827. *Some Aspects of the Solution Chemistry of Zirconium.*

By B. A. J. Lister and (Miss) L. A. McDonald.

Some experiments are described dealing with the chemistry of zirconium in nitric, hydrochloric, perchloric, and sulphuric acid solutions. Ion-exchange techniques have been used to determine the ionic charge of zirconium species and the degree of cation–anion interaction to form complex cations, and to illustrate the presence of anionic complexes in solution. In addition, the rate of diffusion from solution into exchangers of different degrees of cross-linking has given information on ionic size at various acidities. Other experiments include the measurement of the rate of self-diffusion in solution, electromigration studies, and pH determinations.

The results are interpreted as indicating the presence at lower acid concentrations of polynuclear hydrolysis products, and at higher acidities of such complexes as (in nitric acid solution) $[Zr(NO_3)_2(H_2O)_4]^{2+}$, $[Zr(OH)_2(NO_3)(H_2O)_3]^+$, $[Zr(OH)_2(NO_3)_2(H_2O)_2]^{2+}$, and $[Zr(OH)_2(NO_3)_4]^{2-}$.

Great differences are apparent between the behaviour of ionic species of zirconium and thorium in comparable solutions.

Little is known with certainty of the individual zirconium species existing in aqueous solutions and there is lack of agreement on the composition of materials crystallised from solution. An outstanding feature in the chemistry of zirconium in solution is the large degree of hydrolysis, and although claims have been made to have established the existence of the normal nitrate, it is generally agreed that normal salts of quadrivalent zirconium are never crystallised. A short survey of this early work has been made by one of us [Lister, Thesis, London, 1951; A.E.R.E. C/R 801 (1951)].

Several important papers have recently been published, notably those by Connick and McVey (*J. Amer. Chem. Soc.*, 1949, **71**, 3182), Connick and Reas (*ibid.*, 1951, **73**, 1171), and Larsen and Gammill (*ibid.*, 1950, **72**, 3615). Connick *et al.* used a new technique in examining the behaviour of α-trifluoro-α′-thenoylacetone (TTA) for zirconium complexes under different conditions. The degree of anion–cation interaction was examined by Connick and McVey by studying the TTA extraction coefficient as a function of the concentration of complex-forming ion at constant hydrogen-ion concentration and diketone activity. Their results were taken to indicate the presence in 1—2N-nitric and -hydrochloric acid solution of one NO_3^- or Cl^- ion in the respective complexes. Later work by McVey (Hanford Works Report 21,487) has shown the presence of the first and second nitrato-complexes, $ZrNO_3^{3+}$ and $Zr(NO_3)_2^{2+}$ in nitric acid solutions up to 4M.

Connick and Reas examined the hydrolysis of zirconium in perchloric acid solution by similar extraction methods and concluded that formation of polynuclear ions occurs even at 2N-acidity. They quote details of polymerisation under different conditions of zirconium and perchloric acid concentration. A claim is also made that, at very low concentrations of zirconium in 2N-perchloric acid, the zirconium monomer is mainly present as Zr^{4+} although at lower acidities the presence of $Zr(OH)^{3+}$ and $Zr(OH)_2^{2+}$ has been indicated. McVey has also observed the presence of the latter ion and has, by optical-density measurements, confirmed some of the polymerisation data of Connick and Reas.

A study of the titration curves of zirconium and hafnium in perchloric, nitric, and hydrochloric acid solution by Larsen and Gammill (*loc. cit.*) led to some interesting results. For perchlorate solutions, over three quarters of the precipitation range, the logarithm of the hydroxyl-ion concentration was shown to be a linear function of the metal-ion concentration and, from the slope of the curve, the average charge for the ion in solution was shown to be 0·6 and the average number of hydroxyl ions per zirconium atom to be 3·4. This was taken to mean that polymeric species existing in solution over this range had the average composition $[M(OH)_{3\cdot4}^{0\cdot6+}]_n$. Significant differences were found in the behaviour of zirconium and hafnium in nitrate and chloride solution.

Objects of Present Work.—It was hoped that use of a number of different physico-chemical techniques would afford additional information on the state of zirconium in solution, and that further checks might be made of the recent extraction work described above. The experiments now detailed fall under several headings : (*a*) examination of ionic complexity by measurements of the rate of self-diffusion in solution and of the rate of diffusion into ion-exchange resins, (*b*) determination of ionic charge by an ion-exchange technique, (*c*) examination of the degree of cation–anion interaction to form complex cations, and of the presence of zirconium in anionic form, ion-exchange methods being used in both series of experiments, (*d*) electromigration studies, and (*e*) pH measurement on zirconyl salt solutions. Attention has been confined to perchloric, nitric, hydrochloric and, in some cases, sulphuric acid solutions.

It should be stressed that in the ion-exchange experiments the relative accumulation of the species in the resin phase is not identical with that in the solution phase owing to variations in ionic size as well as to the fact that species of higher charge are generally more strongly held in the resin phase than those of lower charge. However, valuable information has been obtained by examination of the resin phase after equilibration with the solution.

In the experiments now described, two cation-exchange materials have been used, Zeokarb 225 and Dowex 50, both sulphonated polystyrene resins cross-linked by addition of about 10% of divinylbenzene. [The properties of such resins are described by Reichenberg, Pepper, and McCauley (*J.*, 1951, 493) and by Topp and Pepper (*J.*, 1949, 3299).]

EXPERIMENTAL

(1) *Rate of Self-diffusion in Solution.*—The diffusion coefficients of zirconium species in solutions of various acidities were measured by Jander and Jahr (*Koll. Beih.*, 1936, **43**, 295) who found a fall in the rate of diffusion with decrease in acidity, their results being in agreement with the formation of highly aggregated hydrolysis products. It was also suggested that the progress of hydrolysis may differ markedly with the anion present, and that nitric acid and perchloric acid solutions of zirconium hydroxide differ fundamentally in their chemical properties.

The availability of radio-isotopes has made it possible, in contrast to previous work, to determine self-diffusion in solution, *i.e.*, diffusion under conditions where there exists no concentration gradient. Anderson and Saddington (*J.*, 1949, 5381) have described measurements of self-diffusion coefficients of tungstic acids, and their technique has been closely followed in the present work. Briefly, it entails measurement of the rate of diffusion of the ion concerned from an active solution contained in a capillary cell into an external solution of the same composition but with no added radio-tracer.

To interpret our results, the expression $\gamma = 8e^{-\theta}/\pi^2$, derived from Fick's law, has been used. In this expression γ = fraction of activity remaining in the capillary cell, and $\theta = \pi^2 Dt/4L^2$, where D = diffusion coefficient at the temperature of the experiment (29·6°), t = time of diffusion, and L = length of capillary cell.

The solutions used were all 1% in zirconyl nitrate (*ca.* 0·04M), the nitric acid concentration varying from 0·02 to 6M. Radioactive tracers for these and other experiments were prepared by irradiating hafnium-free zirconyl nitrate [the hafnium being removed by a cation-exchange technique (Lister, *J.*, 1951, 3123)] in the Harwell pile for 4 weeks. The weak β-activity due to the zirconium daughter-product, niobium, was removed by counting through a 20 mg./cm.^{2} aluminium filter.

The results are shown in Fig. 1. The scatter may be due to the unavoidably low counting rate and to possible small differences in the preparation of the solution which might affect the complexity of the ions.

A complete theoretical treatment of the relation between diffusion coefficient in liquid systems and ionic or molecular weight is lacking. As an approximation, Riecke's relationship (*Z. phys. Chem.*, 1890, **6**, 564) (the molecular weight is considered as inversely proportional to the square of the diffusion coefficient) may be used to evaluate the results; it then appears that between solutions of zirconium in 0·02M- and 6M-nitric acid there is an approximately six-fold decrease in the weight of the ionic species. Jander and Jahr found wide differences in the values of the diffusion coefficient with the interval between preparation of the solution and measurement. After 2—7 weeks they found that, over the range 0·5—3 moles of acid per mole of zirconium salt, the product of the diffusion coefficient and the specific viscosity varied from 1·5 to 1·8. After 10·5 months these values had changed to 1·0—1·8. The first figures represent a factor of 1·45 in the molecular weight at the two acidities, and the latter figures a factor of 3·2. In the present work, over this same range (*ca.* 0·02—0·12M-acid), a factor of 2·1 was found. The results are not directly comparable since Jander and Jahr carried out their experiments in the presence of a large excess of a second electrolyte; however, the general trend is the same.

