, nor can it be induced by cooling.

The relation we have found between conductivity and concentration in the three solutions is shown in Fig. 1. The three curves are similar: each rises to a fairly sharp maximum and then falls in an almost linear fashion. There are, however, real differences too: the solution in sulphuric acid does not reach the highest conductivity until 6·8 mol. % of tetroxide is present, and the lowest conductivity does not drop to that of sulphuric acid itself, whereas the solutions in selenic and phosphoric acids attain their peaks with very little tetroxide and their lowest conductivities are far below those of the respective acids. A reservation (see p. 3145) is necessary regarding our conductivity of selenic acid; by analogy with sulphuric acid, it might be lower. Associated with every maximum is a change from colourless to yellow.

About the solutions in sulphuric acid, especially the dilute solutions, there is a considerable background of knowledge. From crysocopic measurements on solutions up to a concentration of 0·45 mol. % (*i.e.*, far below that giving peak conductivity), Gillespie, Graham, Hughes, Ingold, and Peeling (*J.*, 1950, 2504) conclude that the tetroxide ionises thus

$$N_2O_4 + 3H_2SO_4 = NO^+ + NO_2^+ + H_3O^+ + 3HSO_4^-$$

Gillespie and Wasif (*J.*, 1953, 221) gave electrical conductivities of the liquids up to a concentration of 0·663 mol. % and found values—with which ours closely agree—greater than for a di(hydrogen sulphate), *e.g.*,

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$$

and approximately three times that for a mono(hydrogen sulphate), *e.g.*,

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-,$$

thus substantiating deductions from cryoscopic evidence.

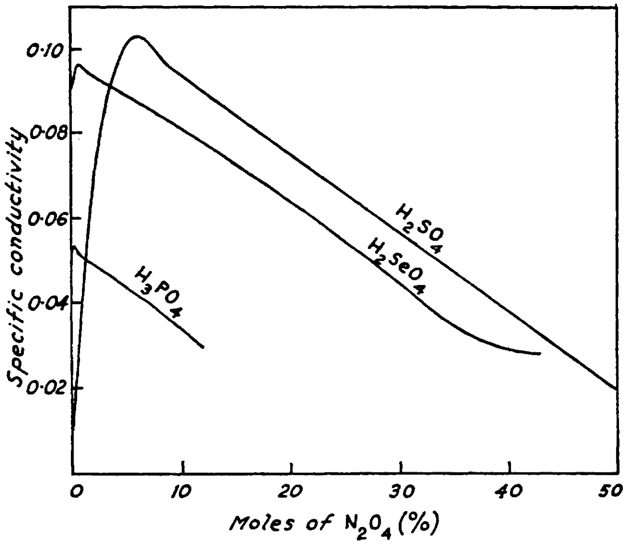


FIG. 1. *Specific electrical conductivities (ohms⁻¹ cm.⁻¹) of solutions of dinitrogen tetroxide in sulphuric, selenic, and phosphoric acids.*

From the Raman spectrum of a solution of 10 mol. % Millen (*J.*, 1950, 2600) infers the presence of sulphuric acid, and the nitronium, nitrosonium, and hydrogen sulphate ions. This concentration is somewhat beyond that corresponding to our maximum conductivity. At 20 mol. %, well beyond the maximum conductivity, Millen observed " an increase in intensity, relative to the molecular sulphuric acid lines of the characteristic lines of the hydrogen sulphate ion, the nitronium ion and the nitrosonium ion," and also the frequencies 680, 1313, and 1670 cm.$^{-1}$. These he attributed to " a spectroscopically detectable quantity of molecular nitric acid formed according to the equation

