FUNDAMENTAL STUDIES ON
THE PHYSICAL CHEMISTRY OF
INORGANIC ION EXCHANGERS.

A THESIS
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for a degree of

DOCTOR OF PHILOSOPHY

by

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PREFACE.

The investigations described in this thesis were carried out in the Chemistry Department of Glasgow University under the direction of Professor J. Monteath Robertson, F.R.S.

Material from Parts II and III has been published in the Journal of Nuclear Chemistry, and a reprint of this paper has been appended at the end of the thesis.

I wish to express my sincere gratitude to Dr. G.H. Nancollas for encouragement, guidance, and supervision during the period of this research. Thanks are also due to Dr. C.B. Amphlett of Harwell for many helpful discussions, and to the United Kingdom Atomic Energy Authority for the provision of a maintenance grant.

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* I and II refer to the sections on experimental methods, and results, respectively.

Part III KINETIC STUDIES

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PART I

GENERAL INTRODUCTION

Ion exchange can take place with any electrolyte, in which the ions of one sign are bound, or incorporated into an insoluble matrix, while those of the opposite sign are free to dissociate into solution. The degree of dissociation of these counter ions, or gegenions, into water is normally very small, due to the formation of an electrical double layer at the solid/solution interface. Ions of the double layer may be considered in dynamic equilibrium with those in the exchanger. When soluble salts are introduced into the aqueons phase, ions of the same charge as the original counter ions, mix with and replace those of the double layer, subsequently entering the solid phase. This is the basis of all ion exchange processes.

The discovery of ion exchange in 1850 is generally attributed to Thompson(1) and Way(2),(3), two British agricultural chemists. It was first observed in soil samples, and traced principally to the aluminosilicate content although evidence also exists now for ion exchange properties associated with soil humus. In 1876, Lemberg(4),(5) discovered that the mineral leucite could be transformed into analcite by leaching with sodium chloride, effectively substituting sodium for potassium ion in the silicate matrix and so stressing the stiochiometry of exchange process. Not, however, until the beginning of the twentieth century was ion exchange used industrially. Studies by Gans(6),(7) on natural and synthetic aluminium silicates, or permutites, were probably the most worthwhile attempts to utilize exchange for this purpose. With the determination of the crystal structures of micas and clays, by Pauling(8),(9), and Bragg(10), correlation between ion exchange properties and structure became possible, giving a much clearer understanding of the ion exchange process on silicates, which culminated in the researches of Matison(11),(12) Barrer(13), and Thomas(14),(15),(16).

As commercial exploitation of these siliceous exchangers was attempted, their limitations became even more apparent. In particular, they were found to be chemically unstable in acidic or basic solutions, and because of their close-knit chemical structure, often exhibited low capacities and rates of exchange. Recently, therefore, interest moved to synthetic organic resin exchangers, for theoretical as well as practical studies.

Organic exchangers are found to occur naturally in soil, in association with humus, which is an indefinite organic colloid, derived from the decay of plant residues. It is generally assumed that the exchange properties of this material are due to the presence of decomposition products of cellulose containing appreciable proportions of carboxylic end groups. Other natural organic products with exchange properties include alginic acid, agar, carrageen, phospholipids, and proteins. These, however, have not found application, because they have low capacities, and are generally of a colloidal or disperse nature in solution.

Synthetic organic ion exchange resins were invented by Adams & Holmes(17), who prepared Sulphonic Acid and polyamine exchangers. This pioneering work was followed by D'Alelio's discovery of polystyrene Sulphonic Acid and polymethacrylic acid exchangers(18). Attempts to prepare a strongly basic anion exchange resin were not successful until 1948, when the Rohm & Haas Coy., (U.S.A.) introduced the quaternary ammonium resin, Amberlite IRA-400(19).

Resins have been used with great success in almost all standard industrial and academic studies. Their properties include, stability to hot water, (with the exception of Amberlite IRA-400) to corrosive chemicals, and they can be obtained monofunctional in a range of either strong or weak, acidic or basic exchange groups. Selectivity can be varied by alteration in the cross linking of the polymer, and in this sense, they can be tailor made for specific applications. Performance data on standard commercial resins(20) shows that, in general, polystyrene sulphonic acid exchangers are stable up to 150°, while quaternary ammonium resins, in the hydroxide form, decompose at temperatures from 30° upwards. Such stability considerations, together with a demand for even more selective exchangers has led to the development of numerous, non siliceous inorganic exchangers. It is, nevertheless extremely unlikely that these will replace the resinous exchangers for normal laboratory studies.

Electrical double layers usually develop upon the surfaces of precipitates, suspensions, and emulsions, and play an essential part in stabilising colloidal sols. Surface changes on these materials may be produced either by preferential absorption of ions or, dissociation of functional groups. When charges arise from absorption of ions from solution, electronentrality is preserved by the formation of a diffuse double layer containing the counter ions: materials of this class exhibit small surface ion exchange capacities. Verwey and Kruyt (21) demonstrated this by electrodialysing a silver iodide sol. to hydrolyse off counter ions, replacing them with hydrogen ions, which were then determined by titration. Insoluble acids, bases, and ampholytes which develop changes by dissociation of functional groups, within the precipitates, exchange ions in much the same way as traditional ion exchangers. To exhibit the greatest number of sites, and hence show the largest capacity such materials are best prepared as gels or microcrystalline solids, which allow maximum penetration of water molecules. In theory, at least, all insoluble hydroxides and acid salts are capable of exchange, and so aroused a great deal of interest. It was hoped, that such exchangers would be capable of functioning without decomposition, in high temperature aqueous systems, and under large dosages of ionising radiation . Exchange properties are retained in the dried material provided the drying temperature is insufficient to remove bound water.

Hydrous oxides and hydroxides have been extensively studied and the exchange properties of many have been discussed, including, Al_2O_3 (23)(24)25)(26), Fe_2O_3 (27),(28), TiO_2 (29), ZrO_2 (29),(30),(31),(32), Nb_2O_3 (30), Ta_2O_5 (30), Cr_2O_3 (30), ThO_2 (29), La_2O_3 (33), WO_3 (29), SiO_2 (34),(35), ZnO_2 (36), and SnO_2 (37). In these investigations, it has been shown that many oxides exhibit amphoteric behaviour, exchanging anions in acidic, and cations in basic solutions. To explain such behaviour, a number of mechanisms have been postulated (29),(38),(30) for anion exchange at low pH, (a) $MOH + H^+ \rightleftharpoons MOH_2^+$, (b) $MOH \rightleftharpoons M^+ + OH^-$; for cation exchange at high pH, (c) $MOH \rightleftharpoons MO^- + H^+$, and (d) $MOH + OH^- \rightleftharpoons MOH.(OH)^-$; where M represents a single metal atom of the oxide matrix. Choice of possible mechanisms of cation or anion exchange on any given oxide is dependent upon its acidic or basic nature. Few, if any, can be regarded as truely amphoteric, exchanging by mechanisms (b), and (c) with the possible exception of aluminium hydroxide. An acidic oxide, therefore, might be expected to exchange cations and anions by (c) and (a), while a more basic oxide might combine (d) and (b) respectively. Zirconia appears to be a special case, since it does not contain the hydroxyl group, and must consequently be termed a hydrous oxide. It has been postulated in Part II that this structure exchanges anions and cations by being protonated in acid, and co-ordinating hydroxyl ions in alkaline solutions respectively.

A choice of suitable hydroxides for exchange purposes is limited by their solubility in aqueous solutions. It is therefore apparent that many potentially interesting oxides would be entirely soluble, for example, the strongly acidic oxides. These can, however, be rendered insoluble as the acid salts of heavy metals, and, as such, exhibit strong acid exchange properties showing no tendency to absorb anions. Since they are usually obtained as gels, they will be referred to as, for example, zirconium phosphate, tungstate, and so on, without implying a specific or stoichiometric composition.

An ever increasing number of papers are being published on these materials, including the acid salts; zirconium phosphate(39),(40),(41) molybdate(42),(43). selenite(44). , tungstate(45),(46). and chromate(47),(48). ; thorium phosphate (22) and tungstate (49) ; titanium phosphate (50) . A similar series of investigations has been conducted into the exchange properties of ammonium - 12 - heteropolyacids (51), (52),(53),(54),(55).

During such investigations materials have been found, with high selectivities, for example caesium ion on zirconium phosphate. In many cases, however, solubility, hydrolysis and the indefinite nature of the compounds formed proved great obstacles to further, and more theoretical investigations into the basic physical chemistry of the exchange processes. It has, therefore, been the object of the present work to prepare stable, well characterised monofunctional exchangers in crystalline or microcrystalline forms, by methods showing a high degree of reproducibility.

PART II

PREPARATION AND PROPERTIES OF INORGANIC EXCHANGERS

PREPARATION OF EXCHANGERS

Zirconia: A 20 l. aspirator containing 15 l. of approximately 0.2 M zirconyl chloride was maintained at 70° by means of a water bath. 0.5 M ammonium hydroxide was added dropwise to the well-stirred solution until it was neutral or faintly alkaline. The solution was allowed to cool slowly overnight, with stirring, after which the gelatinous product was filtered, washed, and air dried at 50°. The resulting glassy solid broke down in water to give a stable material of particle size 30-160 British Standard Sieve. A sieved fraction of particle size 60-160 B.S.S. was used in all experiments on hydrous zirconia.

During the initial stages of precipitation the solution was acid and the zirconia gel absorbed chloride ion by a process of ion exchange while in the later stages as the pH of the precipitant solution became higher more and more ammonium ions were absorbed. This has been observed as 'salt uptake' by Britton (56) and other workers who have studied the precipitation of such hydroxides quantitatively. The Zirconia was therefore present in the chloride and ammonium forms to some extent. Such groups may, however, be removed by hydrolysis when the exchanger is washed with water, and the hydroxide form of the exchanger was prepared in this way by column washing the zirconia sample with distilled water, until no chloride was detectable in the effluent. The sample was then filtered and air dried.

Thoria: Thoria was precipitated by the slow addition of 0.5 M ammonium hydroxide to a solution of 0.2 M thorium nitrate maintained at 70° on a steam bath. Precipitation occurred in the later stages of the addition and the precipitate, although gelatinous, was easily filtered. Normally, however, the product was digested at 70° for several hours to remove excess ammonia from the mother liquor. After washing to remove chloride and drying at 50° a glassy product was obtained.

Two batches, A and B, were prepared. Batch B was digested for a considerably longer period and showed x-ray evidence of greater crystallinity.

Zirconium Phosphate:

1. The method of Larsen Fernilius & Quill:(57)

Larsen Fernilius and Quill described the preparation of a well defined crystalline phosphate, diphosphato-zirconic acid, $ZrO(H_2PO_4)_2$.

Stoichiometric quantities of dilute solutions of zirconyl chloride and phosphoric acid in 10% V/V sulphuric acid were added slowly to a well stirred bath containing 2 - 2.5 l. of 10% V/V sulphuric acid at 75°. In order to prevent the local formation of pockets of high concentration of reagents, the zirconyl chloride and phosphoric acid solutions were sprayed on to the surface, using simple atomisers (figure 1.). The precipitate was digested at 75° for several days, washed thoroughly with dilute ammonium nitrate and dried in at at 50°

The particle size of the material obtained was less than 200 B.S.S., which was too small for normal column operation and the other uses envisaged. Since suitable clay mineral samples for ion-exchange have been prepared from the finely divided material by extrusion, it was decided to compress a sample of the Zirconium phosphate in a hydraulic pill press at a pressure of several thousand pounds per square inch. The product was an opaque disc of good mechanical properties, which, when tested for stability in water broke down to a coarse powder, exhibiting a wide range of particle sizes, suitable for column and other physical investigations. After prolonged immersion in a vigorously stirred bath no further breakdown was observed. Such material was used in all chemical investigations on zirconium phosphate, and will henceforth be denoted by ZrP.