The present results give no evidence of any one ionic species predominating over any range of acidity, but show, instead, a gradual change in molecular weight (the experimentally determined diffusion coefficients representing an average value).

(2) *Rate of Ion Exchange of Zirconium Cations from Nitric Acid Solution.*—If zirconium species of varying complexity and ionic size are present in solutions of different acidity, then these differences should be reflected in the rate at which the species will be taken up by an ion-exchange resin. The method chosen for this study was one in which the degree of reaction was determined *in situ* without separation of resin and solution, measurements being made continuously by means of a radio-tracer technique.

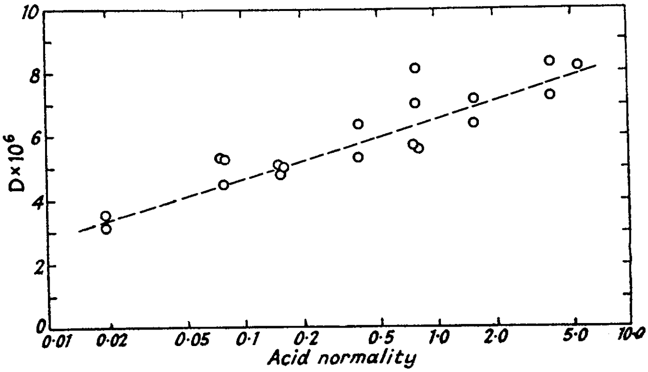


FIG. 1. *Self-diffusion coefficients o, zirconium species in nitric acid solution.*

The apparatus is shown in Fig. 2. A known volume of the solution under examination (seeded with radioactive tracer-^{95}Zr) was admitted to the apparatus at *A* by means of a plunger pipette. A constant-pressure air stream was injected at point *B* *via* a mercury bubbler and a series of needle valves, and the solution was caused to circulate round the apparatus by air rising in tube *C*. The apparatus was built in 0·2-mm. diameter Pyrex capillary tubing with the exception of the reaction cup *D* and the lead-shielded Geiger–Müller tube *E*. In all experiments the solution contained 300 mg. of zirconium nitrate seeded with hafnium-free active material in 30 ml. of nitric acid. The solution in the reaction cup was gently stirred with a constant slow-speed motor and glass stirrer. After addition of 1 g. of oven-dried resin (Zeokarb 225 in the hydrogen form) to the reaction cup, the uptake of zirconium from the solution was measured by observing the counting rate of the solution passing through the flow counter. A small time lag must occur between the reaction and observation of the change in activity, but, as a constant circulation rate of about 25 ml./minute was maintained, this time lag was only important during the first few minutes of the run and a small correction could be applied. The large vertical separation of the reaction cup and Geiger–Müller tube (*ca.* 100 cm.) was necessary to ensure that radiation from the zirconium absorbed on the resin did not affect the observed counting rate of the solution. In addition, the circulation rate is dependent on the vertical distance between the air-injection point and the reaction cup.

The rate of exchange must vary with the pore size of the resin, *i.e.*, with the degree of cross-linking. To examine this effect, two resins were used, the normal production material with 10% of divinylbenzene and a specially prepared resin of similar composition but with only 5% of divinylbenzene and, consequently, a much more open structure.

The results now obtained with zirconium all show that particle diffusion is the controlling mechanism as distinct from film diffusion (Kressman and Kitchener, *Discuss. Faraday Soc.*, 1940, **7**, 90), linear relationships being found between Q_t/Q_∞ and $\sqrt{t}$ at low values of Q_t/Q_∞, where Q_0 = original amount of solute, Q_t = amount taken up at time t, Q_∞ = amount taken up at equilibrium, r = radius of the resin particle, and D = diffusion coefficient.

The determination of Q_∞ presented some difficulty with solutions of lower acidity. In such solutions, a relatively rapid uptake over the first hours was followed by a flattening of the uptake curve to a value which rose extremely slowly, in some cases over weeks. In difficult cases this initial plateau level has been taken as the value of Q_∞. This final very slow uptake may be ascribed to either a resin or a solution effect, *i.e.*, it may arise from a slow permeation of the large ions into the resin structure or to a slow continuous readjustment of equilibrium in solution to produce ions which can exchange more readily. The latter appears more likely since pH measurements have shown a continuous slow change in the hydrogen-ion concentration over many days.

For comparison purposes one run was made with a simpler ion. Thorium was chosen since its uptake has been shown (Kressman and Kitchener, *loc. cit.*) to obey a $\sqrt{t}$ law and the same expression

$$Q_t/Q_\infty = 6Q_0\sqrt{Dt/\pi}/r(Q_0 - Q_\infty)$$

could be used to calculate the diffusion coefficient. The rate of uptake with a solution of thorium nitrate in water (no added acid) was over ten times that in any of the zirconium runs ($D \sim 4 \times 10^{-8}$), indicating a simpler ionic structure.

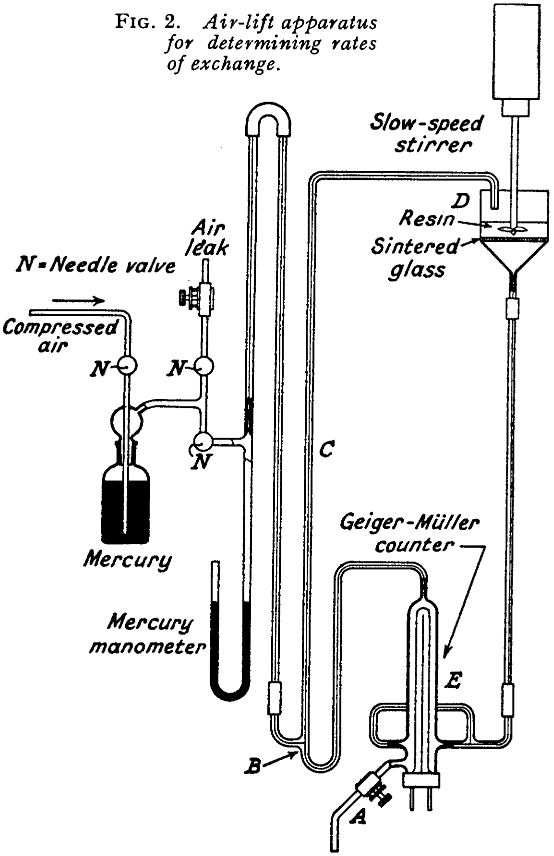


FIG. 2. *Air-lift apparatus for determining rates of exchange.*

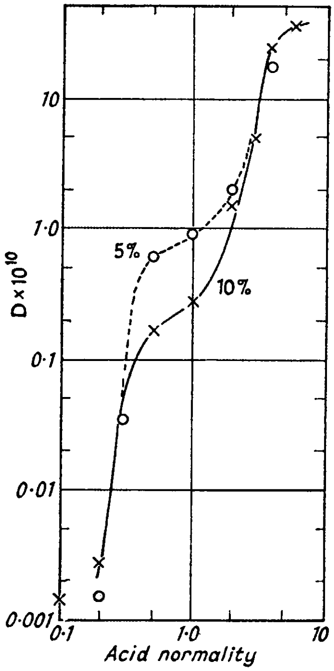


FIG. 3. *Resin diffusion coefficients of zirconium species as function of acid normality and degree of resin cross-linking.*

The results obtained for zirconium are shown in Fig. 3. It is seen that the diffusion coefficient falls away very rapidly with decreasing acidity, this being in agreement with the formation of highly aggregated hydrolysis products. These aggregates appear to be formed even in quite strongly acid solutions. The shape of the curves is interesting and may be explained qualitatively by the following simplified picture. At a limiting acid concentration somewhere above 6N we can suppose that simple ionic species only are present with a certain high mean diffusion coefficient. As we decrease the acidity, larger polynuclear species appear, causing a drop in the average value of D. If no further aggregation occurred we should expect the curve to level out at a value corresponding to the mean diffusion coefficient of these polynuclear ions. Before this state is reached, however, the formation of still more highly aggregated species causes another rapid drop in the diffusion coefficient.