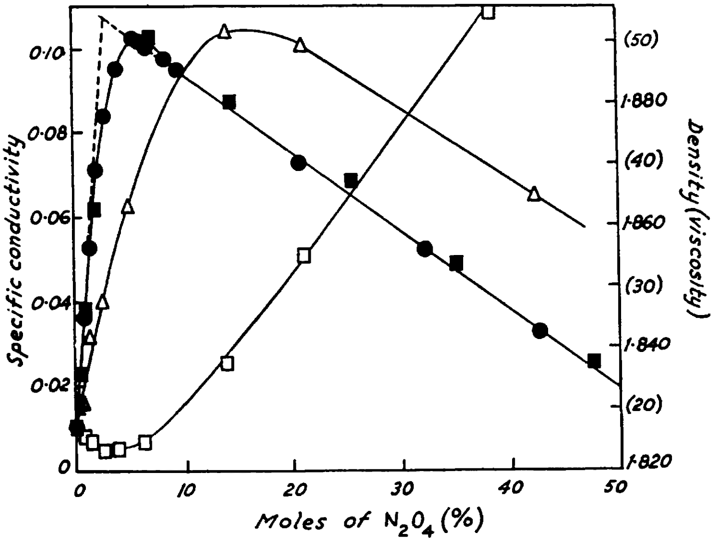
$$NO_2^+ + 2HSO_4^- + H_3O^+ = HNO_3 + 2H_2SO_4\text{"}$$

Since the Raman spectrum is not a very sensitive means of detecting nitric acid, it must have been there in appreciable quantity. Indeed, we found it in the dinitrogen tetroxide layer. This means that the above equilibrium showing the formation of nitric acid, which for dilute solutions lies almost completely to the left, for high concentrations is appreciably reversed. Probably the reversal begins before the yellow colour becomes visible : we imagine, at the concentration where the upward slope of the conductivity curve (Fig. 2) obviously lessens. Below this concentration the dinitrogen tetroxide is completely ionised (cf. Gillespie *et al.* and Gillespie and Wasif, *locc. cit.*), whereas, at the maximum conductivity, about half is un-ionised and beyond that point an increasing proportion remains in the molecular state. Eventually, it separates as a distinct phase.

But Millen's findings show the ionic concentration increases with that of dinitrogen tetroxide, at least up to 20 mol. % of the latter, despite the withdrawal of ions to form sulphuric and nitric acid molecules. Yet the electrical conductivity, due in great part to the hydrogen sulphate ion, HSO_4^-, falls after the concentration of 6·8 mol. % has been passed. In seeking to account for this anomaly, let us consider in turn density and viscosity.

The density of the sulphuric acid solutions (Fig. 2) increases by about 3·8%, being at a maximum with about 16 mol. % of dinitrogen tetroxide, and thence falling regularly. Increase in density suggests molecular association. Such an increase also occurs in dilute solutions of nitric acid in sulphuric acid (Gillespie and Wasif, *J.*, 1953, 215) and can be safely predicted for dinitrogen pentoxide and trioxide. Similar increases are found in solutions of the hydrogen sulphates of ammonium, lithium, sodium, potassium, and barium. Among the plots of density (Fig. 3; from data in Gillespie and Wasif, *ibid.*, p. 217, Figs. 1 and 4) ours for dinitrogen tetroxide lies close to theirs for nitric acid and above all the rest except barium; here the considerable solvation and possibly the mass of the cation are significant. It is noteworthy that they are greatly above that of water (Gillespie and Wasif, *J.*, 1953, 204) which is ionised according to the equation

FIG 2. *Specific electrical conductivity (ohms^{-1} cm.$^{-1}$), density, and relative viscosity of solutions of dinitrogen tetroxide in sulphuric acid.*



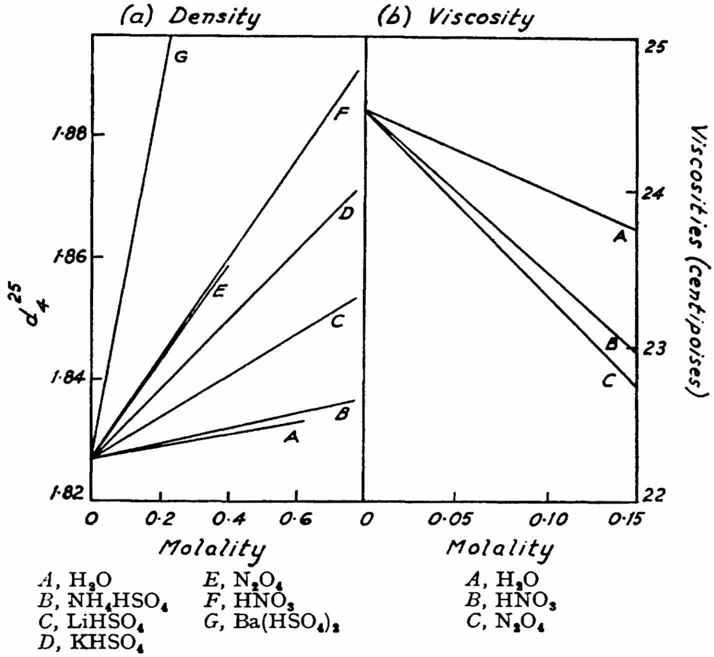
Conductivity: ● *expt.* 1; ■ *expt.* 2. △ *Density.* □ *Viscosity.*