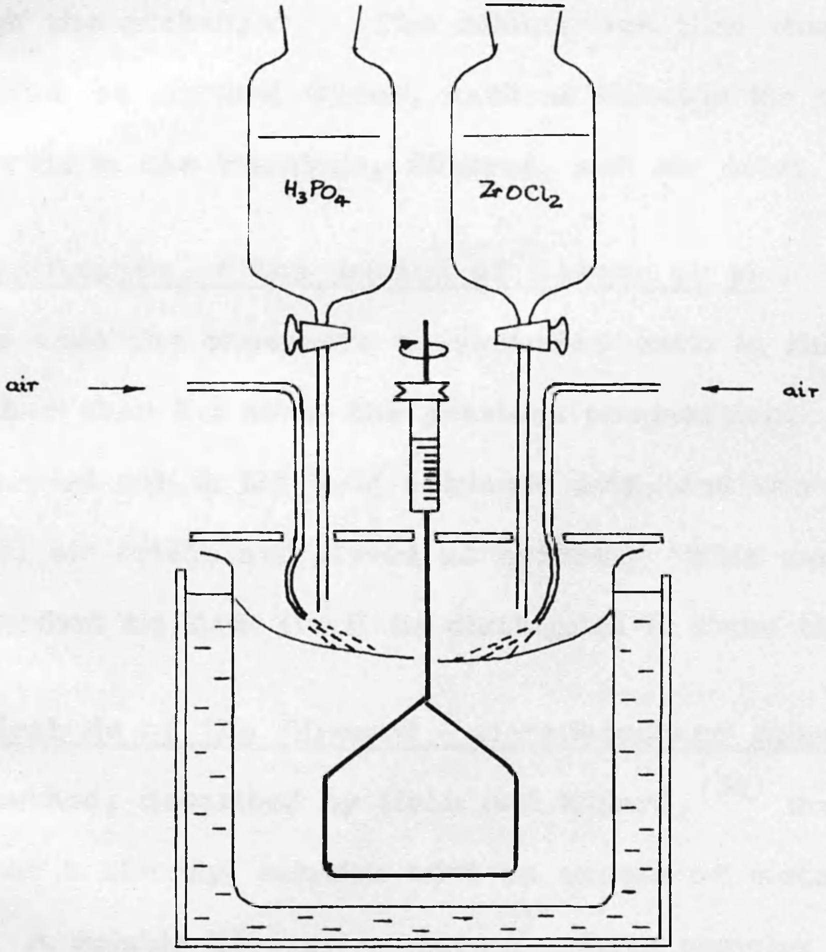


FIGURE 1.

ZrP, H-form:

Samples of ZrP were column washed with 0.1 M HCl until there was no change in the composition of the solution passing through the exchanger. The column was then washed with a minimum of distilled water, until no chloride ion was detectable in the washings, filtered, and air dried.

1a. Modification of the method of Larsen et al.:

In this case the phosphate to zirconium ratio in solution was 1:1 rather than 2:1 as in the previous preparation. Precipitation was carried out in 12% V/V sulphuric acid, and the product washed, air dried, and sieved as before. This material will be described as ZrP (1 : 1) to distinguish it from the original.

2. Hydrolysis of the Zirconyl - metaphosphate complex:

This method, described by Hahn and Willard, (58) involved the mixing of a zirconyl solution with an excess of metaphosphoric acid. A soluble Zirconyl - metaphosphate complex was formed in solution, which on standing over a period of twelve hours at room temperature, hydrolysed to insoluble zirconium phosphate. The product was granular and amorphous.

3. Precipitation in hydrochloric acid solution:

The method of Gal and Gal (59) was also attempted.

A solution of 30 g. of zirconyl chloride in 4 M HCl was added slowly with stirring to 500 ml. of 12% phosphoric acid, in 4 M HCl. The material obtained, after washing and drying the product was a gel.

4. Precipitation by dilution:

Blumental (60) stated that freshly precipitated Zirconium phosphate was soluble in excess of strong mineral acid. It was decided, therefore, to maintain stoichiometric quantities of zirconyl chloride and phosphoric acid in solution in a minimum of concentrated sulphuric acid. Water was then added slowly with stirring and the zirconium phosphate precipitated.

No improvement in the quality of the product was observed since the zirconium phosphate, which formed in local pockets of dilution would not redissolve easily in the bulk of solution.

Insoluble Chromates:

Zirconium Chromates: Such materials appeared to be attractive for studies as ion exchangers, and Briggs (61) described the preparation of a stable chromate of Zirconium; $9\ ZrO_2,\ 5\ CrO_3,\ 12\ H_2O$.

7g. of zirconyl chloride in 50 ml. of water was added to 10 g. of potassium chromate in 80 ml. of water. The precipitate was filtered after 24 hours, washed with water and dried under reduced pressure. 25 g. of the powdered product was heated in a sealed tube for four hours with 6 g. of chromic oxide in 6 ml. of water. An orange-red crystalline powder was obtained, which was washed further, and air dried.

A sample was treated in a column with 50 ml of 0.5 M NaCl and washed free from chloride ion with distilled water. It was then eluted with 0.1 M HCl until the effluent gave a negative test for sodium ion by flame photometry.

Lungren(62) claimed that the material prepared by Briggs did not correspond to a true chemical compound and that on further heating a homogeneous crystalline material, $4\ ZrO_2$, $5\ CrO_3$, $5\ H_2O$, was obtained.

This material was prepared by heating the Brigg's reaction mixture for 7 to 15 days, and consisted of crystals of up to 1 m.m. in length. After washing with 0.1 M HCl, then with water, and air drying, the chromate, which showed no hydrolysis in water, was tested for ion exchange properties.

Batches were equilibrated in solutions of sodium and potassium chlorides and the hydrogen ion release determined by titration with standard sodium hydroxide.

Basic Thorium Chromate:

$Th(OH)_2CrO_4$, was prepared by the method of Lungren and Sillen (63).

A solution of 1 g. potassium dichromate in one litre of water was heated to boiling and a solution of 1 g thorium nitrate in about 10 ml of water added slowly. A flocculent precipitate formed, which, after a few hours became visibly crystalline. The crystals of the chromate were filtered, washed, air dried, and samples equilibrated in water and sodium chloride solutions. Neither hydrolysis nor appreciable exchange of ions was detected.

Analysis of Zirconium phosphate:

The method used was an adaptation of that employed by Larsen et al.(57); in the preparation of zirconia from ZrP.

0.2 - 0.3 g. of finely ground ZrP H-form were treated with 10 ml. of saturated sodium hydroxide at 0 - 10° and the slurry allowed to stand for one hour. A further 10 - 20 ml. of cooled water together with 2 - 3 g. of sodium peroxide were added and the resulting solution digested on a steam bath at 50 - 70° for several hours. During this period the soluble peroxyzirconate was completely decomposed to insoluble hydrous zirconia. The precipitate was filtered hot through a No.4 sintered porcelain crucible, washed thoroughly with dilute ammonium hydroxide to convert it to the ammonium form, and ignited to constant weight at 1000°. On ignition, the precipitate lost water and ammonia, and was weighed as pure anhydrous zirconia. After collecting the filtrate in a weighed flask, it was analysed for phosphate by precipitation of ammonium phosphomolybdate, which was ignited at 500° and weighed as the anhydride.

Thermobalance Studies:

All inorganic exchangers studied contain unknown quantities of bound or interstitial water. There is good reason to believe that the amount of bound water will affect the ion exchange capacity and selectivity (64),(31).

In order to follow the variation of equilibrium weights of these exchangers over a wide range of temperatures a Stanton Thermobalance (model 7825) was used. This is an automatic instrument, with an upper limit of 800°, recording temperature weight loss curves.

The apparatus, shown in figure (2), consisted essentially of an automatic beam balance, the loading beam of which was attached to a silica rod, (A) supporting a platinum crucible. A sample of exchanger of about 0.5 g. was weighed accurately into this crucible and placed in the silica holder. Balance was restored by placing weights on the opposite pan, and the electric furnace (B) then lowered to the position shown. The thermocouple (C), and the balance were connected to a pen recorder so that temperature and weight loss were recorded simultaneously.

Experiments were conducted for zirconia, thoria, and ZrP. To ensure that the plot obtained represented the equilibrium weight loss at each temperature, individual points on the curve were verified by heating similar samples in furnaces at specified temperatures, until they attained constant weight. By this method weight loss curves for zirconia and ZrP were shown to be truly at equilibrium, while for thoria the normal heating rate of 2 deg./min. was too great to allow equilibrium conditions to be attained at each point. In determinations on thoria, therefore, the equilibrium plot of weight loss/temperature

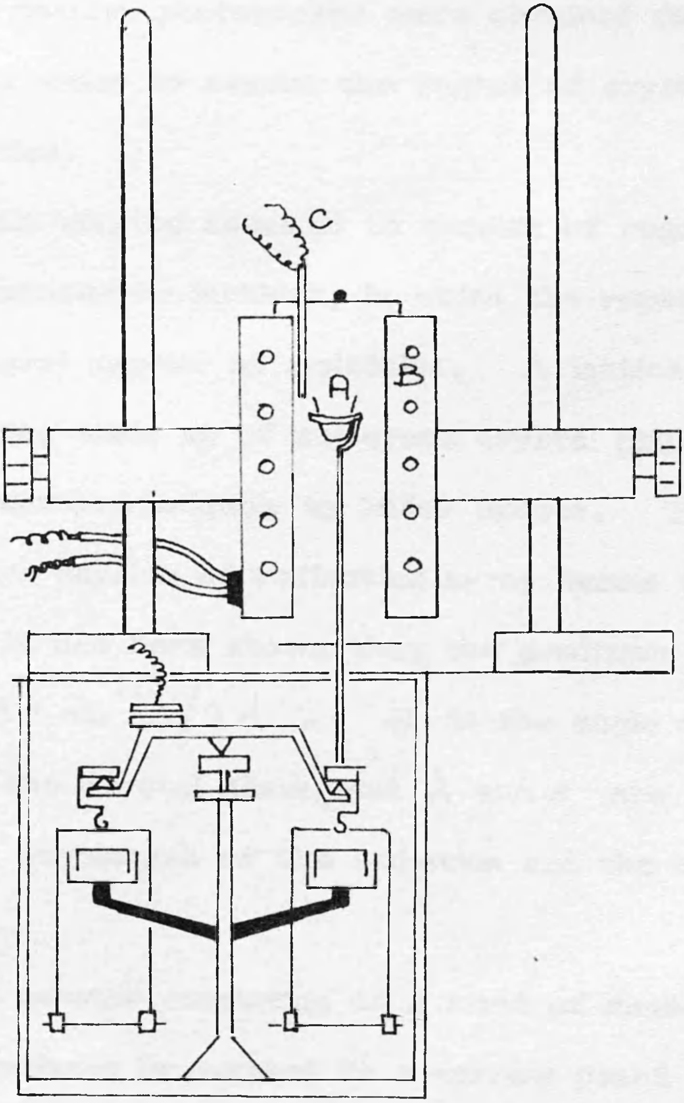


FIGURE 2.

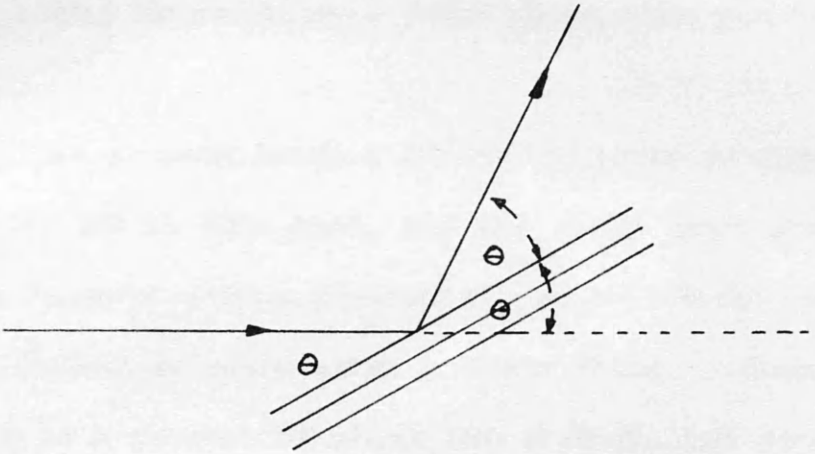
was obtained by heating the sample in steps of 30°, allowing it to reach equilibrium weight at each temperature.

