455. *Electrical Conductances of Solutions in Nitric Acid. Part II.* Solutions of Alkali-metal Nitrates. Transport Numbers and Ionic Conductances of* NH_4^+, K^+, NO_2^+, *and* NO_3^- *Ions.*

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The electrical conductivities of solutions of ammonium, sodium, and potassium nitrates in nitric acid have been measured. The electrode reactions occurring in such solutions are $NO_2^+ + e \longrightarrow NO_2$ and $NO_3^- \longrightarrow NO_2^+ + \frac{1}{2}O_2 + 2e$; these were used to yield transport numbers and ionic conductances of NH_4^+, Na^+, and K^+ ions in solutions of the nitrates. Transport numbers of NO_2^+ and NO_3^- ions in solutions of dinitrogen pentoxide, and of water, in nitric acid have also been determined. The mobilities of both these ions, produced in the self-dissociation of nitric acid, are normal, showing that in this solvent there is no significant contribution from a chain-conductance mechanism. The conductances of the alkali-metal nitrates are interpreted in connection with the self-dissociation of the solvent.

A technique is described in which conductance measurements are used analytically in transport-number determinations.

NITRIC ACID at −10° is an approximately half-molar solution of nitrate and nitronium ions and water.* Its conductivity shows it to be a good ionising solvent for dinitrogen pentoxide, $NO_2^+NO_3^-$, so it might be expected that alkali-metal nitrates, $M^+NO_3^-$, would form highly conducting solutions in it.

Interpretation of the conductivities of the solutions requires the fraction of the conductivity to be ascribed to each ion present to be determined, so we measured transport numbers for the alkali-metal ions, and for the nitronium and nitrate ions, also present in these solutions. The allocation of transport numbers in turn requires investigation of the reactions which occur upon electrolysis.

All these initially colourless solutions become yellow in the cathode compartment of a Hittorf transport cell. This is not due to thermal decomposition, for the contents of the centre and anode compartments remain colourless; it is the result of the cathode process:

$$NO_2^+ + e \longrightarrow NO_2$$

Although nitrogen dioxide is largely ionised in nitric acid solution,[1] sufficient remains un-ionised to produce a yellow colour. The cathodic formation of stoicheiometric nitrogen dioxide was found to be quantitative for the electrolysis both of the solvent and of the

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* Part I, *J.*, 1956, 4463.

[1] Millen and Watson, *J.*, 1957, 1369.

solutions of alkali nitrates: 1 mole of stoicheiometric NO_2 is liberated for the passage of one Faraday.

During electrolysis of the pure acid or of solutions of alkali nitrates, oxygen is evolved at the anode:

$$NO_3^- \longrightarrow NO_2^+ + \tfrac{1}{2}O_2 + 2e$$

Again this process is quantitative: 5·6 l. of oxygen are evolved for the passage of one Faraday.

If the solutions initially contain nitrogen dioxide, an alternative reaction appears to occur preferentially at the anode:

$$NO_2 \longrightarrow NO_2^+ + e$$

Hence, if the anode solution is originally strongly coloured, no oxygen is evolved until the solution has become almost colourless.

EXPERIMENTAL

Materials.—Nitric acid and dinitrogen pentoxide were prepared as described in Part I. Good quality distilled water of specific conductance below 10^{-6} ohm^{-1} at laboratory temperature was used in view of the very high conductance of these solutions. "AnalaR" sodium and potassium nitrates were crushed and dried at 110° for several hours and stored over phosphoric oxide. "AnalaR" ammonium nitrate was not heated, but was kept over phosphoric oxide for some weeks before use.

Verification of Electrode Reactions.—Solutions of dinitrogen pentoxide, and of alkali nitrates, in nitric acid were electrolysed in a Pyrex glass U-tube of about 100 ml. capacity. The anode, of bright platinum gauze, was placed just below the surface of the solution in one arm; this end of the tube was connected *via* a capillary of small dead-space, to a jacketed gas-burette, in which the volume of evolved gas could be measured over saturated brine. The cathode consisted of about 1 cm.^{2} of bright platinum foil, and was fitted into the other arm by a ground-glass joint.