$$H_2O + H_2SO_4 \longrightarrow H_3O^+ + HSO_4^-$$

and that thus neither the HSO_4^- ion, solvated or otherwise, nor the hydroxonium ion can be responsible for the density changes observed. It is therefore necessary to turn to the other entities present: NO_2^+, NO^+, N_2O_4, and, at higher concentrations (20 mol. %), HNO_3. The metal cations are solvated in sulphuric acid; and, though evidence about the molal volume of the nitronium ion does not permit an estimate of the extent, there is good reason to suppose that it is solvated (Gillespie and Wasif, *loc. cit.*), the nitrosonium ion also. This leads us to believe that the rise of the density curve springs from a progressive increase in the number of solvated NO_2^+ and NO^+ ions. Millen's Raman results (*loc. cit.*) indicate that, at about 20 mol. %, equilibrium conditions involve the union of some ions to form nitric acid; and it is not improbable that nitrosyl hydrogen sulphate may be produced in the solution. The maximum of the density curve may very well correspond to the concentration of dinitrogen tetroxide at which the various equilibria lead to the maximum number of solvated NO_2^+ and NO^+ ions. If this be so, then the regular fall of the curve from the maximum with increasing concentration can be regarded as a dilution effect due to molecular dinitrogen tetroxide. Similar behaviour has been observed by Gillespie and Wasif (*loc. cit.*) in solutions of sulphuryl chloride, which does not ionise in sulphuric acid. The curves of conductivity and density show so little parallelism, and the maximum of the latter is displaced so far in the direction of higher concentration, as to make it doubtful whether density and conductivity are intimately connected.

Very closely related to the conductivity curve, however, is that of the viscosity (Fig. 2). The viscosities of dilute solutions of water and nitric acid in sulphuric acid (Gillespie and Wasif, *loc. cit.*) fall with increasing concentration, the latter to much the same extent as we have found for dinitrogen tetroxide (Fig. 3). Our plot of viscosity, however, being carried further, shows a minimum at 2·6 mol. %. This is the concentration at which the initial slope of the conductivity curve when produced meets a continuation of the average slope beyond the peak. It may well represent the concentration up to which all the dinitrogen tetroxide present is ionised and, of course, the point beyond which some is in the molecular form. Solvation has been invoked to explain the change in density; it cannot be used to account for the changes in viscosity. The solvation of metal cations has been given (Gillespie and Wasif, *loc. cit.*) as the cause of the increase in viscosity with concentration, but the argument clearly does not apply to NO_2^+ and NO^+. With these there is first a small fall in viscosity followed by a considerable regular rise. The rise we ascribe to compound formation, since compound formation of one kind or another is possible from about 2·6 mol. % and is progressively more probable up to the final concentration, *viz.*, the point where nitrosyl hydrogen sulphate crystallises. The electrical conductivity curve so closely follows the inverse of the viscosity curve as strongly to suggest that the viscous interference with the translation and rotation of the HSO_4^- ions largely accounts for the observed fall in conductivity. The dilution of the medium by un-ionised dinitrogen tetroxide must also reduce the conductivity, but, we think, not comparably with the change in viscosity.

FIG. 3. *Densities and viscosities of certain dilute solutions in sulphuric acid.*



Our views are set out schematically as four stages, corresponding to four regions of concentration in the dinitrogen tetroxide–sulphuric acid system.

Stage I (up to 2·6 mol. % and minimum viscosity). All the N_2O_4 is ionised :

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

Stage II (from 2·6 to 6·8 mol. % and maximum conductivity). Some at least of the N_2O_4 is in the molecular condition. Compound formation begins and viscosity increases.