Differences in the curves obtained with 5% and 10% divinylbenzene resins are most marked over the region of 0·3—3·0 acid normality, and it is presumably in this region that the ionic species present are comparable in size with the resin pores. At higher acid concentrations the smaller ions can diffuse into either resin with equal ease and at lower acidities both 5% and 10% cross-linked materials have a close enough structure to prevent substantially the diffusion of the larger ions present. A figure of 4—6 Å has been quoted by Kressman (private communication) for the pore size of the 10% cross-linked resin. Thus the simplest zirconium species (*i.e.*, ZrO^{2+} — bond length *ca.* 2·3 Å) would have easy access to the exchange sites, whereas a polymeric ion of the type $(O{=}Zr{-}O{-}Zr{=}O)^{2+}$ with a major diameter of about 8—10 Å would be hindered.

The method, then, as well as giving a qualitative description of the state of the solution with varying acidity, gives a semi-quantitative picture of the ionic size of the species. An important factor which cannot be evaluated is the size of the water sheath associated with the zirconium species and its effect in determining the rate of diffusion of the ion through the resin.

The fact that a stepwise curve is obtained in this series of experiments while a smooth relation is found between acidity and rate of self-diffusion in solution is explained by the sieve-like action exhibited by the cross-linked resin structure.

(3) *Cation–Anion Interaction to Form Complex Cations.*—Interaction of zirconium-containing cations with the anion of the acid solvent to produce complex cations has been proposed by a number of investigators working with different acid solutions, but most of the previous work has resulted in theories that fit the experimental data rather than in unambiguously proved facts, and the nature of the complex cations in solution is still far from certain.

The use of ion-exchange resins seemed to offer a method whereby the combination of an acid anion in the zirconium cationic species could be demonstrated and, at least, a semi-quantitative description given of the variation in the nature of this complex cation with the acid solvent and the acid concentration.

Let us suppose in a solution of a zirconium salt in an acid, HX, there exists the complex cation $[Zr(OH)_pX_m]^{n+}$ where $m + p = 4 - n$. If this is absorbed on to a resin anion we have formed a resinate $R_n[Zr(OH)_pX_m]$. From a knowledge of the general ease of hydrolysis of zirconium ions we could expect, on washing this zirconium resinate with water, either of the reactions

$$(a)\quad R_n[Zr(OH)_pX_m] + (m + n)H_2O = Zr(OH)_4 + mHX + nRH$$

$$(b)\quad R_n[Zr(OH)_pX_m] + mH_2O = R_n[Zr(OH)_{(p+m)}] + mHX$$

Of these two reactions the second is the more likely and this is confirmed by the ease of removal by complex-forming agents of the zirconium species from a water-washed resin and the general similarity in behaviour of washed and unwashed zirconium resins to elution with acids. Further experiments have shown that the zirconium species are in fact in an ionised form after being washed with water and we can confidently ignore reaction (*a*). That hydrolysis does occur on washing, was confirmed by showing that a surface-dried and water-washed sample of resin which had been equilibrated with a hydrochloric acid solution of zirconium nitrate released no chloride ion on regeneration with oxalic acid, which strongly complexes the zirconium.

Hence, water-washing of a resin with absorbed zirconium species, say, $[Zr(OH)_2X]^+$, yields hydrogen ions formed by the hydrolysis of group X according to the equation $R[Zr(OH)_2X]^+ + H_2O = R[Zr(OH)_3]^+ + HX$. The amount of acid released gives a direct measure of the amount of hydrolysable groups on the resin. This can then be compared with the weight of zirconium on the resin and an average value found for the ratio $\overline{X}/\overline{Zr}$ (where the bars refer to the resin phase).

The technique adopted was as follows. A 5-g. sample of oven-dried Dowex 50 in the hydrogen form was shaken with a solution of 2 g. of zirconyl nitrate in 200 ml. of a solution of known acid strength (1—6N). After 24 hours the liquor was separated by suction through a funnel, and the resin surface-dried by rubbing with filter-paper until a freely mobile material was obtained. Experience made this condition quite easy to reproduce. The resin was transferred to a small column and washed with 250 ml. of water, and the acidity of the washings was determined by titration with 0·1N-sodium hydroxide solution (bromothymol-blue). The zirconium held on the resin was removed by elution with oxalic acid solution or 3N-sulphuric acid and determined as oxide.

When a resin is shaken with an electrolyte solution, some of the solution goes into the pores of the resin without the ions being exchanged. This, of course, is also removed on water-washing and in each case a control experiment had to be made with an acid solution containing no zirconium. The difference between the acidity found from washing the mixed zirconium–hydrogen resin and that from the control experiment gave a measure of the hydrolysable groups present on the mixed resin. The quantitative nature of the results may be affected by probably small differences in electrolyte uptake between the pure hydrogen form and the mixed hydrogen–

zirconium form of the resin, but this was minimised by keeping the zirconium–hydrogen ratio on the resin small. The experimental results are shown in Figs. 4 and 5.

With perchloric acid solutions very little excess of hydrogen ion is produced on water-washing, the small amount actually found possibly being due to differences in the electrolyte uptake over a range of zirconium concentrations on the resin. It is therefore clear that there is little, if any, cation–anion interaction to give complex cations in perchloric acid solutions. With nitric and hydrochloric acid solutions, however, the results show a gradual rise in the amount of cation–anion interaction with increasing acid concentration. The curves for these two acids are similar up to a concentration of 3N, but above this the amount of interaction in nitric acid solution increases more rapidly than in hydrochloric acid solution reaching, at 6N, a ratio $\overline{NO_3}:\overline{Zr} = 1:1$. The average formula for the species absorbed from 3N-acids appears to be $[Zr(OH)_{3\cdot84-n}X_{0\cdot16}]^{n+}$, and from 6N-acids $[Zr(OH)_{(3-n)}NO_3]^{n+}$ or $[Zr(OH)_{(3\cdot5-n)}Cl_{0\cdot5}]^{n+}$. It must be remembered that this method examines only the species absorbed on the resin and not directly those in solution, although the results are a reflection of the state of the solution.

An interesting fact arises from the curves of Fig. 5. The equilibrium uptake of zirconium from acid solution varies greatly with the nature of the acid, perchloric acid allowing a much larger uptake than either nitric or hydrochloric acid. In fact, in 5N-solution there is less than one-third of the uptake from hydrochloric acid solution that occurs with perchloric acid. Examination of the activity coefficients of the three acids at high concentrations shows a reason for the discrepancy between the behaviour in nitric acid and in hydrochloric acid solutions, the activity coefficients of the former being far lower than those of the latter. This reasoning is not, however, valid when considering perchloric acid since the activity coefficients of perchloric acid are the highest of the three. An explanation must therefore be sought in the possibility of the presence of anionic complexes or undissociated molecules, or a difference in ionic charge.

FIG. 4. *$\overline{X}/\overline{Zr}$ ratio for species absorbed on resin from various acid solutions.*

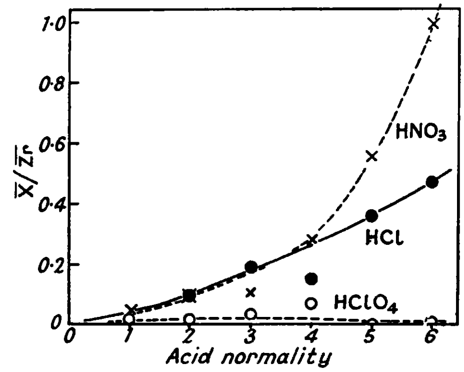
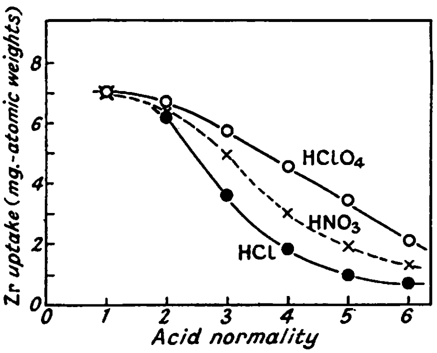


FIG. 5. *Resin uptake of zirconium from various acid solutions after 24 hrs.' contact.*



To examine the effect of increase of nitrate concentration at constant acidity, a series of experiments was carried out similar to those described above but with the nitric acid concentration kept at 1N, and the nitrate-ion concentration increased by addition of lithium nitrate. The results obtained under the two sets of conditions are compared in Table 1.

