189. *Nitration in Sulphuric Acid. Part II. Migration of Nitric Acid to the Cathode during Electrolysis in Oleum Solution.*

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Analysis of the various parts of a solution of nitric acid in oleum of up to 18% SO_3 content, after electrolysis, shows that there is a general migration of nitric acid towards the cathode accompanied by some reduction at this electrode. Experiments in which barium is also present show that in a 16—18% oleum the nitric acid has a mobility of between 2 and 4 times that of the barium ion.

Experiments are also described on the electrolysis of solutions of nitrous acid and of nitrogen pentoxide in oleum and of nitric acid in 98·7% sulphuric acid.

Hantzsch (*Ber.*, 1925, **58**, 941) tried to prove the presence of the nitracidium cations in mixed acids (in which the molar ratio $H_2SO_4/H_2O > 1$) by migration experiments similar to those which were successful for the nitracidium perchlorates in nitromethane (Hantzsch and Berger, *Ber.*, 1928, **61**, 1328). He says (*loc. cit.*, p. 961) : " Experiments for the electrolytic detection of the nitronium (nitracidium) cation have already been undertaken, by the electrolysis of solutions of nitric acid in sulphuric acid, in which the nitric acid should migrate to the cathode. However, these experiments have for the present remained unsuccessful, for the sulphuric acid alone was decomposed—probably because the decomposition potential of the sulphurylium sulphate present in the sulphuric acid is smaller than that of the nitronium sulphate." His observations were confirmed by one of us in collaboration with Miss S. Ram in 1935. It is true that reduction of the sulphuric (and nitric) acids occurs at the cathode, but the passage quoted seems to confuse the electrode processes with the transport in the body of the electrolyte. More recently it seemed to us that, apart from the complication of reduction taking place at the cathode, the detection of the movement of a nitric acid cation in electrolysis was probably prevented by the presence in solution of the OH_3^+ ion. This ion would have great mobility and would consequently carry a large share of the current, so that the movement of the nitric cation might be obscured or appear reversed. It seemed, therefore, that a solution of nitric acid in an oleum of moderate sulphur trioxide content might be a better subject for investigation. The use of oleum as medium has the further advantage that sulphur trioxide is reduced preferentially at the cathode and so furnishes partial protection for the nitric acid.

EXPERIMENTAL.

Materials.—Oleum media were prepared by distilling sulphur trioxide from commercial oleum into sulphuric acid, followed by one or more redistillations. Media were analysed for sulphur trioxide content by titration with water (Brand, this vol., p. 585). Anhydrous nitric acid was made by distilling 70% nitric acid from 98% sulphuric acid at 15 mm. Nitrogen pentoxide was made by distillation of a mixture of anhydrous nitric acid and phosphoric oxide.

Apparatus.—The first experiments were made with a Pyrex U-tube fitted with ground glass stoppers, each carrying (*a*) an outlet tube leading to a sulphuric acid bubbler, and (*b*) the sealed-in platinum leads to the electrodes. These were of smooth platinum, each formed of a horizontal spiral of stout wire (area 1·23 sq. cm.), situated not more than 1 mm. below the meniscus of the electrolyte. Several experiments in which platinised platinum electrodes were used showed so great an increase in the reduction of both nitric and sulphuric acids at the cathode that this type of electrode was abandoned. The U-tube was cooled by immersion in running water at room temperature. After electrolysis, one or more samples were pipetted from the vertical limbs of the U-tube and the residue was poured from the horizontal portion. Pipette samples were always taken from the extreme upper layer of liquid, so that the first samples to be extracted (usually 2 c.c.) contained the liquid nearest to the electrodes. Products and losses due to electrode decomposition were generally concentrated in these. In later experiments (from No. 24 onwards) a more detailed record of the final distribution of solute was obtained by using a W-tube, composed of three vertical limbs (" cathode," " centre," and " anode " in the tables) connected by two horizontal portions. The two extreme vertical limbs carried the electrodes and outlet tubes; the central limb was stoppered. With this apparatus, successive samples were pipetted from the vertical limbs and, finally, two intermediate samples (" cathode middle " and " anode middle ") were taken by pouring the liquid which remained (after withdrawing the electrode and middle samples) simultaneously from the two ends of the apparatus.