Stage III (6·8 to 16 mol. % and maximum density). Viscosity continues to increase. Solvated NO_2^+ and NO^+ ions reach maximum concentration in accordance with following equilibria :

(*a*) Nitric acid formed,

$$N_2O_4 + 3H_2SO_4 \rightleftharpoons NO^+ + NO_2^+ + H_3O^+ + 3HSO_4^- \rightleftharpoons HNO_3 + 2H_2SO_4$$

(*b*) Nitrosyl hydrogen sulphate formed,

$$NO^+ + HSO_4^- \rightleftharpoons NOHSO_4$$

Stage IV (16 to 45 mol. % and crystallisation of nitrosyl hydrogen sulphate). Further compound formation. Dilution of medium by molecular N_2O_4. Further increase in viscosity.

Speculation on the mechanism and intermediates involved in these equilibria is not yet profitable.

There is reason to suppose that the conductivity curve of the solutions in selenic acid has a similar explanation. Clearly, however, the possible concentration of completely ionised dinitrogen tetroxide is smaller in our selenic acid than in sulphuric acid, but whether our selenic acid was absolute is uncertain. If it contained moisture, the conductivity recorded for it will be too high and the true curve would be more like that of sulphuric acid. Nevertheless, since Ingold, Millen, and Poole (*Nature,* 1946, **158**, 480) found nitric acid in selenic acid to give NO_2^+ and $HSeO_4^-$, there is justification for assuming the following equilibria, particularly as crystals of nitrosyl hydrogen selenate are obtained :

$$N_2O_4 + 3H_2SeO_4 \rightleftharpoons NO_2^+ + NO^+ + H_3O^+ + 3HSeO_4^- \rightleftharpoons HNO_3 + 2H_2SeO_4$$
$$NO^+ + HSeO_4^- \rightleftharpoons NOHSeO_4$$

We have not measured densities and viscosities, but appearance leads us to think they follow a similar course to those involving sulphuric acid.

The conductivity of our phosphoric acid suggests that it was near absolute and that the difference in the conductivity curve from that of sulphuric acid is real. In particular there is only a short range of colourlessness; within that range the process of ionisation may well be

$$N_2O_4 + 3H_3PO_4 = NO_2^+ + NO^+ + H_3O^+ + 3H_2PO_4^-$$

We do know that the viscosity increases with the addition of dinitrogen tetroxide, and especially so at higher concentrations.

As all the experiments were done above laboratory temperature, the nitrogen peroxide contained nitrogen dioxide as well as dinitrogen tetroxide. But, since every solution is colourless when sufficiently dilute, it is probable that the presence of a little NO_2 does not seriously upset the course the reaction follows when N_2O_4 is present alone.

EXPERIMENTAL

Preliminary.—Sulphuric acid was shown to absorb about 0·9 mol. of N_2O_4 per mol. of H_2SO_4. The solution appeared colourless up to about 7 mol. %, gradually darkened, and finally deposited $NOHSO_4$ at about 48 mol. % of N_2O_4. Nitrosyl hydrogen sulphate was also obtained on adding sulphuric acid to dinitrogen tetroxide (Found : N, 10·4; S, 24·9%; equiv., 41·9. Calc. for $NOHSO_4$: N, 11·0; S, 25·2%; equiv., 42·3); m. p. 83—84° (decomp.).

Selenic absorbed about 0·75 mol. of N_2O_4 per mol. of H_2SeO_4. Up to about 7 mol. % it remained colourless, gradually darkened and finally deposited $NOHSeO_4$ at about 40 mol. % of N_2O_4. Nitrosyl hydrogen selenate was also obtained by adding selenic acid to the tetroxide (Found : N, 7·5; Se, 46·1%; equiv., 59·0. Calc. for $NOHSeO_4$: N, 8·0; Se, 45·4%; equiv., 58·0); m. p. 85—86° (decomp.).

Phosphoric acid absorbed about 0·13 mol. of N_2O_4 per mol. of H_3PO_4. The solution became yellow at a low concentration; no solid separated from mixtures with either component in excess even on strong cooling.

The three acids, when saturated with dinitrogen tetroxide, were immiscible in it. In the case of sulphuric acid, the layer of tetroxide which separated was shown to contain nitric acid, but no sulphuric acid.