X-ray powder photography:

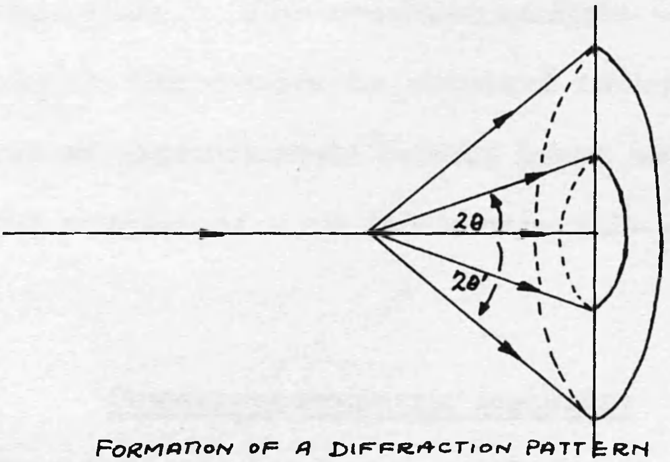
X-ray powder photographs were obtained for samples of exchangers in order to assess the degree of crystallinity in each preparation.

Crystals may be assumed to consist of regular three dimensional structures or lattices, in which the repetitive unit contains an integral number of molecules. A lattice may be considered as being made up of numerous crystal planes each of which may be described uniquely by Miller indices. These crystal planes are capable of reflecting x-ray beams incident upon them, and it has been shown that the condition for reflection is, $\theta = \sin^{-1} \lambda / 2d$. θ is the angle of incidence of the beam on the crystal plane, and λ and d are respectively the wavelength of the radiation and the interplanar spacing.

When a powder consisting of a mass of randomly orientated crystalliteees is exposed to a narrow pencil of monochromatic x-rays, it is probable that the condition for reflection will occur in a number of cases. Provided there are



REFLECTION FROM A SINGLE CRYSTAL PLANE.



FORMATION OF A DIFFRACTION PATTERN

FIGURE 3.

sufficient crystallites, the reflected rays will form a series of cones about the incident beam with vertical angles of 2θ and corresponding to reflections from all possible planes (figure 3)

In the present work a Debije Scherrer powder camera (Phillips P.W. 102 4) was used, and the x-ray beam produced on a copper target; a monochromatic beam of Cu $K\alpha$ radiation λ, 1.543 Å was obtained using a nickel filter. Samples were ground to a powder of about 200 B.S.S. and packed into capillary specimen tubes 0.3 - 1 m.m. in diameter of very thin Lindemann glass. The specimen samples were centred, and film loaded in the camera by standard techniques. An exposure time of approximately twenty hours was required in each case for samples of ZrP (H-form), (Cs - form), and for thoria.

Spectrophotometric Methods:

Determination of trace phosphorus: Trace phosphorus was determined from photometric measurements on molybdovanadophosphoric acid by the method of Michelson (65). Measurements were made using a Hilger Uvispec spectrophotometer (H, 700.307.

The solutions required were:

(a) 2.5 M HCl

(b) 0.234% W/V of ammonium metavanadate, prepared by dissolving 2.34 g. in 500 ml. of hot water, adding 28 ml. of concentrated HCl, and diluting the cooled solution to one litre.

(c) 3.53% W/V ammonium molybdate; prepared by dissolving 35.3 g. of the molybdate in water at 50°, and diluting the cooled solution to one litre.

The reagent was prepared by mixing b, a, and c in the ratios of 1 : 2 : 2 respectively, and diluting 25 times. 25 ml. of this reagent was mixed with 25 ml. of phosphate solution in 0.1 M HCl, in which the phosphate content varied between 10^{-5} and 10^{-4} m.moles. A blank experiment was also made by mixing equal volumes of diluted reagent and 0.1 M HCl. A calibration plot was made of optical density at 315 $m\mu$ against concentration of NaH_2PO_4 solutions, using a blank as reference. Phosphate contents of the unknown solutions were then determined by interpolation.

Determination of trace Zirconium: Thamer and Voigt (66) made a study of coloured zirconium chloranilate complexes in solution and suggested a possible use of the 1 : 1 complex in quantitative analysis of trace zirconium.

25 ml. portions of test solution, containing not more than 1.5 x 10^{-3} m.moles of zirconium, were measured into a 50 ml. standard flask. A further 20 ml. of 4 M perchloric acid were added. After mixing thoroughly, 4 ml. of 0.1% V/W chloranilic acid was added and the solution made up to the mark. Optical densities were measured at 5.50 mμ, using water as a blank and a calibration curve was constructed from solutions of known zirconium contents. These stock solutions were analysed by precipitation of hydrous zirconia in ammonia solutions, and igniting the precipitate at 1000° to obtain the anhydrous oxide. Measurements of ± 1% accuracy were made in solutions of 1×10^{-6} M or greater in zirconium.

Determination of trace sodium and potassium: Analyses were carried out, using an E.E.L. Flame Photometer. Stock solutions of sodium and potassium chlorides were made up by weight or analysed by chloride determination. Standard dilutions in the range 1×10^{-3} to 10^{-4} M were prepared, and using a suitable filter, the scale deflections for distilled water and 10^{-3} M solution were adjusted to zero and 100 respectively. Calibration curves of concentration against scale deflection were then constructed, from which the sodium and potassium contents of unknown solutions were determined.

Hydrolysis of Zirconium Phosphate:

The Hydrogen Form: 1 g. samples of ZrP, ZrP (1 : 1), and commercial zirconium phosphate produced by B.D.H. and Bio-Rad, in the H-forms, were equilibrated with 50 ml. portions of distilled water at 25°. The equilibrium solutions were analysed for trace phosphate (page 19) by the method of Michelson (65) and for hydrogen ion, using the electrode system:

Glass electrode	solution under study	satd KCl	Calomel Electrode

E.m.f. measurements were made with a Pye potentiometer and a Vibron electrometer (E.I.L. model 33B) as a null detector. The electrode system was standardised with 0.05 M potassium hydrogen phthalate, pH 4.005 (67), B.D.H. tabloid phosphate buffer, pH 6.99, and 0.05 M sodium borate pH 9.18. (67)

The caesium form: Samples of zirconium phosphate (ZrP) were converted to the caesium form by eluting (a) with 0.1 M CsCl, and (b) with 0.1 M CsCl in 2.5×10^{-4} M CsOH. The latter was used to ensure complete ionisation of exchange sites.

0.5 g. samples prepared containing Cs^{137} were air dried for several days, added to 50 ml. portions of distilled water and allowed to equilibrate at room temperature for ten days. Standard dilutions of the active 0.1 M caesium solutions were made to 10^{-3} and 10^{-4} molar, 25 ml. samples were evaporated slowly to dryness with an infra-red lamp. Soluble solids were then transferred with washing, and subsequent evaporation to a 2 cm. planchette, and mounted as solid sources. A similar mounting was prepared from the equilibrium solution and its activity compared with those of the standard sources.

In parallel experiments using inactive caesium, samples of the equilibrium solution were withdrawn and analysed for phosphate and hydrogen ions in the usual way (pages 19 + 22)

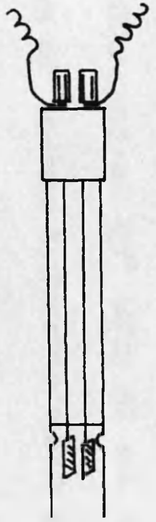
The potassium form: This was prepared by eluting the H-form with 0.1 M KCl for two days, after which the exchanger was washed free of chloride ion, and air dried. 0.5 g. samples were then equilibrated with 50 ml. water and the equilibrium solution analysed for potassium ion, using an E.E.L. flame photometer (page 21). Phosphate and hydrogen ion release were determined in this and a similar experiment where the exchanger was equilibrated with 50 ml. of 0.1 M KCl

Measurement of rates of hydrolysis: The rates of hydrolysis of both the potassium to hydrogen forms of ZrP were studied potentiometrically using the cell: glass electrode/solution/calomel electrode, and the method described on page, 22 . Nitrogen was blown through a sample of 100 ml. water in the cell figure (5a) until a constant e.m.f. was obtained. A 1 g. sample of exchanger 60 - 100 B.S.S., was then added to the vigorously stirred solution, and the fall in e.m.f. plotted against time. Towards the end of the hydrolysis samples of the solution were withdrawn and tested for chloride ion.

Determinations of solubility.

An estimate of the solubility of ZrP in water, and hydrous zirconia in acid solutions was obtained by trace zirconium analysis.

1 g. samples were equilibrated at room temperature with 25 ml. portions of water, and HCl solutions of up to 1 M,



CONDUCTIVITY ELECTRODES
(Phillips PR 95/10).

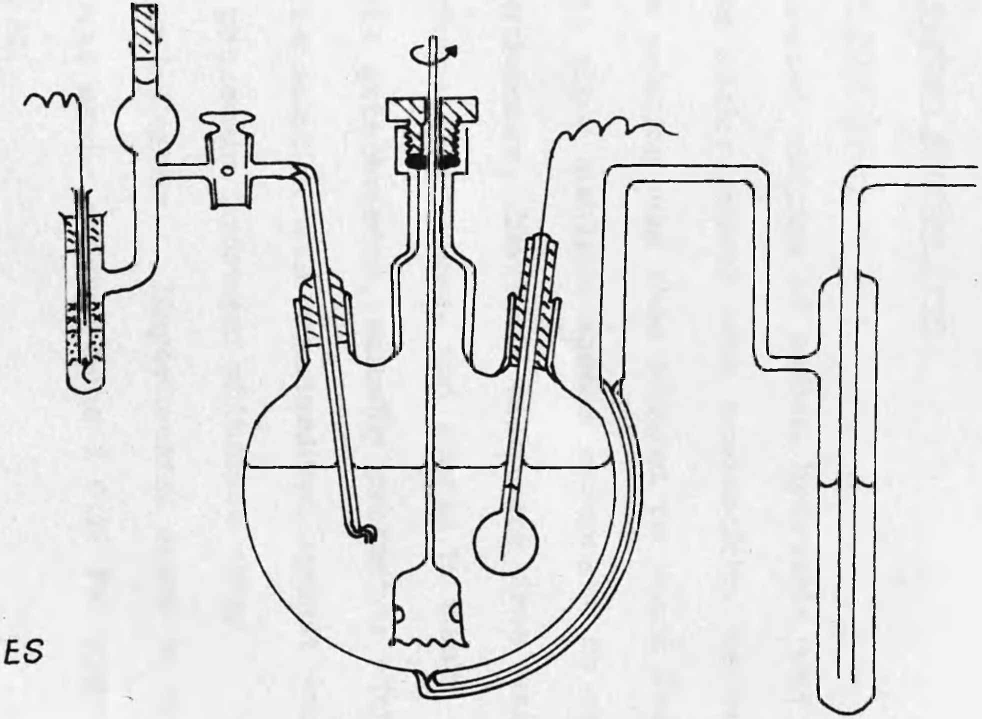


FIGURE 5a.

and analysed for zirconium (page 21).

Preparation of carbon dioxide free sodium hydroxide solutions:

A saturated solution of sodium hydroxide was prepared by shaking excess analar pellets with conductivity water for 24 hours. The solution was then allowed to stand for three to four weeks to allow insoluble sodium carbonate to settle. Samples were withdrawn, diluted in carbonate free water under an atmosphere of nitrogen, and stored in flasks with automatic burette attachments, suitably protected with soda-lime tubes. The solution was standardised against weighed samples of dry potassium hydrogen phthalate using phenolphthalein as indicator. Experimental error in such determinations was never greater than ± 0.1% for hydroxide solutions of 0.1 M.

pH titration curves:-

Zirconium phosphate: 0.5 g. samples of ZrP (H-form) were weighed out and equilibrated at 25^o with 50 ml. samples of varying concentration of sodium hydroxide made up to a total ionic strength of 0.1 M with sodium chloride. After mechanical shaking in a thermostat at 25^0 the equilibrium pH was determined (page 22).