Analysis.—In all samples, the nitric acid was determined, usually by the nitrometer, any nitrous acid formed by reduction being thus included. In a number of experiments, electrometric titration by ferrous sulphate (Treadwell and Vontobel, *Helv. Chim. Acta*, **1937**, **20**, 573) was used to estimate nitric acid alone. When large differences between the results of these two methods revealed the presence of nitrous acid, this was often estimated by ceric sulphate.

Sulphur dioxide formed by cathode reduction interfered with the nitrometer analysis. After a number of experiments this was found to be removable by potassium permanganate. Using a freshly made solution of permanganate in 50% sulphuric acid, it was found that sulphur dioxide present in a sample would not reduce it rapidly if the concentration of the sample was more than 60% H_2SO_4. The first method adopted therefore involved cautious addition of water to the sample in an ice-cooled stoppered tube until the 60% concentration was reached, followed by permanganate in 50% acid drop by drop until a permanent pink colour remained. The sample was then washed into the nitrometer with concentrated sulphuric acid, and the analysis completed as usual. This procedure was in general satisfactory, but the addition of water to an oleum containing more than about 10% of sulphur trioxide caused some loss of nitrous fumes with a consequent error of up to 2% on the result for the nitric acid content.

The second method, suitable for oleums strong in sulphur trioxide, was to remove the sulphur dioxide by adding just enough finely powdered solid potassium permanganate directly to the oleum samples before introduction into the nitrometer, and to shake until the smell of sulphur dioxide disappeared (cf. Lunge and Keane, " Technical Methods of Chemical Analysis," 1908, Vol. I, p. 345). Too great an excess of permanganate interferes with the reaction in the nitrometer, but tests showed that up to 2 mg. of this salt may be added to each g. of oleum without affecting the volume of nitric oxide subsequently developed; and this quantity is enough to destroy the sulphur dioxide in the cathode limb of a typical migration experiment. For example, in analysing a solution of nitric acid in 18% oleum, 1-c.c. samples gave the following volumes (in c.c.) of nitric oxide at N.T.P. :

(1) With no SO_2 present	16·34	(3) SO_2 present (no $KMnO_4$ treatment)	16·6
(2) With 2—3 mg. $KMnO_4$ added (no SO_2)	16·37	(4) Sample (3) with added $KMnO_4$	16·35

Cathode Reduction.—Losses of nitric acid were of two kinds : (*a*) due to formation of gaseous nitrogen oxides, lost to subsequent analysis; (*b*) due to reduction to nitrous acid, included in the nitrometer analysis and sometimes estimated separately. (*a*) The total balance of nitrogen acid revealed a small loss which increased with the time of electrolysis and with the current strength. With oleums of higher sulphur trioxide content the loss of nitrogen acid was less, the reduction of sulphur trioxide to sulphur dioxide then taking precedence. Nitrous fumes were sometimes visible escaping from the solution at the cathode, and frequently white crystals of nitrosylsulphuric acid were deposited on the wall of the tube above the catholyte. As a result of the cathode processes a small volume of electrolyte near the cathode was always distinguishable as having a different density and refractive index and, sometimes, as no longer fuming. This part of the electrolyte had usually a pink or mulberry colour, probably caused by the presence of traces of iron and the reaction of these with nitrous acid. The colour could be reduced or eliminated by taking extreme precautions, redistilling the oleum repeatedly and excluding all dust.

It was found best to remove this coloured layer completely and separately as one sample, since it carried almost the whole of the cathode loss; a second sample then represented the normal cathode concentration. Much of the loss from the solution occurred as nitric oxide. After reaction with air in the apparatus, this was absorbed by the sulphuric acid bubbler and could be estimated by the nitrometer. (*b*) Appreciable amounts of nitrous acid (as nitrosyl sulphate), formed by reduction of nitric acid at the cathode, were also retained within the solution and could be estimated by direct analysis (see Table IV). Conversion into nitrous acid was small in experiments conducted in media containing 17—18% of sulphur trioxide, amounting then to about 5 moles-% of the nitric acid originally present. Here again reduction centres upon the sulphur trioxide of the medium; and the quantity of nitrous acid formed consequently increases if a solution of nitric acid is electrolysed in a weaker oleum or in concentrated sulphuric acid.