The solutions were electrolysed at 25 mA at 0°, the U-tube and burette being surrounded by circulating ice-cold water. The quantity of electricity was measured by a copper coulometer in series; periods of electrolysis were from 6 to 8 hr.

The volume of gas evolved was measured. The gas was transferred to Hempel bulbs and absorbed in 15% alkaline pyrogallol solution; the residual volume of gas never exceeded 10% of the total, and in most cases it was about 5%. After electrolysis all the solution was run out and titrated for stoicheiometric NO_2. Aliquot parts were diluted with water, excess of standard potassium permanganate added, and the excess was determined by addition of potassium iodide and titration with standard thiosulphate solution. At this dilution the nitric acid does not oxidise the iodide. For results see Table 1. The average values are 1·02 moles of nitrogen dioxide and 0·240 mole of oxygen liberated per Faraday.

TABLE 1. *Investigation of electrode reactions.*

Solute	Molality	O_2 at N.T.P. (l. F^{-1})	NO_2 liberated (mole F^{-1})	Solute	Molality	O_2 at N.T.P. (l. F^{-1})	NO_2 liberated (mole F^{-1})
N_2O_5	0·030	5·28	1·20	$NaNO_3$	0·059	5·09	0·95
,, ...	0·036	5·85	1·06	,, ...	0·088	5·61	1·06
,, ...	0·087	5·55	1·07	,, ...	0·093	5·58	0·86
,, ...	0·091	5·59	1·08	KNO_3	0·084	4·95	0·96
,, ...	0·122	4·99	0·90	,, ...	0·362	5·32	—

Transport-number Determinations.—(a) *Solutions of alkali nitrates in nitric acid.* The solutions were electrolysed between bright platinum electrodes in a modified Hittorf apparatus. The compartments, of about 8 ml. volume, were joined by taps sealed with solution. The anode compartment consisted of a bulb joined by about 20 cm. of capillary tubing to the centre compartment. This long path was essential to ensure that the product of the electrode reaction did not subsequently migrate from this compartment. For the same reason it was necessary

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[2] MacInnes, "Principles of Electrochemistry," Reinhold, New York, 1939, p. 33.

to restrict the period of electrolysis at 25 mA to about 4 hr. The gas evolved at the anode escaped through tubes of phosphoric oxide. The quantity of electricity passed was measured by a copper coulometer in series with the cell, the necessary corrections being applied.[2]

After electrolysis the compartments were isolated, and their contents siphoned into weighed, stoppered bottles, and analysed for the alkali cation. Solutions of sodium and potassium nitrates were evaporated to dryness; the residue was carefully warmed with concentrated sulphuric acid and finally ignited to the alkali sulphate, with the addition of a small amount of ammonium carbonate to assist in the decomposition of bisulphate. Solutions of ammonium nitrate were diluted, and excess of concentrated sodium hydroxide solution was added, followed byKjeldahl distillation of the ammonia into excess of standard acid.

(b) *Solutions of dinitrogen pentoxide, and of water, in nitric acid.* The overall effect of electrolysis of these solutions is to change the concentration of dinitrogen pentoxide. Since the solvent may itself be regarded as an 85·7% (w/w) solution of this solute in water, chemical analysis would not be sufficiently accurate to record the change produced by the small amount of electrolysis occurring in a normal transport-number determination. The cell, basically of Hittorf type, was therefore so designed that the change in composition could be derived from measurements of electrical conductivity before and after electrolysis by use of subsidiary electrodes in the anode and centre compartments. These compartments also had capillary side-arms for thorough pre-mixing of their contents with a stream of dry nitrogen. Their cell-constants were measured with 0·1D-potassium chloride as usual.

TABLE 2. *Conductivities of solutions of alkali-metal nitrates in nitric acid at* —10·02°.