Thoria: 1 g. of thoria was introduced into a titration flask containing 100 ml. of water, stirred by nitrogen bubbling. The acidic and basic portions of the titration curve were obtained by following the change in pH on addition of standard acid or alkali.

PART II

RESULTS

Thermobalance Studies:-

Thoria: Thermobalance studies on thorium hydroxide produced a dehydration isobar which showed four distinct regions of weight loss, (figure 4, curve i). (a) probably corresponded to a loss of surface and interstitially absorbed water; while (b), and (c), may be due to the irreversible loss of water molecules by elimination between hydroxide groups in the solid, and (d) represented the equilibrium weight of anhydrous material. Consequently it would be expected that material heated to above 150° would lose some or all of its exchange capacity.

Hydrous Zirconia: This curve, showed a smooth continuous, almost exponential, loss in weight over the temperatures studied, (figure 4 curve iii).

Zirconium phosphate (ZrP): The dehydration isobar, (figure 4, curve ii), showed a steep steady fall in weight with increasing temperature up to 200°, probably corresponding to a loss of interstitial water followed by a plateau of almost constant weight between 200 and 300°. Further slow loss in weight was observed, above 300°, and up to the temperature limit of the thermobalance.

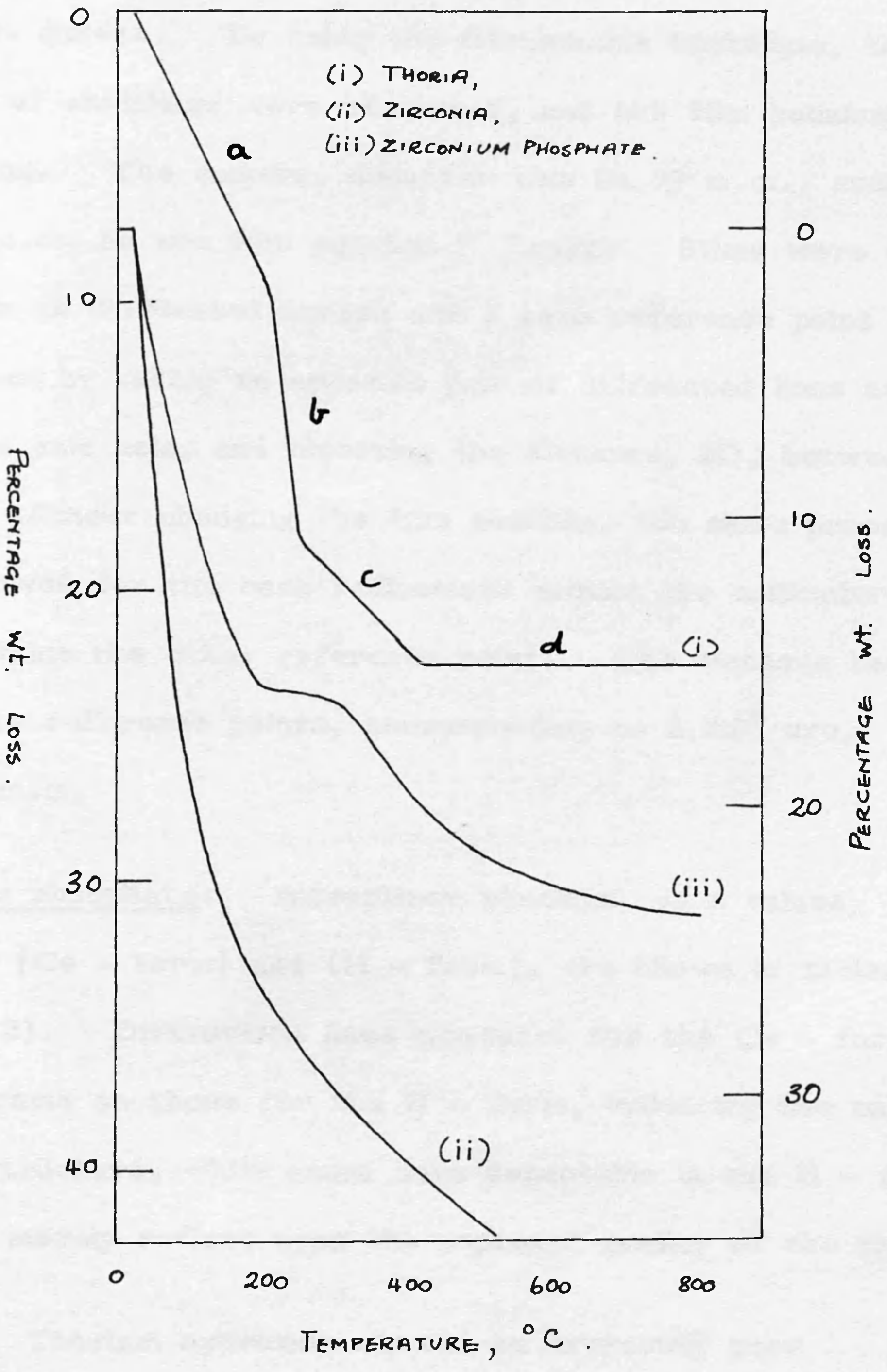

(i) THORIA,
(ii) ZIRCONIA,
(iii) ZIRCONIUM PHOSPHATE.
a
b
c
d
(i)
(ii)
(iii)
PERCENTAGE WT. LOSS.
0
10
20
30
40
PERCENTAGE WT. LOSS.
0
10
20
30
0
200
400
600
800
TEMPERATURE, °C.

FIGURE 4

X-ray powder diffraction:

Any film, after development and drying, shrinks to a certain extent. By using the Straumanis technique, the effects of shrinkage were eliminated, and the film became self calibrating. The camera, diameter was 114.83 m.m., such that 2 m.m. on the film equalled 1° Bragg. Films were laid flat upon an illuminated screen and a zero reference point established by taking an opposite pair of diffracted lines around the beam exit hole, and bisecting the distance, 2D, between them. Without changing the film position, the same procedure was followed for the back reflections around the collimator hole, to determine the other reference point. The distance between these two reference points, corresponding to a 180° arc, was 180 m.m.

Zirconium phosphate: Interplanar spacings, or d values, for ZrP (Cs - form) and (H - form), are shown in tables (1) and (2). Diffraction lines measured for the Cs - form are the same as those for the H - form, indicating the same crystal structure, while extra lines detectable in the H - form pattern, merely reflect upon the improved quality of the photograph

Thoria: Thorium hydroxide showed an extremely poor diffraction pattern, in which the lines were broad and diffuse. Such broadening may be caused by diffraction from crystallites of 1000 Å or less, or by strain within the crystal; both of which are possible.

Table (1)

X-ray diffraction pattern for ZrP, Cs-form
Radiation Cu Kα, λ = 1.542 Å.

Line	Strength	θ°	Sin θ	d (Å)
1	MS	5° 51	0.1020	7.67
2	S	9° 51	0.1170	5.51
3	VS	12° 33	0.2173	3.55
4	S	17° 0	0.2924	2.64
5	VW	18° 0	0.3090	2.50
6	VW	18° 30	0.3173	2.43
7	VW	18° 45	0.3214	2.40
8	W	22° 15	0.3786	2.04
9	W	24° 9	0.4091	1.89
10	W	25° 30	0.4305	1.79
11	W	26° 45	0.4501	1.72
12	W	27° 45	0.4656	1.65
13	W	30° 9	0.5023	1.54

V.S. = Very Strong
S = Strong
M.S. = Medium Strong
W = Weak
V.W. = Very Weak.

Table (2)

X-ray diffraction pattern for ZrP, H-form
Radiation CuKα, $\lambda = 1.542$ Å

Line	Strength	θ	Sin θ	d (Å)
1	M.S.	5° 51	0.1023	7.54
2	S	9° 54	0.1719	5.57
3	V.S.	12° 30	0.2164	3.57
4	V.V.W.	13° 33	0.2342	3.29
5	V.V.W.	13° 45	0.2376	3.25
6	V.V.W.	14° 20	0.2476	3.13
7	S	16° 57	0.2913	2.65
8	V.W.	18° 9	0.3115	2.48
9	V.W.	18° 36	0.3190	2.42
10	V.W.	19° 0	0.3256	2.37
11	V.V.W.	20° 54	0.3567	2.16
12	V.V.W.	21° 24	0.3649	2.11
13	W	22° 9	0.3770	2.04
14	W	24° 9	0.4091	1.89
15	W	25° 45	0.4345	1.78
16	W	26° 33	0.4470	1.73
17	W	27° 45	0.4656	1.66
18	W	30° 20	0.5050	1.53

V.V.W. = extremely weak.

Table (3)

X-ray diffraction pattern for thoria OH - form
Radiation Cu Kα , λ = 1.542 A

Line	Strength	θ	Sin θ	d (Å)
1	S.D.	3° 51	0.0672	11.50
2	S.D.	6° 51	0.1193	6.47
3	W.D.	11° 21	0.1968	3.92
4	S.D.	13° 51	0.2393	3.23
5	W.D.	15° 57	0.2748	2.81
6	S.D.	22° 51	0.3883	1.99
7	S.D.	27° 6	0.4555	1.69

S.D. Strong diffuce
similarly for W.D. etc.

Analysis of Zirconium phosphate:-

Two samples of ZrP, (H - form), were analysed. Sample (I) was material, which had been converted to the hydrogen form using hydrochloric acid, and had subsequently been washed free from chloride using a minimum of distilled water. Sample (II), however, was prepared similarly, using an excess of washing water. From the results shown in table 4, it is seen that the phosphate to zirconium ratio in the solid was about 5% less than for diphosphatozirconia acid and that further reduction in this ratio occurred with washing.

Table 4:

Sample	P04/Zr
I	1.88
II	1.86

Hydrolysis of Zirconium phosphate:-

The Hydrogen form: The results of these studies are shown in Table 5, and it is seen that the hydrolysis characteristics of ZrP, and ZrP (1 : 1) are very similar; suggesting a strong tendency for a fixed ratio or $[H^+]/[PO_4]$, although the ratio

Table 6

Composition of solution for equilibrium	Exchanger form	Equilibrium concentrations in solution			
		pH	$[H^+]$ $Mx10^4$	$[PO_4]$ $Mx10^4$	$[M^+]$ $Mx10^4$
Water	Cs	4.83	0.148	2.08	2.06
Water	Cs^*	5.29	0.051	2.11	2.16
Water	K	5.01	0.098	3.5	3.01
0.1 M KCl	K	3.01	9.7	0.074	-

Note:

(a) 0.5 g. samples were equilibrated with 50 ml. portions of solution

(b) Cs^* represents material prepared by elution with 0.1 M CsCl. in $2.5x10^{-4}$ M CsOH.

Rates of hydrolysis of Zirconium phosphate:

The rate of hydrolysis of ZrP is shown as a plot of pH against time in figure (5b), in which it is seen that 90% of hydrolysis occurred in the first 5 - 6 minutes, indicating a very rapid release of hydrogen ion. Final pH's of the equilibrium solutions were 4 and 5 for the hydrogen and potassium forms respectively.