A smell of ozone was obvious at the anode and peroxidic substances were formed there.

Electrolysis of Solutions containing Barium.—The nitric acid was determined, as usual, with the nitrometer : the barium by diluting the sample and collecting the precipitated sulphate in a porous porcelain crucible and igniting at 800°. The precipitates, which were of about 10 mg., were weighed on a Sartorius micro-balance.

Electrolysis of Oleum containing s-*Trinitrobenzene.*—In the course of experiments aimed at checking whether the observed migration of nitric acid was real or due to a contrary motion of the medium, trinitrobenzene was chosen as an inert solute, known from the cryoscopic evidence not to produce ions in sulphuric acid. Unfortunately, this substance is decomposed by oxidation at the anode and is therefore not a satisfactory neutral indicator; nevertheless, the experiment, upon examination, has significance.

Solutions of trinitrobenzene in oleum were electrolysed for 5 hours with a current of 0·06 amp., and the liquid then taken for analysis in several divisions. The organic matter in each sample was determined by dilution, extraction with benzene, and evaporation and weighing of the residue. Nitric acid was also determined. The results are summarised in Table I.

TABLE I.

Electrolysis of s-*Trinitrobenzene in* 13·7% *Oleum.* (Time : 5 hrs. Current : 0·06 amp.)

			After electrolysis.				
	Concn., mol./l., of :	Original solution.	Cathode.	Cathode middle.	Centre.	Anode middle.	Anode.
Expt. 26.	T.N.B.	0·435	0·445	0·430	0·439	0·386	0·387
	HNO_3	0	0·010	0·019	0·008	0·099	0·101
	[T.N.B.] + $[HNO_3]/3$ ...	0·435	0·448	0·436	0·442	0·419	0·421
Expt. 27.	T.N.B.	0·464	0·464	0·462	—	0·431	0·419
	HNO_3	0	0·026	0·014	—	0·075	0·108
	[T.N.B.] + $[HNO_3]/3$ ...	0·464	0·473	0·467	—	0·457	0·455

Calculation shows (1) that 3 moles of nitric acid appear for each mole of trinitrobenzene lost, and (2) that a total balance of 99·7% of the original trinitrobenzene is accounted for if allowance is made for that which produces nitric acid. It is, moreover, apparent that destruction of the trinitrobenzene occurs at the anode and that nitric acid has spread from that end of the solution towards the cathode. The last line of figures for each experiment gives a corrected concentration of trinitrobenzene, and this shows a rise at the cathode and a fall at the anode amounting, in each instance, to 2—3%. It is evident, however, that some of this apparent movement may be due to migration of the nitric acid liberated at the anode, so that the figure of 2—3% represents an upper limit to the possible transport of sulphuric acid under consideration. A comparison of this result with those of the experiments with nitric acid shows that the migration of nitric acid observed (Tables II—IV) was several times greater than this maximum effect of movement of sulphuric acid. The electrolysis of a solution containing both the indicator substance and the nitric acid, which would be the best evidence, could not be conclusive here in view of the confusion arising between nitric acid from the trinitrobenzene indicator and the nitric acid added as solute.

DISCUSSION OF RESULTS.

Table II gives full particulars of the experimental conditions, with results in terms of the volume of nitric oxide evolved from 1-c.c. or 2-c.c. samples after electrolysis.