$NaNO_3$ (m)	$10^4\kappa$ (ohm^{-1})	KNO_3 (m)	$10^4\kappa$ (ohm^{-1})	KNO_3 (m)	$10^4\kappa$ (ohm^{-1})	NH_4NO_3 (m)	$10^4\kappa$ (ohm^{-1})
0·0338	365·7	0·0515	386·0	0·3828	571·9	0·1067	421·5
0·0725	382·6	0·1007	409·2	0·5919	698·8	0·2002	479·0
0·1881	467·9	0·1685	455·3	0·7737	789·8	0·2480	507·3
0·2951	522·1	0·2152	476·7	1·0682	883·8	0·3879	586·6
0·4052	565·8	0·2943	535·9	1·2301	902·9	0·5325	685·3
0·4862	593·8	0·3355	538·0	1·5825	924·6	0·6929	757·2
0·5874	640·6					0·9053	835·5
0·7017	681·9					0·9881	876·5
0·8038	700·8					1·0551	890·1
1·1290	798·8						

TABLE 3. *Densities* (*d, g. ml.*$^{-1}$) *of solutions of alkali-metal nitrates in nitric acid at* —10·02°.

$NaNO_3$ (m)	*d*	KNO_3 (m)	*d*	NH_4NO_3 (m)	*d*
0·2786	1·5773	0·2427	1·5794	0·3183	1·5661
0·3580	1·5810	0·4958	1·5937	0·5597	1·5720
0·5210	1·5893	0·7021	1·6075	0·9208	1·5763
0·7019	1·5982	0·7478	1·6078	0·9561	1·5775
0·9459	1·6094	1·0480	1·6249	1·1841	1·5801

TABLE 4. *Transport numbers of the* Na^+, K^+, *and* NH_4^+ *ions in solutions in nitric acid at* —10·02°.

$NaNO_3$ (m)	$t(Na^+)$	KNO_3 (m)	$t(K^+)$	NH_4NO_3 (m)	$t(NH_4^+)$
0·1706	0·132	0·0992	0·106	0·1121	0·094
0·2920	0·186	0·2591	0·191	0·2488	0·190
0·4618	0·233	0·2714	0·218	0·3302	0·215
0·5982	0·247	0·4605	0·273	0·4375	0·253
0·7071	0·263	0·5877	0·297	0·5289	0·258 *
0·859	0·278	0·7575	0·324 *	0·6325	0·276

* One result only; other values are means of the results obtained from analysis of anode and cathode compartments.

The cell was filled with solution, the compartments were isolated, and the initial conductivities determined. The compartments were then joined and a current of 25 mA was passed for about 4 hr. The cells were then isolated, the contents of each was mixed by the passage of dry nitrogen, and their final electrical conductivities were determined. The conductivity–concentration data from Part I then yielded the changes in composition.

Conductivities of Solutions.—Conductivities were determined as described in Part I, the same type of cell and the same temperature, $-10°$, being used.

Results.—Solutions of alkali-metal nitrates in nitric acid. The electrode reactions which occur on electrolysis of these solutions are:

$$NO_3^- \longrightarrow NO_2^+ \times \tfrac{1}{2}O_2 + 2e \text{ (anode)}; \quad NO_2^+ + e \longrightarrow NO_2 \text{ (cathode)}$$

There is a net gain of alkali nitrate, MNO_3, in the cathode compartment, and a net loss in the anode compartment in each case of $t(M^+)$ moles per Faraday, where $t(M^+)$ is the transport number of the alkali-metal cation for the solution. No change is expected in the centre compartment.

As these solutions contain two cations, M^+ and NO_2^+, the value of $t(NO_3^-)$ cannot be obtained directly from $t(M^+)$. Again, the graph of $t(M^+)$ against concentration does not extrapolate to a non-zero value for $t^0(M^+)$ as the concentration of alkali nitrate tends to zero since

$$\lim_{m \to 0} t(M^+) = \lim_{m \to 0}[m.u(M^+)/\textstyle\sum mu] = 0$$

where u is the mobility of the ion of molality m.

Results are in Tables 2, 3, and 4 for sodium potassium, and ammonium nitrates in nitric acid.

The solvent used, prepared and purified as described in Part I, is not quite anhydrous, but as exact corrections for the effect of the small quantity of water cannot be made the tabulated values are those directly observed. Such corrections would lead to slightly higher values for the specific conductances, but would not change the reported ionic conductances significantly.