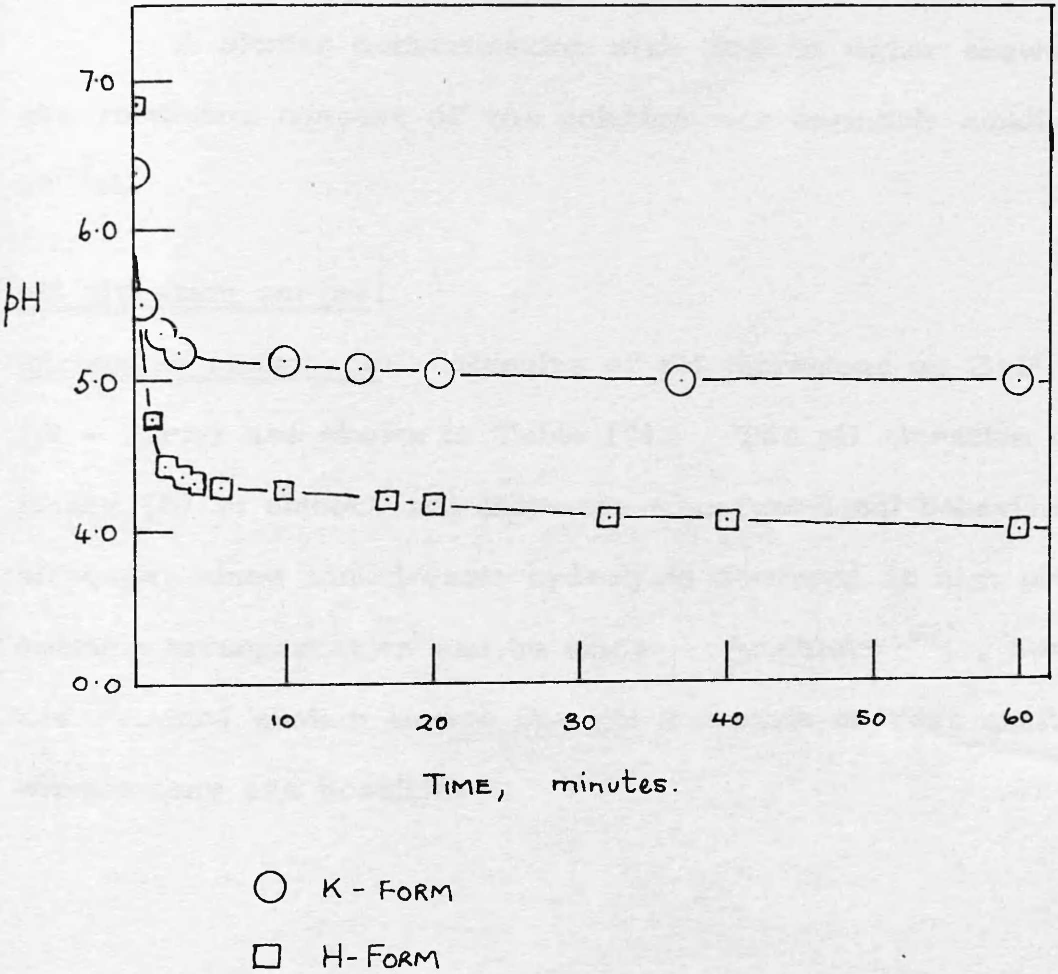


FIGURE 5b.

Solubility determinations:

Of the samples of zirconia equilibrated with water and HCl solutions only in the case of 1 M HCl was a trace of zirconium detected, ($5x10^{-5}$M). Zirconia is therefore extremely insoluble in the acid and alkaline solutions normally encountered in ion exchange.

A similar determination with ZrP in water showed that the zirconium content of the solution was negligibly small 10^{-7}M.

pH titration curves:

Zirconium phosphate: Results of pH titrations on ZrP (H - form) are shown in Table (7). The pH titration curve, figure (6) is smooth and indicates monofunctional behaviour, although, since considerable hydrolysis occurred at high pH, no definite interpretation can be made. Amphlett (39), however, has obtained similar curves for gel materials so that qualitative comparisons are possible.

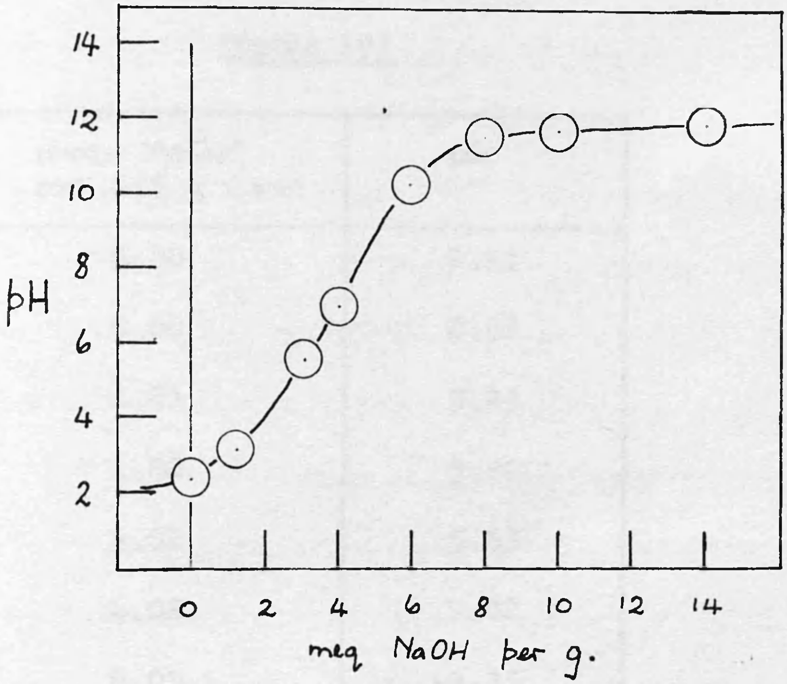


FIGURE 6.

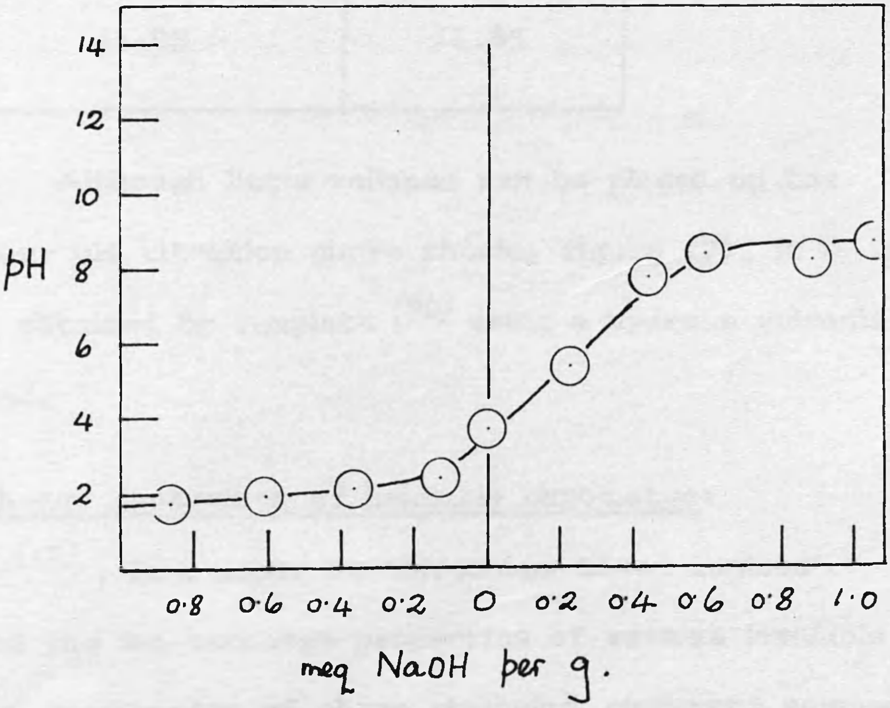


FIGURE 7.

Table (7)

meq. NaOH per 0.5 g ZrP	pH
0.00	2.41
0.60	2.82
1.21	3.23
1.82	3.89
3.02	5.63
4.02	7.02
6.03	10.35
8.04	11.67
14.05	11.85

Thoria: Although little reliance can be placed on the preliminary pH titration curve thoria, figure (7), it is similar to that obtained by Amplett (29) using a hydrous zirconia exchanger.

Ion exchange properties of insoluble chromates:

Bresler (47), in a paper on 'Zirconium based Ionites'. discussed the ion exchange properties of various insoluble zirconium compounds; of these zirconium chromate seemed most interesting. The material described was amorphous and chemically ill-defined, corresponding to those prepared by Montignie(69) and Haber(70). A more suitable material was that described by Briggs(61) which was prepared as described on page 13. This showed a sodium ion capacity of 0.51 meq./g. and had an equilibrium pH of 3, in equilibrium with water, indicating a degree of hydrolysis similar to that of ZrP. The homogeneous crystalline solid obtained by Lungren(62), on further heating of the reaction mixture, showed no hydrolysis and negligible capacity (0.02 meq./g.) for the alkali metal ions. No further study of the compounds was contemplated since Lungren's pure crystalline form showed no exchange properties, while Brigg's material, although showing exchange properties was chemically unsatisfactory.

PART II

DISCUSSION

ZIRCONIA:-

Structure: Hydrous zirconia has been shown to have formulae ranging from ZrO_2, $6H_2O$ for the air dried material to ZrO_2, $1.5H_2O$(71) when dried over phosphorus pentoxide. Dehydration isobars (72)(73) showed, that the aqueous vapour pressure over zirconia fell continuously as the temperature was slowly raised, and dehydration progressed. There were no discontinuities to indicate the presence of hydrated compounds. These results were verified in thermobalance experiments on zirconia, as seen in figure (4, curve iii).

Maximum stability of the zirconium dioxide crystal skeleton is achieved by orbital hybridisation, and since aquo groups could only be bound to surface zirconium atoms through orbitals which remained unoccupied in crystal bonding, their attachment is extremely weak. Larsen and Gammill (74) have shown the presence of $ZrOOH^+$ in solutions of pH 2, which were on the point of precipitation. Since the zirconium content of these solutions was close to 0.02 M, the ionic product was therefore: $ZrOOH^+ \times OH \simeq 2 \times 10^{-14}$

The formation of hydrous zirconia by the addition of ammonia to an aqueous solution of zirconyl chloride appeared therefore to be made up of the following steps:-

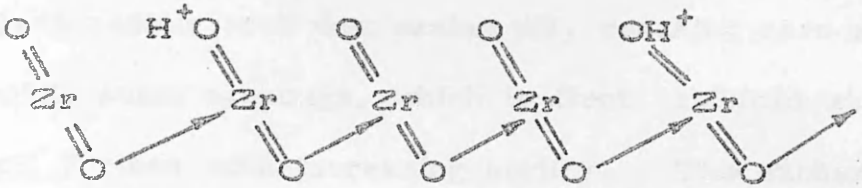
$$ZrOCl_2 + H_2O \rightleftharpoons ZrOOH^+ + H^+ + 2Cl^-$$

$$ZrOOH^+ + OH^- \xrightarrow{2} \left[ZrO(OH)_2\right] \xrightarrow{3} ZrO_2,\ nH_2O.$$

Since step 2 was irreversible, there could be no possibility of digestion of the solid to larger crystals when aged, and the material should therefore be in an amorphous or microcrystalline state. Freundlich (75) in an x-ray study on zirconia observed no crystallinity, and this has been confirmed in the present work. Recently, however, electron diffraction studies have shown that the particles resulting from precipitation are of the order of 0.01 microns in diameter (60), too small to give x-ray diffraction patterns.

Mechanism of ion exchange: The absence of bound water in the structure of zirconia leaves the problem of the mechanism of the observed exchange properties. Blumental (60) suggested that during the formation of hydrous zirconia, individual molecules must coalesce to form micro-crystals.

For precipitation in an acid environment containing the species $ZrOOH^+$ it is reasonable to suppose that a number of these ions will take the place of ZrO_2 as structural units. Therefore, in a one dimensional crystal model we have:



These hydrogen ions can presumably migrate from one oxygen atom to another regardless of its position, resulting in what is in effect a protonated oxide.

We may therefore regard hydrous zirconia, precipitated in acid solution as being a polyelectrolyte cation. Associated with these positive charges will be negative counter ions; in this case chloride ions. Provided the same basic structure is present in the air dried material, we can explain the anionic exchange of zirconia in acid solution as an exchange of negative counter ions. The fact that zirconia is a cation exchanger in alkaline solutions cannot, however, be reconciled with the oxide structure shown above unless the protons of this structure are neutralised and further hydroxyl ions become associated by co-ordination or absorption, giving the matrix an overall negative charge: this possibility was suggested by Kraus (30).

Both Amphlett (29) and Kraus (30) have described the variation in capacity of zirconia with pH. Cation capacity falls rapidly with decreasing pH, reaching zero at pH 9, while anion exchange, which is first exhibited at approximately pH 7 rises with increasing acidity. The exchange capacity is largely suppressed at the isoelectric point, which lies between pH 7 and 9, while the low capacity for both anions and cations in this region indicates a degree of heterogeneity of the exchange sites.