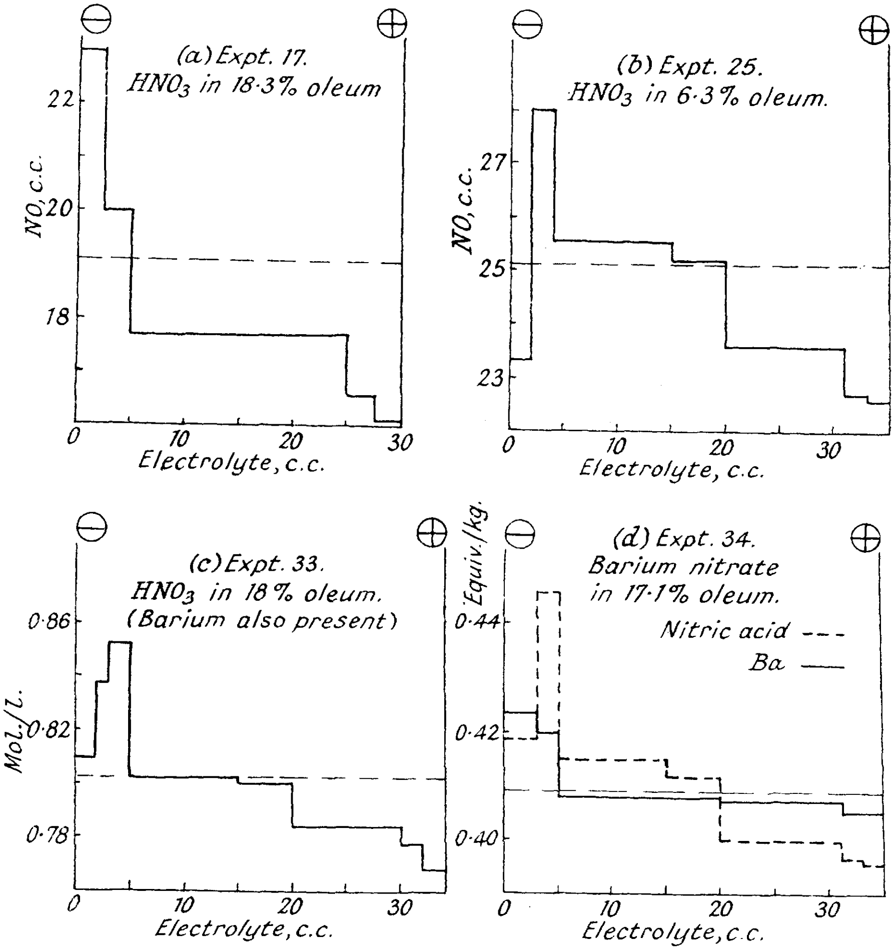
The results, essentially the same with both types of apparatus, are most easily appreciated graphically. Examples are shown in the figure, representing the distribution of nitric acid after electrolysis of originally homogeneous solutions. Apart from a fall due to loss by reduction to gaseous products in the immediate neighbourhood of the cathode (seen best in the W-tube experiments), there is a general accumulation of nitrogen acids at the cathode and a deficit at the anode after electrolysis.

It is necessary, however, to prove that the observed movement of nitrogen acid from anode to cathode is real and not merely an apparent migration caused by transport of other components in the opposite direction. For this purpose it would be desirable to repeat the migration experiments in presence of a solute known to be a non-electrolyte in oleum, since any change of concentration of such a material after electrolysis would be due to migration of the solvent. But to find a substance which is a non-electrolyte in oleum solution and is also chemically stable to oleum (and preferably to nitric acid as well) is not easy. Some experiments with *s*-trinitrobenzene have been referred to in the experimental section. Satisfactory results were obtained by carrying out simultaneous migrations of nitric acid and of the barium ion.

Hammett and Lowenheim (*J. Amer. Chem. Soc.*, 1934, **56**, 2620; cf. Riesenfeld and Feld, *Z. Elektrochem.*, 1920, **26**, 286; Meyer and Friedrich, *Z. physikal. Chem.*, 1922, **101**, 498) studied the electrolysis of barium sulphate in anhydrous sulphuric acid. Using trichloroacetic acid as a neutral indicator substance, they found a small but real migration of barium into the cathode compartment. They measured an apparent transport number $n_c = 0{\cdot}012$ for the barium ion, which fell to 0·007 after correction for movement of the medium; and they concluded that conduction must be largely by the proton-jump mechanism (Grotthuss conduction), which means that transfer of solvent molecules will be correspondingly small. Although this in itself makes it unlikely that our observed migration of nitric acid towards the cathode could be entirely caused by solvent movements, we have nevertheless used the barium ion as an indicator in further migration experiments in which barium and nitric acid were simultaneously present in oleum solution.