TABLE 1. *Dependence of* $\overline{NO_3}/\overline{Zr}$ *on nitrate concentration.*

Nitrate concn. (N)	1	2	3	4
$\overline{NO_3}/\overline{Zr}$ (HNO_3 only)	0·051	0·088	0·109	0·286
$\overline{NO_3}/\overline{Zr}$ (1N-HNO_3 + $LiNO_3$)	0·051	0·045	0·043	0·065

It is apparent from these figures that an increase in nitrate concentration without an increase in acidity does not affect the $\overline{NO_3}/\overline{Zr}$ ratio of the cations absorbed on the resin. Hence, any further nitration of the ionic species must yield either uncharged molecules or anionic species. The zirconium uptake after 24 hours' contact was similar in both series of experiments.

These results are further discussed on p. 4326.

(4) *The Presence of Zirconium in Anionic Form.*—To obtain an indication of the presence of

zirconium in complex anionic form, the degree of uptake from solution on an anion-exchange resin was examined. 2-G. samples of air-dried highly basic resin (De-acidite FF) were shaken for 24 hours with 25 ml. of solutions of different acidity containing 1·0 g. of zirconium nitrate seeded with radioactive hafnium-free zirconium tracer. The resin and solution were separated, and the activity of the final solution was compared with that of the original solution by counting 5-ml. samples contained in a glass cell centred beneath a Geiger–Müller tube. Three separate portions of each solution were counted in this way. The results obtained are collected in Table 2.

TABLE 2. *Uptake of zirconium by anion-exchange resin.*

Acid	N	Uptake, %	Uptake (1N-HNO_3 + $LiNO_3$), %	Acid	N	Uptake, %	Uptake (1N-HNO_3 + $LiNO_3$), %
$HClO_4$	2	4·3	—	HNO_3	2	0 *	0 *
	4	0·9 *	—		4	2·0 *	0 *
	6	1·1 *	—		6	10·2	8·9
HCl	2	0 *	—	H_2SO_4	0·5	57·5	—
	4	5·3	—		1·0	21·5	—
	6	8·1	—		1·5	10·0	—

* Within statistical deviations.

In assessing the results certain facts should be considered. The stability of the anion exchanger to solutions of high ionic strength and particularly of high acidity must always be in doubt, although De-acidite FF is claimed to be one of the most stable anion exchangers. Depression of the uptake by total anion concentration is marked as shown by figures obtained with sulphuric acid solutions. Although it is known from other results that the amount of zirconium existing in anionic form in solution increases with the concentration of sulphuric acid, the present work has shown a rapid decrease in uptake as the acid concentration is raised from 0·5 to 1·5N.

Thus the method is probably of limited value in a quantitative assessment of the complex anion content of the solution, particularly as our knowledge of the reactions of anionic resins is more limited than is the case with cationic resins. Nevertheless, the results with hydrochloric and nitric acid solutions indicate strongly that, at the higher acidities, some zirconium does exist as anionic complexes.

An explanation of the results with perchloric acid (lower uptake with higher acidity) can be found in the probability of resin decomposition in the presence of more concentrated perchloric acid. The resin was, in fact, greatly darkened in 4N- and 6N-perchloric acid solutions, whereas no change was noticed in the appearance of the resin in contact with other acids.

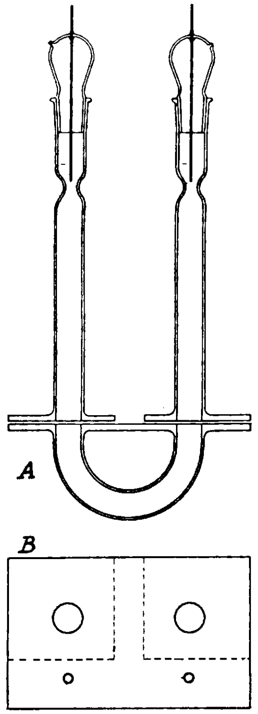
Results from comparable experiments with mixtures of nitric acid (1N) and lithium nitrate to a total nitrate concentration of 2—6N show no significant differences (Table 2).

(5) *Electromigration Experiments.*—To obtain further information on the existence of anionic complexes of zirconium and the degree to which such complex-formation occurs, experiments were made on the electromigration of zirconium species in different acid solutions. An apparatus was constructed similar to that made by Coehn (*Ber.*, 1902, **35**, 2676) and used by Ruer (*Z. anorg. Chem.*, 1904, **42**, 94) when studying zirconium solutions. It was essentially a Pyrex glass U-tube so designed that the catholyte, anolyte, and central solution could be separated without the need for constrictions at stopcocks where local heating would arise. As illustrated in Fig. 6, the anolyte and catholyte sections (diameter *ca.* 0·8 cm.) were mounted in ground-glass Pyrex plates which, with the aid of a thin layer of lubricant, were able to slide smoothly over a third ground-glass plate (9 × 6 cm.) carrying the central U-shaped section. Thus each section of the apparatus could be filled separately and brought into contact at the start of the experiment with very little disturbance of the boundary. The electrodes were platinum wires of *ca.* 1 mm. diameter held in position in ground-glass joints containing a small hole for the escape of gas. They were immersed about 1 cm. in the solution which was filled to a mark on the upper part of the vessel. The electrode compartments held *ca.* 4 ml. of liquid and the central compartment *ca.* 8 ml. At the end of the run, the two electrode compartments were again separated from the central section and were emptied by sliding them over two vertical exit tubes sealed into the base plate as shown in Fig. 6 (*B*).

In all the work described, the zirconyl nitrate used (previously freed from hafnium impurity) had been pile-irradiated so that the migration could be followed radiochemically. The central compartment was filled initially with a solution containing 100 mg. of activated zirconyl nitrate per 10 ml. of solution of given acidity, and the electrode compartments with the same acid solution but no zirconium. Aliquots of the original and final central solutions and the final anolyte and catholyte were counted by using standard β-counting equipment. A control run was carried out under identical conditions but with no current, so that a correction for diffusion across the boundary could be applied in each case. The current used in all runs was 40 ma., and the time of electrolysis 2 hours. Other experiments (to be published later) have shown that the amount of anode-directed migration is not a linear function of time.

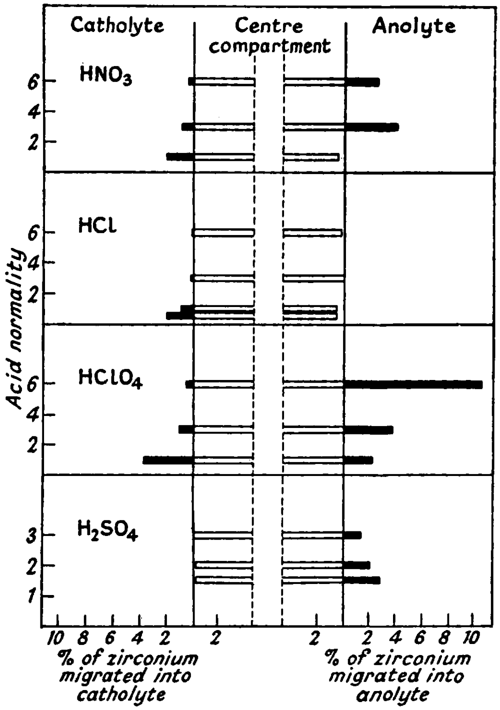
The results obtained with solutions in perchloric, hydrochloric, nitric, and sulphuric acids are shown in Fig. 7. The percentage migration to the two compartments shown pictorially has been corrected for diffusion. In some cases the amount of zirconium transferred in the diffusion control experiment was slightly greater than that found in the comparable run during electrolysis, *i.e.*, the diffusion into, say, the cathode compartment has been overcome by electromigration towards the anode. This is shown in the diagram by a retraction of the migration line back into the central compartment. As the acid strength increases, competition with the acid anion will result in less transference of zirconium for the same amount of the same zirconium ions in solution.