Stability to acids and bases: Zirconia is completely insoluble in alkaline solution as shown by the ionic product: $[ZrOOH^+].[OH^-] = 2 \times 10^{-14}$. In acid solution, however, a tendency for the matrix to dissolve would be expected. This has been shown to be negligibily small from solubility determinations (page 36) in acid solutions and supports the suggestion, that the process of precipitation involves an irreversible step

Loss of capacity: Kraus and Phillips (31), in their early investigations into the exchange properties of zirconia, discovered that exchange capacity was lost when their material was fired at temperatures of 300° or greater. The thermobalance studies of the present work show a continuous loss of water in the temperature range up to 600°.

Russian workers (76) have shown that zirconia may exist in two crystalline states, tetragonal and monoclinic. The former is stable at low and the latter at high temperatures and the temperature of transition is 290°. The conversion of microcrystalline hydrous zirconia for the more compact monoclinic form at 300°, coupled with the probable growth of crystallites at the transition temperature, may account for the loss of exchange capacity observed.

Thoria:

Structure: Investigators agree that Th^{4+} undergoes extensive hydrolysis in solution. Kraus and Holmberg (77), and Hietman (78), have concluded independently that in the later stages of hydrolysis a series of polynuclear complexes are formed containing thorium atoms bonded through oxygen or hydroxyl groups: e.g. $Th\left[(OH)_3\,Th\right]_n^{n+4}$. It would appear that such complexes are chain like although hydrolysis data alone permit no conclusions as to their shape. Dobry, Guinard, and Mathieu - Sicaud (79) have studied colloidal thorium hydroxide by a number of techniques, including electron microscopy, and concluded that the particles were thread-like with a diameter of about 18 Å and an average length of 700°A.

The structure corresponds to bundles of about 30 chains, each made up of some 300 molecules of thorium hydroxide. Chains of the type, $ThOH_2^{2+}$ have been found by Lungren and Sillen (63),(80) in the crystal structures of basic thorium chromate, $Th(OH)_2CrO_4 \cdot H_2O$, and sulphate $Th(OH)_2SO_4$. Both chain models postulated are virtually equivalent, since a dehydration process would yield:

$$Th\left[(OH)_3Th\right]_n^{4+n} \longrightarrow Th\left[(O)(OH)Th\right]_n^{4+n} + nH_2O.$$

Basic thorium chromate, however, was prepared and found to have no exchange properties. This implies, either that the structure of this material is fundamentally different from that of precipitated thorium hydroxide, or more probably that ion exchange is prevented by the compact nature of the single crystals formed. It is therefore assumed that the thoria (thorium hydroxide) exchanger is in fact the ultimate product of the condensations described. Further indication that the exchanger crystallites correspond to the chains described by Dobry et al (79) is shown by the broadening of the diffraction lines in a powder photograph of thoria. This broadening has been attributed to crystal strain or to crystallites of less than 1000 Å (68) and such is very likely to be the case.

We might therefore consider thoria as a polymeric cationic structure, in which electroneutrality is preserved by a number of counterions. The displacement of these ions in acid solution would account, for the observed anion exchange, although the possibility of cation exchange, in alkaline solutions, on this model is more difficult to explain since the fundamental positive charge of the matrix must change to a negative one. Furthermore, Dobry et al (79) have obtained by diallysis a colloidal solution of thorium hydroxide, which is free from adsorbed ions, and is stable in solution for periods of several weeks. This suggests that the thoria matrix is uncharged, corresponding to the molecule, (1) (figure 8). The dehydration isobar obtained in thermobalance studies, (figure 4, curve 1), is similar to those reported by Weiser (81) for $Al_2O_3 \cdot 3H_2O$ and $WO_3 \cdot H_2O$, which have been characterised as hydrous hydroxides, containing both bound and interstitial water. The bound water will therefore be present as hydroxide groups, which may be eliminated as water on heating; figure 8, (2). This elimination may also occur between chains giving the thoria matrix a crosslinked three dimensional structure, possibly conferring the entranced chemical stability of the dried material: figure 8 (3).

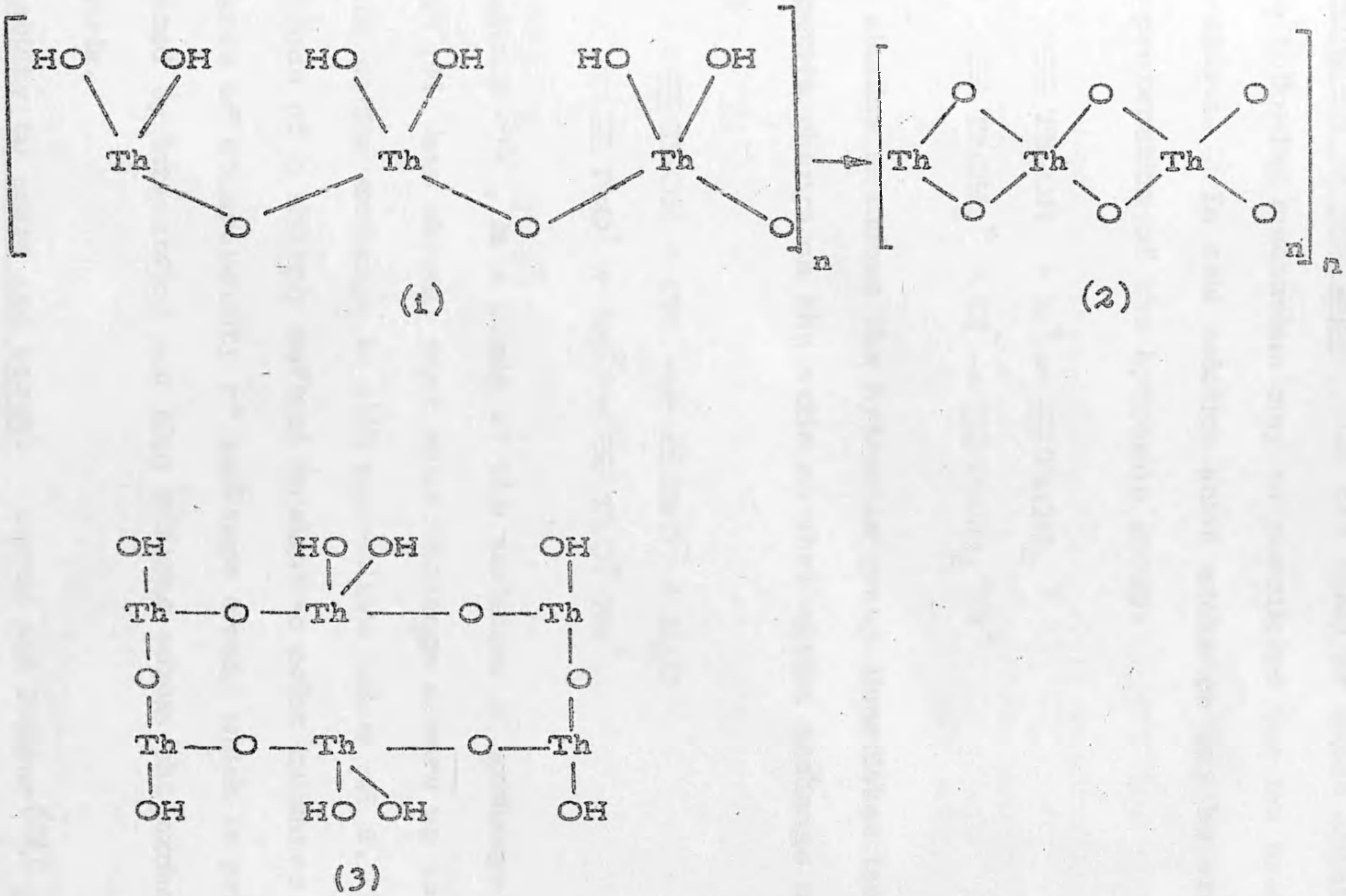


Figure 8.

Mechanism of exchange: On the basis of these hypotheses, the following mechanism may be postulated for ion exchange on thoria. In acid solution anion exchange may be explained by protonation of the hydroxide group:

$$\equiv \mathrm{Th{-}OH} + \mathrm{H}^{+} \longrightarrow \equiv \mathrm{ThOH_2}^{+}$$
$$\equiv \mathrm{ThOH_2}^{+} + \mathrm{Cl}^{-} \longrightarrow \equiv \mathrm{ThOH_2}^{+}\mathrm{Cl}^{-}$$

In alkaline solutions the hydroxide group dissociates leaving a negative charge on the oxide so that cation exchange may occur as:

$$\equiv \mathrm{ThOH} + \mathrm{OH}^{-} \longrightarrow \equiv \mathrm{ThO}^{-} + \mathrm{H_2O}$$
$$\equiv \mathrm{ThO}^{-} + \mathrm{Na}^{+} \longrightarrow \equiv \mathrm{ThO}^{-}\,\mathrm{Na}^{+}.$$

Amplett (39), in a study of the variation of exchange capacity with pH has shown, that anion exchange occurs up to pH 10, while cation exchange is still appreciable below pH 8. The absence of a sharply defined isoelectric point indicates a degree of heterogeneity of exchange sites, which is probably caused by interaction and site effects within the exchanger matrix.

Stability to acids and bases: Gayer and Leider (82) have studied the solubility of freshly precipitated thorium hydroxide in solutions of perchloric acid and sodium hydroxide.

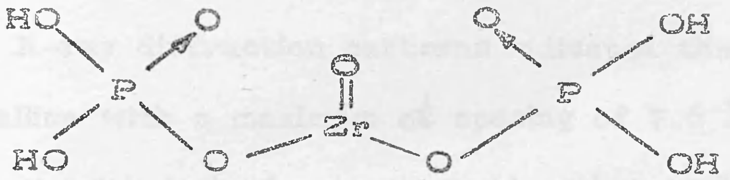
In sodium hydroxide solution above 0.2 M they observed a Th^{4+} concentration of approximately 1 x 10^{-6} M and extrapolation to a solubility in pure water indicate a Th^{4+} concentration of 5 x 10^{-5}M. In perchloric acid, however, the precipitate is very soluble, the solubility increasing linearly from Th^{4+} = O to 0.2 M when the acidity increases to 0.4 M. Solubility of the gel material, which was dried at 50° is much reduced, owing to deswelling and crosslinking of its structure. It is observed, nevertheless, that on prolonged exposure to acid solutions of 0.1 M and above, breakdown of the solid occurs, producing a milky solution. Thoria exchanger may therefore be regarded as a practicable ion exchanger in solutions of pH $\geqslant$ 2.

Zirconium phosphate:

Stability in aqueous solutions: Freshly precipitated zirconium phosphate is soluble in concentrated mineral acid (60). Hevesy and Kimura (83) have shown, however, that the solubility of the dried gel material is only 2 x 10^{-5} M in 10 M HCl and therefore solubility in acidic solutions may be neglected.

In all work with zirconium phosphates, equilibration with distilled water caused a release of hydrogen ions into solution. This could be due only to hydrolysis of phosphate groups or solubility of zirconium phosphate itself. Either would release phosphate and hydrogen ions, but only the latter would release detectable amounts of zirconium. It has been shown that zirconium is absent, so that hydrolysis of the phosphate groups must occur. Larsen and Vissers (84) described a gel material, with a low phosphate to zirconium ratio, and claimed that little hydrolysis occurred in water. Accordingly a modification of the method of Larsen et al. (57) was attempted, in which the phosphate to zirconium ratio in solution was 1 : 1 rather than 2 : 1 as in previous preparations. The product, however, showed similar hydrolysis characteristics to those of ZrP, (Table(5)).

Structure: Analysis of samples of ZrP, Table (4), and of the zirconium phosphates produced by Hevesy and Kimura(83) and Blumental(85) showed a phosphate to zirconium ratio of 2 : 1. Blumental(85),(60) suggested that the most probable formula for such compounds would be:



corresponding to diphosphatozirconic acid. Blumental's model, however, included a water molecule bound to the zirconyl group which, if it existed, could not be strongly co-ordinated, since thermobalance studies on ZrP indicates that the water present is held interstitially.