Solutions of dinitrogen pentoxide in nitric acid. The electrode reactions are the same as for solutions of alkali-metal nitrates. Passage of one Faraday leads to a net gain of $[0{\cdot}5 - t(NO_2^+)]$ moles of dinitrogen pentoxide in the anode compartment. The amount of dinitrogen pentoxide in the anode compartment did increase, showing that $t(NO_2^+) < 0{\cdot}5$; from this increase the transport numbers were evaluated. No change should occur in the centre compartment.

The change in the cathode compartment could not be used, since one mole of nitrogen dioxide is liberated per Faraday passed. This is a strong electrolyte[3] and its presence will offset the decrease in conductivity due to loss of dinitrogen pentoxide. However, in this case it is permissible to put $t(NO_3^-) = 1 - t(NO_2^+)$, since there are only two ionic species present in the solution.

Transport numbers obtained from measurements on the anode compartment are in Table 5.

TABLE 5. *Transport number of the* NO_2^+ *ion in solutions of dinitrogen pentoxide in nitric acid at* $-10{\cdot}02°$.

N_2O_5 (initial molality)	0·056	0·082	0·107	0·195	0·211	0·350	0·515
$t(NO_2^+)$	0·363	0·365	0·375	0·385	0·389	0·421	0·436

DISCUSSION

Ionic Conductances.—For a solution of specific conductance κ, of several ions, u_i being the mobility of the ion of molarity m_i, t_i its transport number and l_i its ionic conductance:

$$\kappa = \sum_i \frac{m_i u_i \boldsymbol{F}}{1000} \qquad t_i = \frac{m_i u_i}{\sum_i m_i u_i} \qquad l_i = u_i \boldsymbol{F} = \frac{1000\,\kappa\, t_i}{m_i}$$

Ionic conductances calculated from these equations for the concentration range 0—1M are recorded in Table 6. The transport numbers have been interpolated at intervals of 0·1 molarity from the molal data in Table 4.

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[3] Unpublished work.

The conductance of each ion varies only slowly with increasing concentration. Thus good evidence is provided to support the assumption made in certain calculations in Part I, that ionic conductances can be taken as approximately independent of concentration over the range 0—1M.

The ionic conductances of the nitrate and nitronium ions cannot be similarly calculated since, in the absence of data concerning activity coefficients, the molarities of these ions in solutions of dinitrogen pentoxide in nitric acid are unknown, but the ionic conductances in the special case of the solvent, nitric acid, can be obtained for the molarity is known (Part I). Combining the equivalent conductance of the solvent with the appropriate nitrate and nitronium ion transport numbers, we obtain the ionic conductances. Values of l, compared with those of the alkali-metal cations, are: NO_3^-, 46·6; NO_2^+, 25·1; Na^+, 21·7; K^+, 27·2; NH_4^+, 22·8. The values for nitrate and nitronium ions refer to the solvent. The values for alkali-metal cations were obtained by extrapolation of the data of Table 6 to zero cation concentration.

TABLE 6. *Ionic conductances of* Na^+, K^+, *and* NH_4^+ *ions in solutions of the nitrates in nitric acid at* —10·02°.

Molarity ...		0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
Na^+	t	0·057	0·103	0·143	0·175	0·197	0·216	0·232	0·245	0·255	0·263
	l	21·7	21·8	22·3	21·9	20·9	20·2	19·5	18·8	18·1	17·5
K^+	t	0·070	0·127	0·170	0·206	0·234	0·256	0·273	0·285	0·297	0·309
	l	27·2	27·1	26·4	26·0	25·5	24·9	24·3	23·6	23·2	22·9
NH_4^+ ...	t	0·058	0·107	0·154	0·189	0·217	0·243	0·267	0·281	0·315	0·340
	l	22·8	23·3	24·4	24·2	23·9	23·9	24·2	24·0	25·6	26·7

The mobility of the nitronium ion is comparable with that of the alkali-metal cations. Although the mobility of the nitrate ion is higher, Table 5 shows that under certain conditions $t(NO_2^+) = 0{\cdot}436$ and $t(NO_3^-) = 0{\cdot}564$. If it is accepted that the conductance of the nitronium ion is normal, then it is unlikely that under these conditions there is a contribution to the conductance of the nitrate ion from a chain mechanism. Although, with decrease of concentration, $t(NO_3^-)$ increases to 0·637, it does not seem probable that within this range a change in conductance mechanism occurs.