The results are given in Table III. Expt. 28 confirms the small cathode migration of the barium ion on electrolysis of a solution of barium sulphate in oleum. The remaining experiments in this table were performed with solutions prepared by dissolving barium nitrate in oleum; and the distribution of barium after electrolysis was determined gravimetrically. The results show (cf. section *d* of figure) that, during electrolysis, migration of nitrogen acid is 2—4 times more pronounced than that of barium (cf. Table V). Since barium is known to undergo a real migration, the reality of the nitric acid migration is thus confirmed.

It may still be objected that the nitrometer method of analysis records both nitric and nitrous acids and it remains to be proved that the observed migration is in fact migration of *nitric acid.* To test this point, samples after electrolysis were divided and analysed (*a*) for total nitrogen acids by nitrometer, (*b*) for nitric acid by electrometric titration with ferrous sulphate, (*c*) for nitrous acid by quantitative oxidation with ceric sulphate. The results are given in Table IV, which includes a number of duplicate analyses to show the reproducibility of the experiments.



Distribution of nitric acid after electrolysis in oleum solution.
Horizontal broken line : Solution before electrolysis.
In (a) *and* (b) *ordinates show c.c. of* NO *given by* 2 *c.c. of electrolyte.*

TABLE II.

*Electrolysis of Solutions of Nitric Acid in Oleum.**

Expt. No.	Medium, % SO_3.	HNO_3, mol./l.	Time, hrs.	N Acids recovery, %.	Original solution.	C.c. of NO at N.T.P. from 2 c.c. of electrolyte. After electrolysis : Cathode. I.	Cathode. II.	Cathode middle.	Centre.	Anode middle.	Anode. I.	Anode. II.
A. *Solution prepared from oleum and anhydrous nitric acid.*												
14	4·5	0·414	5	95	18·2	18·8		—	17·5	—	16·7	
15	18·3	0·427	5	97	19·1	19·4		—	18·4	—	18·0	
17	18·3	0·427	21	96	19·1	23·0	20·0	—	17·7	—	16·6	16·1
21	9·6	0·357	20·5	92	15·97	16·77	16·81	—	14·38	—	14·18	14·09
22	9·6	0·357	10	96	15·97	18·49	17·03	—	15·37	—	15·00	14·86
24	6·3	0·560	10	98	25·05	25·25	28·23	26·08	24·41	23·00	23·03	23·51
25	6·3	0·560	7	98	25·05	23·31	27·99	25·54	25·20	23·58	22·75	22·61
B. *Solution prepared by dissolving barium nitrate in oleum.*												
C.c. of NO at N.T.P. from 1 c.c. of electrolyte.												
31	16	·0·805	6·8	99·8	18·03	18·67		18·30	18·04	17·69	17·46	
32	18·1	0·832	6·75	99·4	18·46	18·19	18·97	18·78	18·47	17·98	17·95	17·58
33	18·3	0·803	6·7	99·5	18·02	18·2 18·8	19·1	17·93	17·90	17·58	17·45	17·21
C. *Solution of nitrogen pentoxide in oleum.*												
42	16·9	—	7·3	99·5	12·90 12·97	14·1	13·21	13·06 12·92	12·82 12·83	12·60 12·70	12·31	12·17

* The current was 0·06 amp. except for Expts. 14 and 15, where it was 0·1 amp., and Expt. 17, where it was 0·07 amp.

TABLE III.

*Electrolysis of Solutions of Barium Sulphate and Nitric Acid in Oleum.**

Expt. No.	Medium, % SO_3.	Solute, mol./kg.	Time, hrs.		Re-covery, %.	Original solution.	Analysis of samples of electrolyte (mol./kg.). After electrolysis.					
							Cathode. I.	Cathode. II.	Cathode middle.	Centre.	Anode middle.	Anode.
28	13·6	0·247 $BaSO_4$	5	Barium	100·1	0·2470	0·2511		0·2473	0·2468	0·2468	0·2465
30	16	0·219 $Ba(NO_3)_2$	6·9	Barium	—	0·2217	0·2259		0·2230	0·2226	Deposition of solid prevented analysis	
				N-acid	—	0·443	0·459		0·441	0·440		
34	17·1	0·205 $Ba(NO_3)_2$	7·2	Barium	99·96	0·2044	0·2119	0·2102	0·2040	0·2040	0·2038	0·2028
				N-acid	99·7	0·410	0·419	0·446	0·415	0·412	0·400	0·397, 0·396
35 †	18·2	0·190 $Ba(NO_3)_2$	7·5	Barium	99·95	0·190	0·1951	0·1920	0·1902	0·1900	0·1892	0·1874
				N-acid	99·5	0·395	0·400	0·423	0·400	0·393	0·384	0·379

* The current in each experiment was 0·06 amp.