FIG. 6. U-*Tube apparatus for electromigration experiments* : *A*, *side view*; *B*, *plan of base plate.*



Note.—Marks on stems of apparatus near electrodes are marks to which apparatus is filled with solution.

FIG. 7. *Results of* U-*tube electromigration experiments.*



Perchloric acid solution. A very pronounced anion migration was observed even in 1N-solution. This anode-directed movement increased considerably with increase in acidity, the amount of zirconium moving towards the cathode decreasing correspondingly.

Nitric acid solution. In 1N-solution only cation migration was noted, but at the higher acidities there was very marked movement of zirconium towards the anode, the somewhat smaller migration at 6N possibly being accounted for by hydrogen-ion competition. The cation migration gradually decreased with rise in acidity.

Hydrochloric acid solution. Very little movement of zirconium in either direction was found. At 0·5N- and 1N-acidities definite migration to the cathode occurred but at higher acid concentrations the increase in zirconium concentration found in the catholyte and anolyte was within experimental error (<0·2%).

Sulphuric acid solution. As expected, considerable anion transference was found, this decreasing with rise in acidity between 1·5 and 3N, presumably owing to sulphate-ion competition (cf. results of section 4).

The two most striking features of this series of experiments are the apparent lack of migration in hydrochloric acid solutions and the large anion transference in perchloric acid solutions. The experiments are direct ones and considerable reliance can be placed on them. The only similar experiments on record are those of Ruer, who used 2% solutions of zirconyl chloride in 0·5N- and saturated hydrochloric acid and in 0·5N-sulphuric acid. In the first solution he found considerable cathode-directed migration of zirconium and negligible movement to the anode, in agreement with the present results. The movement in saturated acid solution was considerably less to the cathode but rather more to the anode. Ruer's measurements of small migrations must, however, be less precise than the present results using radio-tracer methods. Unfortunately, there is little comparison of migrations in other acids, the only other quoted result being a twenty-fold larger migration to the anode than to the cathode in 0·5N-sulphuric acid.

The present results can be explained on the basis of complex equilibrium systems involving the presence in solution of cations, anions, and uncharged molecules. These results are correlated with those obtained by other methods on p. 4326.

(6) *Determination of Ionic Charge of Zirconium Cationic Species.*—The general scheme followed in the present work was an equilibration of a batch of cation-exchange resin with the solution under investigation, and determination of the weight uptake of zirconium by gravimetric means, and of the equivalent uptake of zirconium species on the resin. A full investigation into methods and technique was carried out with the system zirconyl nitrate–nitric acid and the major part of the work described in this section deals with this system.

0·5-G. samples of Dowex 50 in the hydrogen form were shaken with solutions of 0·25 g. of zirconyl nitrate in 25 ml. of nitric acid solution varying in concentration from 0·1 to 6·0N. After a given time interval the resin was transferred to a small column (1 cm. in diameter) and supported on a sintered-glass disc. The weight of zirconium held on the resin was found by precipitating the hydroxide from the original and final solutions with ammonium hydroxide, drying it, igniting it to the oxide in silica crucibles, and weighing it.

The resin in the mixed zirconium–hydrogen form was washed with water till the washings were neutral to litmus solution, and then about 100 ml. of N-sodium chloride solution were allowed slowly to percolate through the resin bed. The hydrogen ions liberated from the resin by sodium ions were determined by titration with 0·1N-sodium hydroxide (bromothymol-blue). The zirconium on the column was removed with 0·5% oxalic acid solution, and the resin treated with N-sulphuric acid to reconvert it into the hydrogen form. After being washed with water to remove excess of acid, the column was again eluted with N-sodium chloride solution, the acidity of the eluate being a measure of the total equivalent capacity of the resin sample. The difference between the two alkali titration values gave the number of resin equivalents occupied by the zirconium ions.

The effect of washing a resin in the zirconium form with water has been considered in Section 3. Further experiments have shown that less than 20 p.p.m. of zirconium are removed from the resin by such treatment.

If a is the number of mg.-atoms of zirconium taken up by the resin (from gravimetric data), e the number of m.-equiv. of resin occupied by the zirconium, and n the number of zirconium atoms in the ionic species, then the number of complex ions on the resin $= a/n$, and the charge on the complex ion $= V_c = en/a$. If $e/a = V_s$, the measured quantity, from now on called the mean specific ionic charge, then $V_c = nV_s$. It is clear that by this method the charge on a polynuclear ion can only be found if the number of zirconium atoms in the polymer is known.

The values found for V_s are shown graphically in Fig. 8. For simplicity, only the mean values of many determinations are shown. The results obtained with solutions between 2N and 6N in nitric acid could be explained on the basis of a simple equilibrium, involving mononuclear species,

$$[Zr(OH)_m(NO_3)_{(2-m)}]^{2+} + H_2O \rightleftharpoons [Zr(OH)_{(m+1)}(NO_3)_{(2-m)}]^+ + H^+$$

or, more generally, $[ZrA]^{2+} \rightleftharpoons [ZrB]^+ + H^+$. The values for V_s move in the expected direction, *i.e.*, a higher ionic charge in more concentrated acid solutions. Below 2N-acid, however, the V_s values behave abnormally, a sharp increase being noted with increasing acid dilution. The results in this region are far less easily reproducible, suggesting that some less rigid secondary process is becoming operative.

This rapid rise in specific charge can only be explained if some sort of steric effect is assumed at the lower acidities. It is suggested that at acidities below 2N, there are formed large polynuclear hydrolysis products, and that these complexes when absorbed on the resin tend to block some of the pores (which in this class of resin are, on the average, of the order of 4—6 Å in diameter). This blocking effect prevents the eluting sodium ions from reaching some of the hydrogen sites and thus the hydrogen-ion concentration found in the sodium chloride eluate is too small. The equivalent zirconium concentration on the resin thus appears too high, and with it the value of V_s. This supposition is supported by a series of experiments carried out with solutions of varying zirconium concentration but constant acidity (Fig. 9). Further evidence in support of this is a reduction in the value of V_s when a 5% cross-linked resin is used (Fig. 8). Although this reduction could certainly be caused by a smaller degree of pore blocking, yet it could equally arise by a relatively greater uptake of polynuclear ions when the specific charge is unity or less.

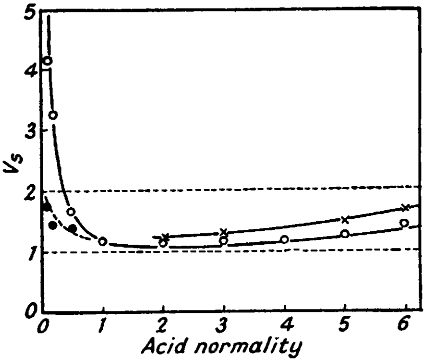


FIG. 8. *Variation of V_s with acid normality (mean experimental values) showing effect of resin cross-linking.*

○ *Nitric acid*; 10% *cross-linked resin.*
● *Nitric acid*; 5% *cross-linked resin.*
× *Perchloric acid*; 10% *cross-linked resin.*

FIG. 9. *Effect of zirconium concentration on value of V_s for nitric acid solutions.*

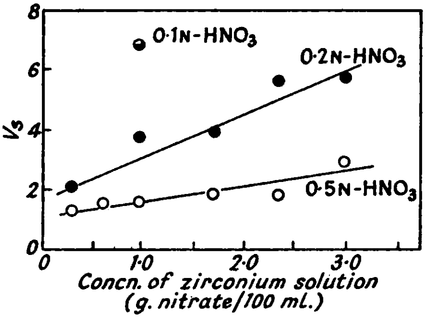
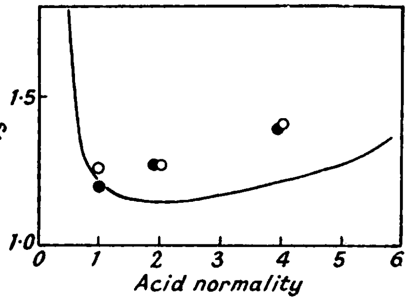


FIG. 10. *Effect of contact time on value of V_s for nitric acid solutions.*



—— 2 *Hrs.' contact.*
○ 2 *Days' contact.*
● 6 *Days' contact.*

Further to test the blocking mechanism theory, experiments were made to determine the mean specific ionic charge in solutions of ammonium chloride and tetraethylammonium iodide (major diameter 7·2 Å). Although the results tend to confirm the theory, ions of larger diameter would have to be used for a complete test.