In acid solutions the exchange properties of ZrP may be explained in terms of acid dissociation and replacement of one hydrogen ion in each phosphate grouping. In alkaline solution, however, phosphate groups were easily hydrolysed from the crystal matrix:

$$ZrO(H_2PO_4)_2 + OH^- = ZrO(OH)H_2PO_4 + H_2PO_4^-$$

This hydrolytic reaction prevented any quantitative study of pH titration data, since alkali was used in the processes of hydrolysis and neutralisation, as well as in ion exchange. Nevertheless, the smooth pseudo-monofunctional titration curve obtained for ZrP, figure 4 was in sharp contrast to the results of Amphlett (39) on gel materials, which showed a number of kinks or discontinuities, indicating a variety of exchange sites.

X-ray diffraction patterns indicated that ZrP was crystalline with a maximum d spacing of 7.6 Å, which was invarient with ionic form, suggesting that exchange may only take place on the surface of the crystallites and would hence cause little or no distortion to the basic crystalline structure of the material. The postulated structure of the ZrP exchanger particles is further discussed in Part IV in terms of capacity and equilibrium data for caesium/hydrogen ion exchange.

PART III

KINETIC STUDIES

A knowledge of the overall reaction rates, and the Kinetic processes from which they are derived, is of fundamental importance in the study of ion exchangers from both practical and theoretical considerations.

Study of the Kinetics of cation exchange dates from the classical work of Way (2)(5) who found the rate of exchange on soil silicates to be quite rapid, and only slightly affected by temperature. Weigner (86) considered the rate of exchange on silicates to be dependent upon the location of exchanging sites, and so ultimately upon the physical characteristics of the exchanger matrix. Although Nachod and Wood (87), Thomas (88), and Juda and Carron (89), have interpreted exchanges in terms of a bimolecular reaction, it is now almost generally accepted that the rates of exchange reactions are governed only by ion transport or diffusion processes. It is interesting, however, to note that this is not always true in exchangers which bind ions by other than pure electrostatic forces. Turse and Rieman (90), for instance, have recently substantiated a chemically controlled rate determining step in the exchange of calcium and sodium ions on the chelating resin, Dowex A - 1.

Boyd, Adamson and Myers (91), have shown that transport processes in exchange reactions could be interpreted in terms of a Nernst film (92),(93),(94) at the surface of the exchanger. According to this theory the bulk of solution was instantaneously mixed by stirring, but close to the solid surface, there was a thin film of immobile solution in which transport could only occur by diffusion. With a stirred suspension of particles the problem is much more complex. Nevertheless, since it is impossible to mix a solution right up to the surface of a solid phase, the complicated hydrodynamics may be represented schematically by considering the solution as a completely mixed volume, and an unstirred static layer of thickness δ. The thickness of this film is usually deduced from Kinetics, and not vice versa. Its dependence upon viscosity, temperature, and stirring is problematical, and so this concept has been of little theoretical importance.

In general, therefore, a cation exchange reaction such as, $Y^+ + XR = YR + X^+$ may be regarded as taking place through a number of steps; (1) film diffusion of Y^+ ions through the solution up to the surface of the exchanger particle, (2) diffusion of Y^+ ions to an exchange site XR within the solid, (3) chemical exchange between Y^+ and XR (4) diffusion of X^+ ions in the solid to the surface, and (5) film diffusion of X^+ ions through the solution away from the particle.

Neglecting the chemical step (3), the rate of reaction may then be controlled by two simultaneous processes; diffusion of ions through the film, and through the exchanger base. Since non steady state conditions apply, diffusion is governed by Fick's second law, in the form, $\partial C_x / \partial t = - D \; (\partial^2 C_x / \partial x^2)$. $\partial C / \partial t$ is the rate of diffusion of the X^+ ions, D is the diffusion coefficient, and $\partial^2 C_x / \partial x^2$ is the rate of change of concentration gradient in the medium. Each diffusing ion will follow this law in both film and exchanger particle, and the problem is further simplified by the fact that solid diffusions are coupled. Diffusion of X^+ ions in one direction is conditional upon diffusion of Y^+ ions in the opposite direction due to the overall maintainence of electroneutrality in both solution and exchanger. Not only are the fluxes of X^+ and Y^+ equal and opposite, but so also are the concentration gradients, $\partial C_X / \partial x$ and $\partial C_Y / \partial x$ A given pair of exchanging ions must therefore share a common diffusion coefficient D_i for particle diffusion. Since concentration changes and movement of co-ions are possible within the film, it is usual to consider the film diffusion coefficients of X^+ and Y^+ ions to be independent, D_{X^+} and D_{Y^+} respectively.

Further simplyfying assumptions are necessary before a more manageable Kinetic expression can be derived. It is assumed that equilibrium is maintained at the resin/solution interface, governed by the usual mass action expression, $K_x^y = \bar{Y}X^+ / \bar{X}Y^+$, where $\bar{Y}$ and $\bar{X}$ refer to concentrations in the exchanger phase. K_X^Y, D_{X^+}, D_{Y^+}, and D_i, and δ are assumed constant throughout the exchange, and conditions must be chosen accordingly.

Methods for studying the Kinetics of rate processes on exchanger particles fall into two categories; limited, and infinite bath techniques. In a limited bath experiment samples of exchanger are reacted with volumes of solution by a batch method, so that during exchange the composition of the solution changes. On the other hand, in infinite bath experiments, shallow beds of exchanger particles are flushed with reacting solution so that the exchanging particle is in contact with a solution of constant composition throughout the exchange. The mathematics of the latter problem are much simpler.

Expressions for the overall Kinetics are very complex, having been derived in only a few selected cases. The most successful appear to be those of Edeskuty and Amundson (95) and Adamson and Grossman (96),(97), for shallow bed diffusion studies. Boyd et al.(91), however, pointed out that in most practical cases either diffusion across a film, or in the exchanger particle would offer negligible resistance, and hence the overall reaction could be classified as predominantly a particle, or a film diffusion mechanism.

Film diffusion: (I). In shallow bed diffusion Boyd et al. expressed transport of ions across the Nernst film by a single diffusion coefficient, D^1. The thickness of the film around the exchanging particles is taken as δ, and it is assumed that chemical equilibrium is maintained at the surface of the particles throughout exchange. Fick's law was applied, and the resultant expression was $(1 - F) = - Rt$, where F = the amount of exchange at time t / the amount of exchange at infinite time. $R = 3D^1/r$ where K is the distribution coefficient of Y^+ ions in the solid, and r_o is the mean radius of the particles. K is taken to be a constant throughout the exchange, and it is usual to maintain the exchanging ion Y^+ as a microcomponent in the system.

A further interpretation of film diffusion in infinite bath experiments, by Adamson and Grossman (96)(97), is more general, including the separate diffusion coefficients D_{X^+} and D_{Y^+}. The final expression of the rate equation is, however, similar to that of Boyd et al. Both treatments show that the rate of an exchange, controlled by film diffusion, is dependent upon the rate of flow and concentration of the external solution, and varies inversely as the radius of the particle size of the exchanger.

II Kressman and Kitchener (98) have developed an expession for film diffusion Kinetics in limited bath experiments. A resin of capacity Q meq. of X^+ ion was allowed to react with a solution containing an equals amount of Y^+ ions. The final expression $(1 - F) = Ct\, Q_0/Q_{co}$, is very similar to that derived by Boyd et al. Q_{co} is the amount of reaction at equilibrium, and $C = D' K'/\delta$; K' is a constant of proportionality.

In I and II therefore, the rate of exchange through film diffusion is proportional to the rate of stirring, the concentration of ions in solution, and inversely proportional to the radius of the resin particle. The dependence of rate upon concentration of exchanging ion is not immediately obvious from the final rate expressions. In their derivation, however, the rate of exchange was calculated from a concentration gradient across the film, and so is dependent upon the concentration of external electrolyte solution.

Particle diffusion: The Kinetics for particle diffusion in an infinite bath have been derived by Boyd et al.(91), where the exchanging ion is present as a microcomponent of the system. The mathematical treatment was based on conduction of heat into a sphere from an infinite source, and the final expression was,

$$F = 1 - 6/\pi^2 \sum_{n=1}^{n=\infty} 1/n^2 \text{ exp. } (-Btn^2)/n^2.$$

$B = \pi^2 Di/r^2$ where Di is the mutual diffusion coefficient of X^+ and Y^+ ions in the exchanger.

The corresponding theory for a limited bath experiment was given by Carslaw and Jaeger (99). Their treatment was, however, less convenient than that of Paterson (100) which expressed the amount of reaction, F in terms of a parameter $\tau = (D_i/r^2)\ t$. The rates of exchange for particle diffusion are therefore independent of solution concentration, and are defined by parameters which vary as $1/r^2$.

Plots of t and Bt against t should therefore be linear and of slope B, provided Di is constant. For particle diffusion in infinite bath studies therefore, the ratio , $B_1/B_2 = r_2^2/r_1^2$ where r_1 and r_2 are the corresponding radii of the particles in each determination.

Chemical Control: When the reaction rate is controlled by a chemical step, the final expression for the Kinetics as the form, $\ln (1 - F) = - St$.

$S = K_1 m_x{+} + K_2 M_Y{+}$, where K_1, and K_2 are the specific rate constants of forward and backward exchange and $M_X{+}$ and $M_Y{+}$ are the concentrations of these ions in solution. The form of this expression is identical with that given by Boyd et al for film diffusion Kinetics S however, differs from the constant R in that it is independent of particle size and of flow (stirring), being dependent only on the concentration of ions in solution, and temperature.

It is therefore possible to distinguish each rate controlling mechanism by observing the changes in rates which occur by varying stirring, flow rates, particle sizes, or the concentration of the exchanging electrolyte.

Investigations on particle diffusion by Helfferich (101)(102)(103)(104) have shown that the flux of moving ions in an exchanger can be expressed in terms of the concentration and an interdiffusion coefficient which depends upon the ratio of concentrations of the exchanging ions. It is a problem of non linear diffusion and has to be solved by numerical integration. Application of this advanced treatment requires the exchanger in the form of solid homogeneous rods, which is at present impossible for inorganic exchangers. The common assumption that D_i is constant throughout exchange must then be regarded as an approximation in all but isotopic exchange. It is, however a useful postulate giving a mean diffusion coefficient for exchange. Furthermore its application provides valid criteria for distinguishing rate controlling mechanisms

In the present studies upon the rates of sodium/hydrogen exchange on thoria and ZrP and Cs^+/K^+ on ZrP, the original theories and especially those of Boyd et al(91) have been tested.

PART III

EXPERIMENTAL

Particle sizes: A knowledge of the ratio of the radii of the particle sizes was necessarly for the interpretation of reaction rates of different sieved fractions. In the first method an optical microscope was used to measure 100 particle diameters of each sample, and the average taken. Since many of the particles were of irregular shape, a second and independent estimate of the relative surface areas of the samples was made using a dye adsorbtion method similar to that of Kolthoff and O'Brien (105).

Weighed samples of the exchanger were equilibrated with solutions of Brilliant Cresyl Blue, having a pK value well outside the pH range encountered. Concentrations of the dye were determined spectrophotometrically on a Hilger Uvispec at 630 mμ, after verifying Beer's Law. The ratio of the effective surface areas of samples in two particle sizes was obtained from the amounts of dye adsorbed.

Exchange Experiments

Limited bath: Sodium/hydrogen ion exchange was studied on thoria, prepared by the method described in Part II, page Conversion of thoria to the hydrogen form was made difficult by its amphoteric properties. Batches were washed in a column with distilled water for prolonged periods, the hydrogen form being produced by a hydrolytic reaction;

A and B were obtained in this way. In addition the hydrogen form of B_2 was made by treating samples with 0.01 M HCl. solutions and washing free from chloride ion with distilled water. A further method was attempted, based upon the exchange reaction between two resins in aqueous suspension, demonstrated by Kressman and Kitchener (98). Samples of thoria, were therefore shaken several days with a mixed bed of the resins Amberlite I.R.A. 400 in the hydroxyl form, and Amberlite I.R. 120 in the hydrogen form. The organic resins, subsequently removed by flotation, were shown to replace quantitatively any ions orginally held by the thoria, and batch B_3 was obtained.