† Owing to a defect in the nitrometer, the analyses for N-acids in Expt. 35 are high throughout by approximately 3%.

TABLE IV.

Expt. No.	Medium.	Time, hrs.*		Re-covery, %.	Original solution.	Analysis of samples of electrolyte (mol./l.). After electrolysis.						
						Cathode. I.	Cathode. II.	Cathode middle.	Centre.	Anode middle.	Anode. I.	Anode. II.
Electrolysis of nitric acid solutions.												
41	SO_3 17·1%	7·6	N-acids	99·5	0·645	0·658	0·699	0·649	0·643	0·628	0·618	0·614
			HNO_3	94·8	0·642	0·300	0·61	0·648	0·633	0·630	—	0·610
			HNO_2		0·0	(0·358)	(0·09)	(0)	(0)	(0)	(0)	(0)
37	H_2SO_4 98·7%	8·5	N-acids	96·5	0·649 0·650	0·473	0·633	0·664 0·670	0·651 0·651 0·657	0·648 0·652 0·658	0·618	0·592
38	H_2SO_4 98·7%	8·5	N-acids	97·5	0·662 0·666 0·663	0·578	0·654	0·678 0·673	0·660 0·662	0·657 0·658	0·613	0·595
			HNO_3	66	0·671	0·027	0·286	0·405	0·553	0·556	0·612	—
			HNO_2	31	0·0	0·556	(0·366)	0·259 0·262	0·098	0·187	(0)	—
Electrolysis of nitrosyl sulphate in oleum.												
39	SO_3 18%	17·9	N-acids	99·7	0·615	0·660	0·632	0·625 0·630	0·618 0·611	0·596 0·592	0·581	0·575
40	SO_3 17·1%	19·2	N-acids	98·6	0·517 0·508 0·512	0·578	0·536	0·512 0·520	0·499 0·494	0·484 0·485	0·484	0·478
			HNO_3	49	0·0	0·0	0·062	0·145	0·044	0·440	0·482	
			HNO_2	49		(0·578)	(0·474)	0·362	—	0·041	—	

Note.—HNO_2 concentrations in parentheses are determined by difference, not by direct analysis for HNO_2.

* The currents were : Expts. 37 and 38, 0·07 amp.; Expts. 39 and 40, 0·05 amp.; Expt. 41, 0·06 amp.

Experiment 41 is conclusive for electrolysis in oleum solution. It shows, as usual, a deficit of nitrogen acid at the anode and an increment at the cathode, less marked in the sample " Cathode I " withdrawn from the immediate vicinity of the cathode than for " Cathode II," taken from a layer of liquid not immediately touching the cathode, because of cathode reduction of nitric acid to gaseous products which are lost. But the significant feature of the experiment is that, after electrolysis, nitrous acid is present only in the cathode limb and mainly in the sample " Cathode I," drawn from the immediate vicinity of the electrode. No nitrous acid is found in other parts of the apparatus.

It must therefore be *nitric acid* which migrates from anode to cathode, to suffer partial reduction at the cathode. Taken together with the final distributions observed in the other migrations, the result of Expt. 41 also disposes of the alternative supposition that destruction of nitric acid at the cathode is the prime cause, and that compensatory thermal diffusion sets up the inequalities of concentration observed after electrolysis. This supposition cannot be maintained, because it would require a deficit in the middle instead of at the anode, where it is found; and could not account for the increment observed in the cathode limb in samples not drawn from the immediate neighbourhood of the cathode.

The results of Tables II—IV therefore prove that, in oleum solution, nitric acid migrates from anode to cathode during electrolysis; and must exist in oleum solution in the form of a cation. The experimental arrangement is not sufficiently elaborate for the measurement of transport numbers; but it is useful to compare quantitatively the extent of transport of the nitro-cation with that of the barium ion under the same conditions. In Table V calculations are given for the transport of both ions from the anode in the W-tube experiments.