Several methods have been tried to avoid the difficulty of resin blocking at low acidities, all of them based on a complete regeneration of the mixed zirconium–hydrogen resin (*e.g.*, with oxalic acid and sodium and ammonium oxalate solutions), and examination of the eluate from the regeneration. In no case, however, were useful results obtained.

The work described in Section 2 showed the rate of uptake of zirconium from solution to be slow. The effect of this slow exchange on the value of V_s was examined. Similar experiments were performed with solutions in 1N-, 2N-, and 4N-acid after contact times of 2 hours, 2 days, and 6 days. The results (Fig. 10) show increases in V_s between 2 hours' and 2 days' contact but after this no differences occur, equilibrium having been reached. The rise may be caused either by further blocking of the resin pores by larger ions which have slowly entered the resin structure or by a slow change in the solution equilibrium producing smaller, highly charged ions. The state of the solution would probably be best indicated by resin uptakes at low contact times before the very slow rate of exchange mentioned in Section 2 has become important, and most of the results have been obtained with a contact time of 2 hours. Over this time interval the laws of resin diffusion mechanism are obeyed.

A few experiments were carried out with zirconium solution in perchloric and hydrochloric acids. Similarly shaped curves were obtained to those with nitric acid solutions, *i.e.*, a slow decrease in V_s with decreasing acidity and a rapid increase at acid concentrations less than 1N. With perchloric acid solutions the values of V_s were somewhat higher than with nitric acid (see Fig. 8); insufficient experiments were carried out with hydrochloric acid to enable the exact path of the V_s curve to be determined.

FIG. 11. *Comparison between zirconium and thorium uptake (m.-equiv.) from acid solution.*

A – Zr *from* HNO_3 (2 *hrs.' contact*).
B – Zr *from* HNO_3 (6 *days' contact*).
C – Th *from* HNO_3 (2 *hrs.' contact*).
D – Th *from* $HClO_4$ (2 *hrs.' contact*).
E – Zr *from* $HClO_4$ (2 *hrs.' contact*).

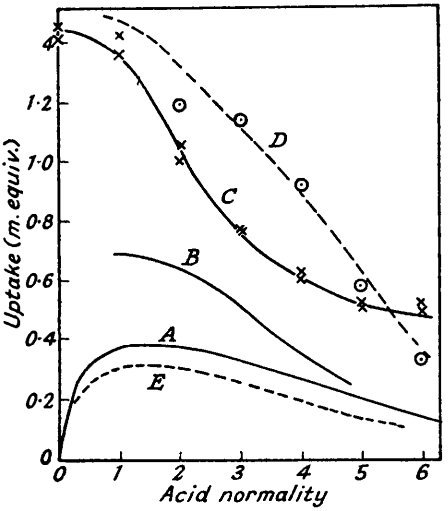


FIG. 12. *Determination of V_s for zirconium in nitric acid–lithium nitrate mixtures.*

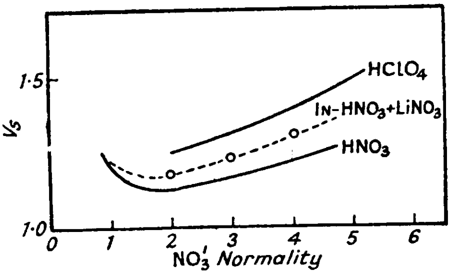
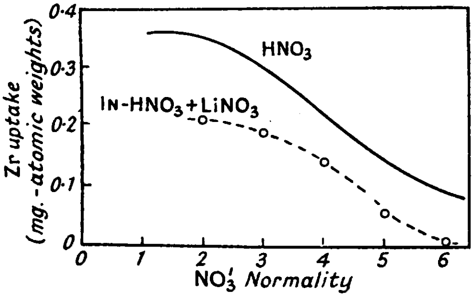


FIG. 13. *Uptake of zirconium from nitric acid–lithium nitrate mixtures.*



As a comparison, runs were carried out with nitric and perchloric acid solutions of thorium in place of zirconium. The equivalent uptake after 2 hours was much greater than with the zirconium solutions (see Fig. 11) and the lowest value of V_s (with no added acid) was found to be 3·4. This emphasizes once again the great differences between the state of aqueous solutions of zirconium and of thorium salts.

To determine the effect on V_s of increasing the nitrate content of the solution without altering the acidity, a similar series of experiments was carried out using 1N-nitric acid and increasing the nitrate content by addition of lithium nitrate. The values of V_s, shown in Fig. 12, were slightly higher than when nitric acid only was used. Although this might mean an increase in the specific ionic charge of the zirconium species, it can equally well be explained by a small decrease in the hydrogen-ion concentration of the solution on addition of lithium nitrate; a slight shift in this direction will cause a considerable increase in the apparent value of V_s due to the formation of more polynuclear hydrolysis products, and approximate calculations show that this effect will adequately explain the observed rise in V_s. The low zirconium uptake (Fig. 13) can be attributed to the formation of uncharged or anionic species, this being in agreement with the values for the $\overline{NO_3}/\overline{Zr}$ ratios observed in the work described in Section 3. It should be noted, however, that after a contact time of 1 day, the uptakes when using nitric acid only or nitric acid with lithium nitrate are very similar.

(7) pH *Measurements on Zirconyl Nitrate Solutions*.—pH Measurements have been made on solutions of zirconyl nitrate of different concentrations, a glass electrode being used in conjunction with a saturated calomel half-cell. Two methods were employed : (*a*) successive additions of zirconyl nitrate were made with mechanical stirring to 200 ml. of water and the pH was measured after 2 or 3 minutes; (*b*) a concentrated solution (1M, pH = 0) was diluted to give solutions of a number of different concentrations, and the pH measured over several days. The zirconyl nitrate concentration in each case varied between about 10^{-4} and 1M.

No measurements have been possible of the thermodynamic activities of the zirconium ions in solution and hence no satisfactory calculations can be made leading to the reaction mechanisms.

The results from the two methods are shown in Fig. 14. Curve *A* represents the best line through points obtained from six series of experiments using two different materials by method (*a*), and curve *B* shows the pH values found 10 days after dilution by method (*b*). It is seen that there are wide differences in the two curves over the whole concentration range, illustrating the slow attainment of equilibrium in the system. Indeed, it is not certain that the equilibria are completely reversible, since after 2—3 months' standing the corresponding curves still did not coincide. The obvious lack of equilibrium conditions in the solutions studied makes any calculations leading to the hydrolysis mechanism of little value, but further work on these lines might prove profitable.

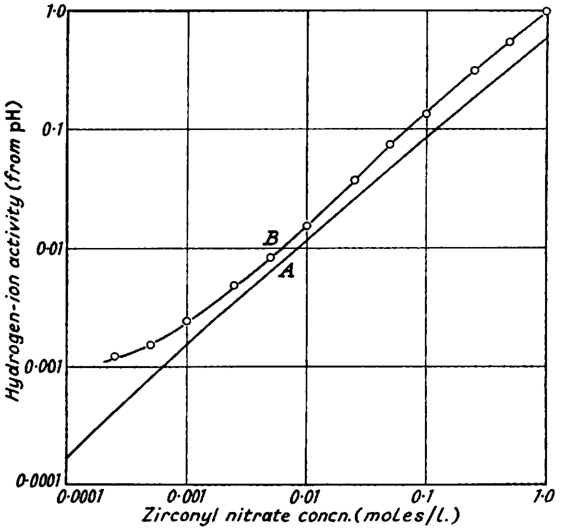


FIG. 14. *Relation between zirconium nitrate concentration and hydrogen-ion activity* (*from* pH *measurements*).

DISCUSSION

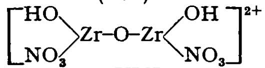
The results obtained emphasize the complex nature of solutions of zirconium salts. Apart from the number of different species coexisting in solution, we have the additional complication of slow adjustment of equilibria; this difficulty may cause deviations in results observed with solutions prepared by somewhat different methods or even in the same solutions after different time intervals. As far as possible, similar methods of preparation have been employed for the solutions used, but small difference may easily enter in this way.