The solids were separated from their mother-liquors by filtration through a glass frit, and dissolved in water under conditions which avoided loss of oxides of nitrogen. In the solution nitrogen was determined by reduction with Devarda's alloy in a Kjeldahl apparatus, sulphur by precipitation as barium sulphate, selenium by reduction to the element. Direct titration of an aqueous solution, using carbonate-free 0·1N-sodium hydroxide with methyl-red as indicator, gave the acid equivalent weight. The $NOHSeO_4$ was less easy to isolate and showed slight decomposition at the ordinary temperature. Both nitrosyl hydrogen sulphate (see Elliott, *J.*, 1926, 1219) and selenate (Meyer and Wagner, *J. Amer. Chem. Soc.*, 1922, **44**, 1032) are known.

Materials.—Absolute sulphuric acid was made by dilution of high-quality dilute oleum with conductivity water until the minimum conductivity was attained. Selenic acid (B.D.H.) was used without further purification, the sample with the lowest conductivity being chosen. The same applies to phosphoric acid which was B.D.H., 100%. Both are solid, but as they readily supercool after melting, conductivities on the liquids at 25° could be measured. Crude dinitrogen tetroxide from copper and concentrated nitric acid was passed with oxygen over phosphoric oxide and condensed on to phosphoric oxide at −180°. After standing, this material was fractionated in a vacuum by bulb-to-bulb distillation with rejection of head and tail fractions, and stored in tubes fitted with break-seal joints.

Manipulation and Measurement.—To avoid atmospheric moisture, the materials were handled and the mixtures made in a vacuum, or under air dried by phosphoric oxide and protected with phosphoric oxide guard tubes.

The measurement of conductivity will be dealt with in a later paper; we merely record that results were accurate to ±0·00002 ohm^{-1} cm.$^{-1}$ at 25·00° ± 0·01°. The densities were determined by weighing a standard volume of liquid under conditions which protected it from atmospheric moisture. An accuracy of ±0·01 g. per c.c. was sufficient for our purpose and more is not claimed. The viscosities except for those of very dilute solutions (used in Fig. 3) are on an arbitrary scale, being for comparative purposes only.

Results.—The specific conductivities, κ, in ohms^{-1} cm.$^{-1}$ at 25° for solutions of dinitrogen tetroxide in the three acids are given in the Tables.

Expt. 1				Expt. 2					
Concn. (mol. %)	100 κ	Concn. (mol. %)	100 κ	Concn. (mol. %)	100 κ	Concn. (mol. %)	100 κ	Concn. (mol. %)	100 κ
				Sulphuric acid.					
47·56	2·551	1·808	6·299	42·66	3·246	6·871	9·956	2·077	7·215
35·02	4·938	0·8065	3·807	32·11	5·282	6·113	10·15	1·291	5·426
25·56	6·925	0·3746	2·313	20·24	7·246	5·655	10·30	0·6440	3·725
14·54	8·736	0·1433	1·438	9·593	9·467	3·921	9·409	0·0000	1·045
7·181	10·26	0·0000	1·045	8·611	9·595	3·031	8·559		

Selenic acid.

Expt. 1				Expt. 2		Expt. 3		Expt. 4	
43·29	2·919	13·46	7·733	27·60	4·654	19·48	6·372	15·38	7·272
39·37	3·082	9·464	8·355	18·01	6·653	9·033	7·912	7·921	8·485
35·31	3·455	4·699	8·993	10·56	7·818	4·205	8·922	3·821	8·864
30·94	4·414	0·5545	9·576	5·371	8·887	2·246	9·141	2·266	9·233
26·73	5·184	0·3120	9·625	1·075	9·481			1·280	9·430
20·46	6·439	0·0000	9·105					0·6146	9·569
16·64	7·174							0·2706	9·624
								0·0000	9·092
				Phosphoric acid.					
11·50	3·132	2·43	4·803	0·893	5·054	0·135	5·216	0·013	5·207
6·94	4·084	1·69	4·944	0·500	5·126	0·0595	5·232	0·000	5·192
4·53	4·483	1·36	4·982	0·252	5·170	0·0305	5·220		

This work was carried out during the tenure of a Salters' Fellowship (G. H.).

KING'S COLLEGE, NEWCASTLE-ON-TYNE, 1.

[*Received, March 31st*, 1955.]