TABLE V.

Transport of Barium and Nitric Acid from the Anode in Oleum.

Expt. No.	Solute. Substance.	Solute. Concn.	Medium, % SO_3.	Transport, in equiv./Faraday. HNO_3.	Transport, in equiv./Faraday. Ba.
25	HNO_3	0·560 mol./l.	6·3	0·034	—
28	$BaSO_4$	0·247 mol./kg.	13·6	—	0·008
30	$Ba(NO_3)_2$	0·219 mol./kg.	16·0	Anode not analysed	0·007
31	$Ba(NO_3)_2$	0·402 mol./l.	16·0	0·019	Not analysed
32	$Ba(NO_3)_2$	0·412 mol./l.	18·1	0·022	,,
33	$Ba(NO_3)_2$	0·401 mol./l.	18·3	0·019	,,
34	$Ba(NO_3)_2$	0·205 mol./kg.	17·1	0·021	0·007
35	$Ba(NO_3)_2$	0·190 mol./kg.	18·2	0·022	0·004
38	HNO_3	0·663 mol./l.	98·7% H_2SO_4	0·014	—
40	$Ba(NO_3)_2$	0·322 mol./l.	16·9	0·018	Not analysed
42	N_2O_5	{0·577 equiv./l. 0·288 mol./l.	16·9	0·016	—

In competitive experiments, the cation of nitric acid in oleums of sulphur trioxide content of 16—18% has a mobility of 2—4 times that of the barium ion.

Migration in Concentrated Sulphuric Acid.—It is obviously desirable to extend the proof of cathode migration of nitric acid from oleum media to concentrated sulphuric acid media, free from sulphur trioxide. The effect of electrolysing solutions of nitric acid in 98·7% sulphuric acid is shown in Table IV (Expts. 37 and 38). After electrolysis there is a marked fall in concentration of nitrogen acids in the anode limb and there is a general movement of such acid towards the cathode. But when sulphur trioxide is absent, nitric acid becomes the principal target for cathode reduction, as Hantzsch observed. Gaseous losses (mainly nitric oxide) at the cathode are greater than in oleum solutions, and cathode reduction to nitrous acid is so extensive and disturbing that nitrous acid becomes distributed, during electrolysis, as far as the " anode middle " section of the electrolyte (Expt. 38). Disregarding the cathode compartment, it is clear in both Expts. 37 and 38 that nitric acid migrates away from the anode. The extent of transport from the anode is comparable with that observed in oleum media (Table V, Expt. 38).

Migration of Nitrous Acid in Oleum Media (cf. Angus and Leckie, *Trans. Faraday Soc.*, 1935, **31**, 958).—For comparison with the experiments of the preceding paragraph, nitrosyl sulphate was electrolysed in 18—19% oleum (Table IV). Migration of nitrogen acids from anode to cathode takes place, but only to about two-thirds of the extent observed with nitric acid in a similar medium. At the same time, anodic oxidation of nitrous acid to nitric acid is very great (after electrolysis the anode limb contains 94 mol.-% of nitric acid) and nitric acid is found even in the cathode limb (Expt. 40). The experiments give no clear evidence about the electrolytic migration of the NO^+ ion and it might even be argued that the greater part of the current is carried by the nitric acid cation.

Migration of Nitrogen Pentoxide in Oleum Medium.—When electrolysed in oleum solution, nitrogen pentoxide migrates from anode to cathode (Table II, C). The nitrogen pentoxide employed contained 94% (w/w) of N_2O_5, the remainder being N_2O_4. Migration of the impurity is quite insufficient to account for the effect observed. The transport is comparable in magnitude (Table V) with that observed for nitric acid in oleum. After electrolysis, 99·5% of the initial material is accounted for by the nitrometer analyses, so loss of gaseous reduction products is negligible. This result, indicating that nitrogen pentoxide ionises in oleum, has an obvious bearing upon the discussion in the preceding paper of the supposed formation of nitrogen pentoxide in mixed acids.

Our thanks are due to the Chief Scientific Officer of the Ministry of Supply for permission to publish this paper.

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[*Received, March 7th*, 1946.]