The evidence regarding ionic size obtained by measurements of resin diffusion coefficients and self-diffusion coefficients in solution confirms in a general way the results obtained by other workers, and it is abundantly clear that polynuclear-ion formation occurs even in solutions of quite high acidity. The resin diffusion method gives a semi-quantitative picture of the size of the ions, but satisfactory evidence is still lacking on the mechanism of hydrolysis and polymerisation. The process of oxygen bridging is suggested as a probable mechanism, but the slow equilibrium changes, shown by the difference (and slow drift) in pH measurements when equilibrium is approached from the two sides, make any quantitative treatment rather suspect. Indeed, no direct evidence is yet forthcoming that the equilibria involved are truly reversible.

Nitric Acid Solution.—From the results on resin diffusion coefficients we can divide the system into three approximate acidity ranges. At acid concentrations less than 0·3N we have large polymerised species predominating, between 0·3 and 3N the species are approximately the size of the resin pores, and above 3N smaller ions which diffuse easily into the resin are most important. However, even these ions are larger than the cations from thorium nitrate solution which have been shown to be mainly of charge 4^+.

We can draw up a table (Table 3) which includes the most probable species, and proceed to eliminate certain of them by consideration of size, ionic charge, or nitrate content. For reasons of space, all possible species have not been included. Supposition of cationic species with a mean specific ionic charge greater than 2 or with a NO_3/Zr ratio greater than 2 is not necessary to explain the observations. If such species exist they are only present in very small amounts and have been omitted from the Table.

TABLE 3. *Possible zirconium species in nitric acid solution.**

Mean specific ionic charge :					
−2	0	0—1	+1	+2	NO_3/Zr
$[Zr(NO_3)_6]^{2-}$ (I)	—	—	—	—	6
$[Zr(OH)_2(NO_3)_4]^{2-}$ (II)	$[Zr(NO_3)_4]^0$ (II*a*)	—	—	—	4
—	$[Zr(OH)_2(NO_3)_2]^0$ (III)	—	$[Zr(OH)(NO_3)_2]^+$ (IV)	$[Zr(NO_3)_2]^{2+}$ (V)	2
—	$[(O{=}ZrNO_3)_2{=}O]^0$ (VI)	—	$[Zr(OH)_2(NO_3)]^+$ (VII)	$[Zr(OH)(NO_3)]^{2+}$ (IX)	1
			 $\left[(HO)(NO_3)Zr{-}O{-}Zr(OH)(NO_3)\right]^{2+}$ (VIII)		
—	$[Zr(OH)_4]^0$ (X)	$[Zr_3O_5]^{2+}$	$[Zr(OH)_3]^+$ (XI)	$[Zr(OH)_2]^{2+}$ (XII)	0
		$[Zr_4O_7]^{2+}$, etc. (XIV)	$[(HO)_2Zr{-}O{-}Zr(OH)_2]^{2+}$ (XIII)		

* For diagrammatic purposes simple formulæ have been incorporated in Table 3 (and in other places in the text). It would, however, be more correct to regard the species as being derived from the parent cation $[Zr(H_2O)_n]^{4+}$, where *n* may well be considered to be 6. Thus the relation between species (XII) and (XI) would be written as $[Zr(OH)_2(H_2O)_4]^{2+} \rightleftharpoons H^+ + [Zr(OH)_3(H_2O)_3]^+$ and so on. The reactions then fall into three types : (*a*) Competition of NO_3^- and OH^- with H_2O for positions in the co-ordination complex; (*b*) acid–base reactions often combined with (*a*); (*c*) condensation to form polynuclear cations with elimination of water.

The resin diffusion and self-diffusion data indicate, at low acid concentration, the existence of highly polymerised ions such as (XIV) in Table 3. With increasing acidity these will depolymerise to give the " dimer " (XIII), which may be one of the ions responsible for the " loop " in Fig. 3. The possible " depolymerisation " product $[Zr(OH)_3]^+$ is eliminated on account of its size, although at very much lower zirconium concentrations it may become important. The formation of $[Zr(OH)_2]^{2+}$ is not considered, since its specific charge of 2 is too high to agree with experimental data. From the dimer (XIII) we can proceed in a number of directions to (VII), (VIII), (IX), (V), or (IV). Species (VIII) can be eliminated on size considerations. Examination of the $\overline{NO_3}/\overline{Zr}$ ratios found on a cation exchanger (see Section 3) gives us information on this point. Let us assume equilibria between species (XIII) and (VII) :

$$[Zr_2O_3]^{2+} + 2H^+ + 2NO_3^- \overset{K_1}{\rightleftharpoons} 2[Zr(OH)_2(NO_3)]^+ + H_2O$$

Let us call $[Zr_2O_3]^{2+} = A$ and $[Zr(OH)_2(NO_3)]^+ = B$, and let X be the nitrate concentration. Then we have the relationships $K_1 = AX^4/B^2$ and $2A + B = \mathrm{Zr}$ (Zr = total zirconium concentration). There also exist the cation-exchange equilibria :

$\frac{\dot{A}}{\overline{\overline{\mathrm{H}}}^2} = K_2 . \frac{\bar{A}}{\overline{\overline{\mathrm{H}}}^2}$; $\frac{\bar{B}}{\overline{\overline{\mathrm{H}}}} = K_3 . \frac{B}{\mathrm{H}}$ and $2A + \bar{B} = \overline{\mathrm{Zr}}$, where the bars represent the resin phase. From these relationships we arrive at an expression

$$k = \overline{\mathrm{Zr}}f^2/(1 - f)X^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $f = \bar{B}/\overline{\mathrm{Zr}}$ and $k = K_3^{\,2}/2K_1K_2$. From this we obtain an equation for f:

$$\frac{f}{2} = \frac{X^2\sqrt{k/4\overline{\mathrm{Zr}}}}{1 + X^2\sqrt{k/4\overline{\mathrm{Zr}}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For a species containing one nitrato-group, the value of f is the value $\bar{X}/\overline{\mathrm{Zr}}$ shown in Fig. 8. By substitution of experimental values at one value of X into equation (1) we can arrive at a value for k. Inserting this into equation (2) in conjunction with the value for $\overline{\mathrm{Zr}}$ obtained from Fig. 9, we can see how the calculated values of f agree with the experimental $\bar{X}/\overline{\mathrm{Zr}}$ curve (Table 4). Although the agreement is not very good, examination of the relations involved shows that the theoretical curves obtained by deriving similar equations from other possible reactions, *i.e.*, the formation of species (IX), (IV), or (V), do not agree nearly so well with the experimental curves.

TABLE 4.

X	$\overline{\mathrm{Zr}}$	$\bar{B}/\overline{\mathrm{Zr}}$ (calc.) *		$\bar{X}/\overline{\mathrm{Zr}}$ (exptl.)	X	$\overline{\mathrm{Zr}}$	$\bar{B}/\overline{\mathrm{Zr}}$ (calc.) *		$\bar{X}/\overline{\mathrm{Zr}}$ (exptl.)
		(*a*)	(*b*)				(*a*)	(*b*)	
1	7·0	0·01	0·02	0·05	4	3·0	0·28	0·33	0·28
2	6·3	0·06	0·07	0·09	5	2·0	0·48	0·56	0·56
3	5·0	0·14	0·16	0·16	6	1·3	0·72	0·83	0·98

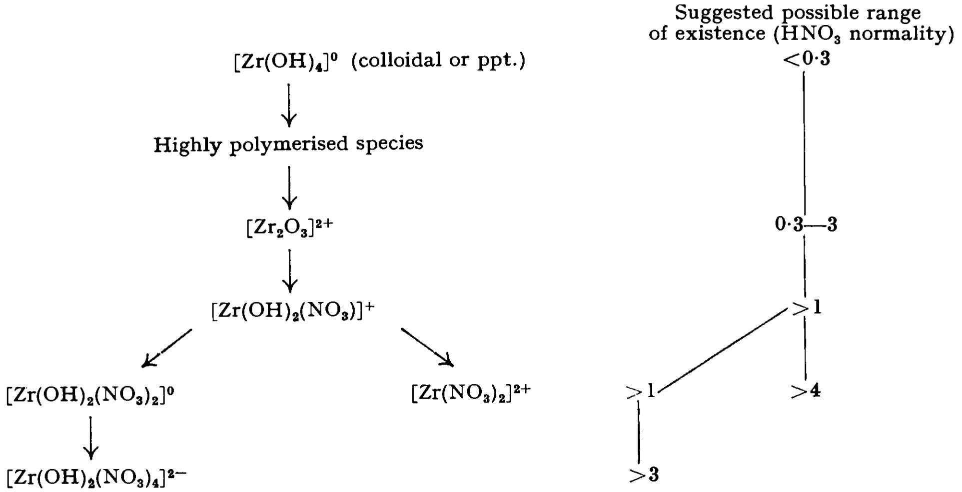
* (*a*) k found by matching at $X = 4$; (*b*) k found by matching at $X = 3$.