Interpretation of Conductances.—The conductance of a solution of an alkali-metal nitrate in nitric acid can be divided into contributions from the added salt and from the ions produced in the self-dissociation of the solvent. The contribution of the latter falls as the alkali-metal nitrate concentration increases, but remains dominant until a concentration of about 0·4M-alkali nitrate is reached. The rate of increase of conductance with concentration for dilute solutions of alkali-metal nitrates is consequently markedly dependent on the self-dissociation equilibrium constant. The contribution of the metal cation to the conductance is known from transport measurements. The remainder of the conductance provides a measure of the concentrations of nitrate and nitronium ions which are related through the self-dissociation equilibrium constant. The dependence is complicated to some extent by the variations of ionic mobilities and activities with changing concentration. Lack of information about both of these factors limits the accuracy with which the extent of the self-dissociation of nitric acid can be evaluated from conductance data on solutions of alkali-metal nitrates.

For a solution of alkali metal nitrate MNO_3, of molarity m and density d, the composition of 1 litre of solution can be expressed as n moles of NO_2^+ and H_2O, $(n + m)$ moles of NO_3^-, m moles of M^+, and $c = (1000d - \sum xM)/63{\cdot}03$ moles of NHO_3, where x is the molarity of species of molecular weight M. The classical equilibrium constant, in terms of molar fractions, is given by:

$$K = \frac{n^2(n + m)}{c^2(c + 3n + 2m)} = K'X \quad \ldots\ldots \quad (1)$$

where $K' = n^2(n + m)$ and $X = 1/[c^2(c + 3n + 2m)]$

Calculation shows that X varies only slowly with m; over the range $m = 0{\cdot}1$ to $1{\cdot}0$, X varies by only 0·35%. Neglecting this slight dependence of X on m, we have from eqn. (1):

$$\mathrm{d}n/\mathrm{d}m = -n/(3n + 2m) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The specific conductance of the solution, in terms of the ionic mobility l for each species present, can be written:

$$1000\,\kappa = n.l(\mathrm{NO_2^+}) + (n + m).l(\mathrm{NO_3^-}) + m.l(\mathrm{M^+}) \quad . \quad . \quad . \quad . \quad (3)$$

If, in this approximate treatment, we may neglect the variation of the ionic mobilities with concentration, we have:

$$1000\,\mathrm{d}\kappa/\mathrm{d}m = l(\mathrm{NO_2^+}).\mathrm{d}n/\mathrm{d}m + l(\mathrm{NO_3^-}).(1 + \mathrm{d}n/\mathrm{d}m) + l(\mathrm{M^+}) \quad . \quad (4)$$

By combining equations (2) and (4) an expression is obtained for the measured quantity $\mathrm{d}\kappa/\mathrm{d}m$, in terms of the unknown quantity n:

$$1000\,\mathrm{d}\kappa/\mathrm{d}m = -l(\mathrm{NO_2^+})[n/(3n + 2m)] + l(\mathrm{NO_3^-})[(2n + 2m)/(3n + 2m)] + l(\mathrm{M^+})$$

For the limiting case $m \longrightarrow 0$, $n \longrightarrow a$, the equilibrium concentration of dissociation products in the pure solvent, we can write: $l = 1000\kappa t/a$ for the nitrate and nitronium ions, where t is the appropriate transport number. The expression for a then simplifies to:

$$a = \frac{\kappa[2t(\mathrm{NO_3^-}) - t(\mathrm{NO_2^+})]}{3[\mathrm{d}\kappa/\mathrm{d}m - l(\mathrm{M^+})/1000]}$$

in which all quantities are limiting ones for $m \longrightarrow 0$. Evaluation of a yields, from the data on solutions of sodium, potassium, and ammonium nitrates respectively, the values 0·64, 0·59, and 0·56M. Differences between the values are to be expected, since no account has been taken of the variations with concentration of activity coefficients and ionic mobilities, on neither of which is there any information. The values for a agree reasonably with that evaluated from conductance measurements on solutions of water and dinitrogen pentoxide for which, because of the special relation between the two solutes and the solvent, another method of evaluation was possible.

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