The above calculations make many approximations and neglect all activity coefficients. In addition, recognition is only made of the existence of two species, whereas the solution is almost certainly not so ideal. In the circumstances it is considered probable that the mononitrato-species is in fact $[Zr(OH)_2(NO_3)]^+$.

The experimental curve (Fig. 4) indicates that at acidities greater than about 4N a second species containing more nitrato-groups exists, and this, from considerations of ionic charge and size, is assumed to be $[Zr(NO_3)_2]^{2+}$. Electromigration studies and anion-exchange experiments show the presence of an anionic species at the higher acid concentrations. This may be $[Zr(OH)_2(NO_3)_4]^{2-}$ (II) or $Zr(NO_3)_6{}^{2-}$ (I) or possibly an intermediate uni-charged species. An uncharged species probably $[Zr(OH)_2(NO_3)_2]^0$, must be suspected and, although no direct proof is given, evidence for its presence is found in the experiments with mixed nitric acid–lithium nitrate solutions.

Nitric Acid and Lithium Nitrate Solutions.—The values obtained with mixed nitric acid–lithium nitrate solutions show that an increased nitrate concentration without increased acidity does not affect the nitrate content of the zirconium cationic species. We cannot therefore, under these conditions, suppose that a dinitrato-cationic complex makes any large contribution to the system. However, the initial cationic uptake on an exchange resin from the mixed nitric acid–lithium nitrate solutions is much smaller than for the corresponding pure nitric acid solutions and this, together with the facts that no significant differences in the zirconium uptake occur on an anionic resin and that there is little, if any, alteration in the value of the specific ionic charge, leads to the conclusion that an uncharged species is being formed under these conditions, probably $[Zr(OH)_2(NO_3)_2]^0$. It is probable that, by adjusting the nitrate–acidity conditions, a wide range of zirconium hydroxynitrato-complexes may be formed.

From these considerations, the following scheme is suggested :



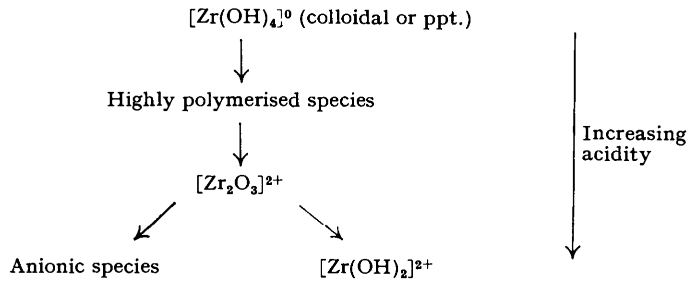
Perchloric Acid Solutions.—In perchloric acid solution we have very little, if any, complex cations formed by cation–anion interaction and, from an examination of the mean specific ionic charge curves, one must assume the formation in strongly acid solutions of the simple zirconyl radical $[Zr(OH)_2]^{2+}$. Connick and Reas (*loc. cit.*), by using extraction methods, have claimed that Zr^{4+} is the main monomeric zirconium species present in 1N- and 2N-perchloric acid solutions. The unlikely nature of this in solutions of the present concentrations seems to be confirmed by the fact that the uptake of zirconium from perchloric acid by a cation exchanger is rather slower than from nitric acid and very much slower than the uptake of thorium ion from nitrate solution. As with ion-exchange methods, the extraction technique (only Zr^{4+} ions will give an uncharged TTA complex soluble in the organic phase) favours the removal of more highly charged ions, and this tends to move the equilibria. This feature is, however, almost certainly more marked in extraction methods.

Electromigration and anion-exchange experiments show clearly the presence of zirconium in anionic complexes but the nature of these complexes is not clear. From this work, as well as from recent work by Sutton (*Nature*, 1952, **169**, 71) on the iron–perchlorate system, it is apparent that we must be much more careful before we assume that perchloric acid has no ability to form complexes. Indeed, some of the earlier work might well be reviewed in the light of this new information. It should, perhaps, be pointed out that Connick and his co-authors assume, but offer no experiments to prove, the absence of perchlorate complexing of zirconium.

The greater difficulty in removing zirconium from a cation-resin column with perchloric acid than with nitric acid (Lister, *J.*, 1951, 3123) may be explained by the small $[Zr(OH)_2]^{2+}$ ion being bound more tightly than the larger nitrato-ions found in nitric acid solution. In addition, the mean specific ionic charge of the zirconium species in perchloric acid solution is somewhat higher, but this fact alone is insufficient to explain the much higher degree of retention. Although a considerable proportion of zirconium may be present as anionic species, the introduction of the cation exchanger will cause a very large shift of the equilibria. A further explanation to correlate the difference in column behaviour of nitric and perchloric acids with the electromigration and anion-uptake data might be found in the relative amounts of anionic and uncharged species present in solution.

The greater ease of removal of zirconium from a column with sulphuric acid is easier to explain, since the cationic zirconium content of solutions in sulphuric acid is much smaller than in perchloric acid solution, and a smaller shift in the equilibrium would be expected to arise from the introduction of a cation-exchange resin. However, further experimental evidence on the position of the equilibria and the kinetics of all these systems is needed before a reliable explanation can be given.

We can then, for perchloric acid solutions of zirconium, suggest a scheme



Hydrochloric Acid Solution.—An examination of the results obtained with hydrochloric acid solutions again leads to the conclusion that a complex equilibrium system exists involving cationic, anionic, and uncharged species. The $\bar{X}$-$\overline{Zr}$ curves for hydrochloric acid solutions (Fig. 8) can be explained by the formation of a monochloro-complex and it is not necessary to assume the presence of any dichloro-complex. Electromigration experiments show very little movement of zirconium species in either direction, possibly indicating that an uncharged species is the predominating one. Anion-uptake experiments show that anions are present in solution, the equilibria involved moving to accommodate the removal of the small amount of anions originally taken up by the exchanger. The electromigration results may also be explained if similar amounts of cationic and anionic species are present with a very rapid adjustment of equilibria.

Similar conclusions as to the existence of cation–anion complexing have been arrived at by Adolf and Pauli (*Kolloid Z.*, 1921, **29**, 173) by measurements of conductance, pH, freezing points, and electromigration of $ZrOCl_2$ in solutions of different acid concentration. They have suggested complexes such as $[Zr(OH)_4,ZrO]^{2+}$, $[Zr(OH)_2Cl_4]^{2-}$, and $[Zr(OH)_4Cl_2]^{2-}$. The existence of the last ion has also been quoted by Blumenthal (*J. Chem. Educ.*, 1949, **26**, 472).

Sulphuric Acid Solution.—The existence of zirconium in complex anionic form in sulphuric acid solution was first demonstrated by Ruer (*loc. cit.*), and this has been amply confirmed by the present electromigration studies, by ion-exchange uptake experiments, and by column-elution behaviour (Lister, *loc. cit.*). We may again assume equilibria between cationic and anionic species, these equilibria lying far more to the anionic side than with any of the other acids studied. Electromigration and cation-exchange experiments have shown that in 1·5N-sulphuric acid solution the cationic species have disappeared completely and we are presumably left with equilibria between anionic and uncharged species. The presence of more than one anionic species has not been ruled out by these experiments.

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