0.1 g. samples of the thoria were added to 30 or 50 ml. portions of 0.01 M NaOH solution, containing 0.01, 0.1, or 1.0 M NaCl, and shaken mechanically in a thermostat at 25°. The procedure was similar to that by Conway et al (106), and the amount of hydroxide used was in each case larger than the ion exchange capacity of the thoria samples. After a given time, the amount of exchange was determined by titrating portions of the supernatant liquid against standard 0.01 M HCl. For periods shorter than about 5 minutes, the technique described by Amphlett et al (39) was used. Reaction was carried out in a sintered - glass funnel which could be connected to suction for rapid removal of solution samples for analysis, or to slight air pressure to prevent drainage.

Rates of exchange at 25° were also followed potentiometrically using the cell

Glass electrode	Solution under study	Sat. KCl	Calomel electrode ,

incorporating a stirrer as shown in figure (5a). E.m.f. measurements were made with a Pye potentiameter and vibron electrometer (E.I.L. model 33 B) as a null detector. Electrode Systems were standardised with 0.05 M potassium hydrogen phthalate, pH = 4.005 (67), B.D. H tabloid buffer pH = 6.99, and 0.05 M sodium borate, Ph 9.18 at 25° (67)

In thoria experiments, the cell incorporated a device for the rapid addition of 0.5 g samples of exchanger, slurried with 5 ml of distilled water, to 145 ml. of sodium hydroxide chloride mixture. Nitrogen was bubbled through the solution during experiments. Since 'Alki' glass electrodes showed small, but reproducible drifts in e.m.f. at the high pH's of these studies, corrections were made from blank experiments.

In the experiments with zirconium phosphate (ZrP), a stronger acid exchanger, 0.5 g samples were added to 145 ml. of carbonate free water in the cell. After an initial rapid fall in e.m.f. due to hydrolysis, the reading became steady. 5 ml. of sodium chloride solution were then added from a fast delivery pippette, giving initial concentrations of 0.01 and 0.1 M. The change in e.m.f. was followed with time. Rates of change of e.m.f.'s for the smaller sized particles were, however, too rapid for manual operation, and were recorded by rapidly photographing both vibron and time scales.

Cs^+/K^+ exchange on ZrP: A number of experiments were made on zirconium phosphate, using a shallow bed method, similar to that described by Boyd et al.

The extent of exchange was determined by counting active solid samples containing Cs^{137}. These were transferred to a planchette, and evenly distributed over the counting area, ensuring constant solid geometry of sources. In a trial experiment, the poorest possible distribution of solid sources resulted in a counting loss of less than 5%. Errors due to varying geometry in properly mounted sources were therefore considered negligible. The β activities were determined by standard counting techniques, using an end window Geiger Muller tube, and an I.D.L. scaler (type 1700). 10^4 counts were made each time, reducing counting errors to

± 1%. Further correction of counting rates for background and coincidence errors were applied, and hence the percentage attainment of equilibrium was calculated. The overall accuracy of the determinations was estimated at ±5%.

A 50 or a 100 mg. sample of ZrP was introduced into the small glass cell of 6 m.m. diameter shown in figure (9), covered at each end with 200 B.S.S. nylon gauze. The cell was connected by a quick fit joint to three reservoirs, any one of which could be selected by three-way taps. After flushing with distilled water to remove air bubbles, the exchanger was conditioned by passing an inactive solution of 5×10^{-5} M CsCl in 0.1 M KCl for three hours. Following this pre-treatment, a solution of the same bulk concentration, but containing Cs^{137} as tracer, was forced through the shallow exchanger bed for a pre-determined time, and immediately washed with water. The zirconium phosphate was then flushed from the cell, filtered, and dried with acetone, before placing on a counting planchette. No activity was removed from the exchanger during these operations. Amounts of Cs^{137} in the solid were then obtained by the standard counting techniques described above.

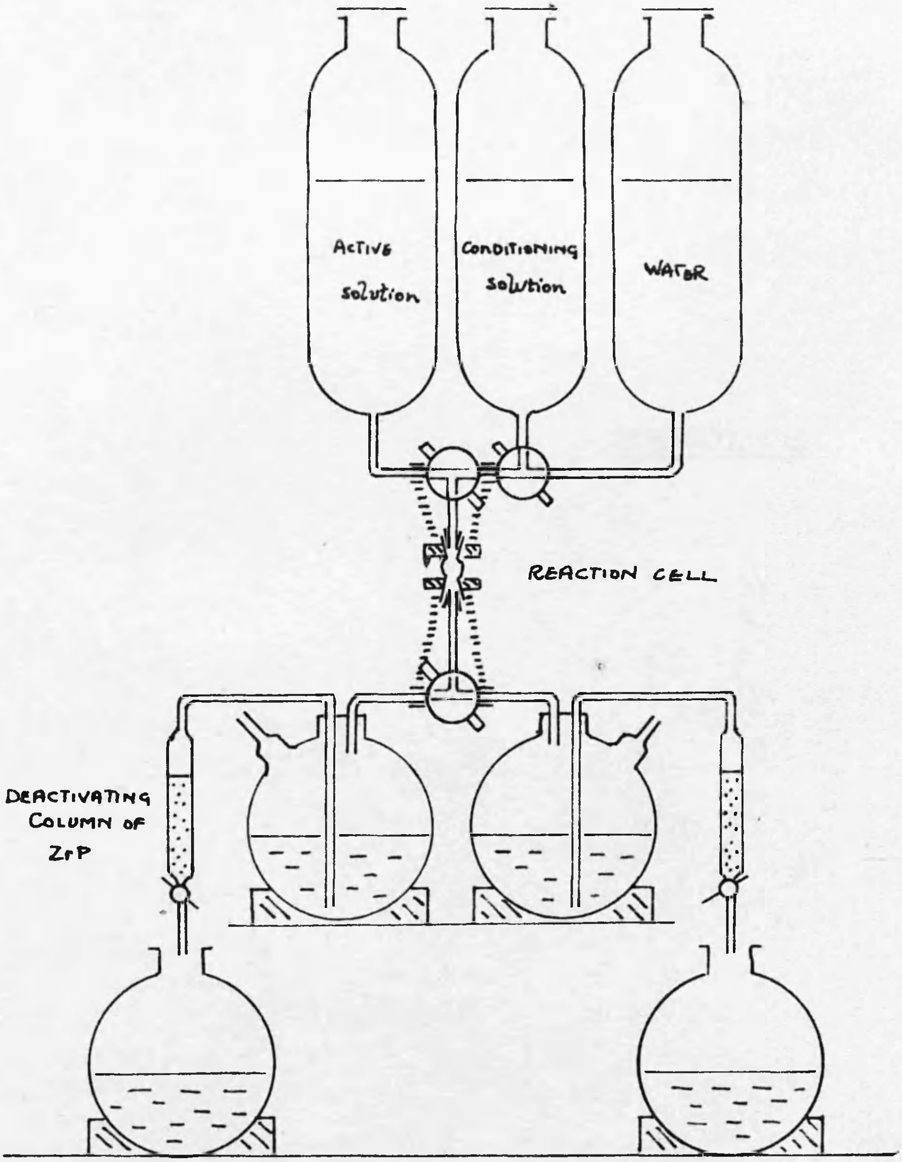

ACTIVE solution
CONDITIONING solution
WATER
REACTION CELL
DEACTIVATING COLUMN OF ZrP

FIGURE 9.

PART III

RESULTS

THORIA.

Sodium/hydrogen exchange: Data for the two particle sizes used in the study of sodium/hydrogen exchange on hydrated thoria are shown in table (8), and figures (10) and (11).

Table (8):

Experiment number	Batch	Sodium chloride (Molar)	Particle size			B (min^{-1})	$D_i \times 10$ cm^2/sec
			Sieve (B.S.S.)	Mean diameter (μ)	Radius from dye (Arbitrary)		
1_T	A	1.00	60-100	250	1.84	0.17	4.4
2_T	A	0.10	60-100	250	1.84	0.17	4.4
5_T	A	0.10	60-100	250	1.84	0.17	4.4
3_T	A	0.10	160-200	134	1.00	0.51	4.9
4_T	A	1.0	160-200	134	1.00	0.51	4.9
14_T	B_1	0.01	60-100	250	1.84	0.58	15.3
12_T	B_1	0.10	60-100	250	1.84	0.58	15.3
15_T	B_2	0.01	60-100	250	1.84	0.58	15.3
11_T	B_3	0.10	60-100	250	1.84	0.12	3.2

Zirconium phosphate.

Sodium/hydrogen exchange: Rates were followed by the e.m.f. method, and the results for two particle sizes 60-100 and 160-200 B.S.S. are summarised in table (9). Plots of F against t are given in figure (12).

Table (9):

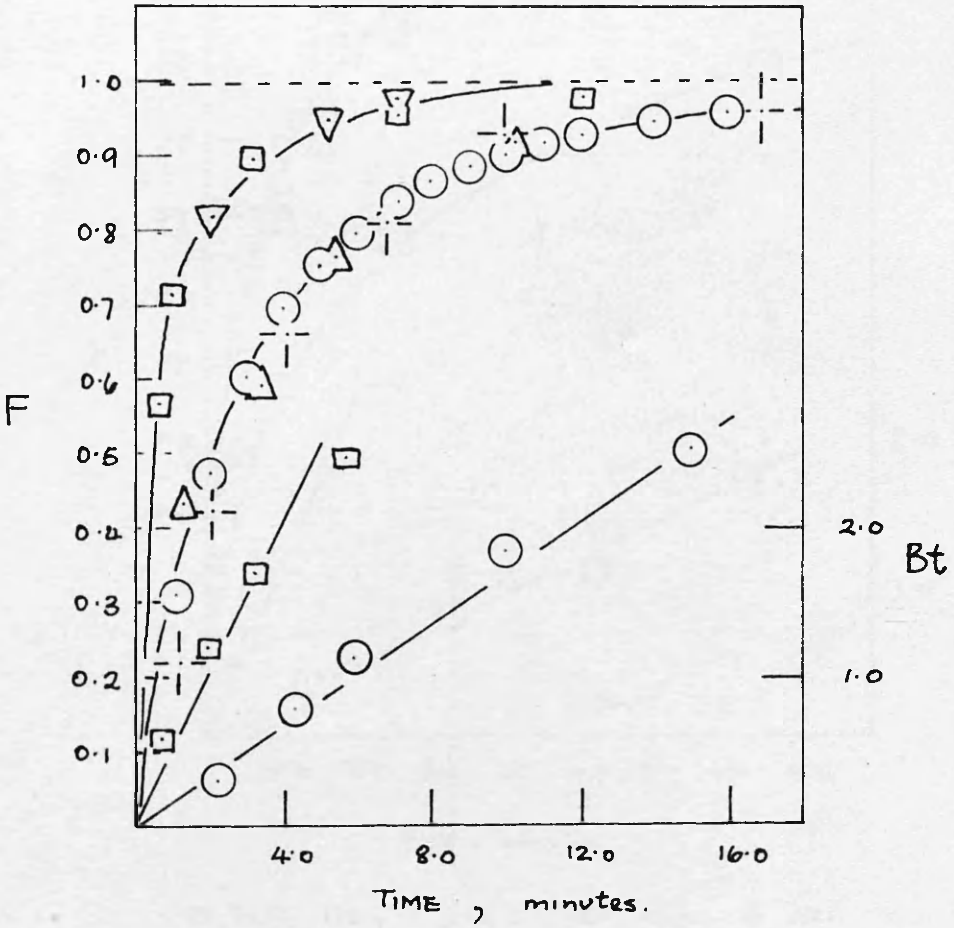
Experiment number	Sodium chloride (Molar)	Particle size			B (min^{-1})
		Sieve (B.S.S.)	Mean diameter (μ)	Radius from dye (Arbitrary)	
17_p	0.01	60-100	360	1.9	2.6
18p	0.10	60-100	360	1.9	2.6
24p	0.10	160-200	119	1.0	6.7
25p	0.01	160-200	119	1.0	6.7

Caesium/potassium: Results of exchange experiments on both particle sizes using infinite bath techniques are given in Table (10) and figure (13).

Table (10):

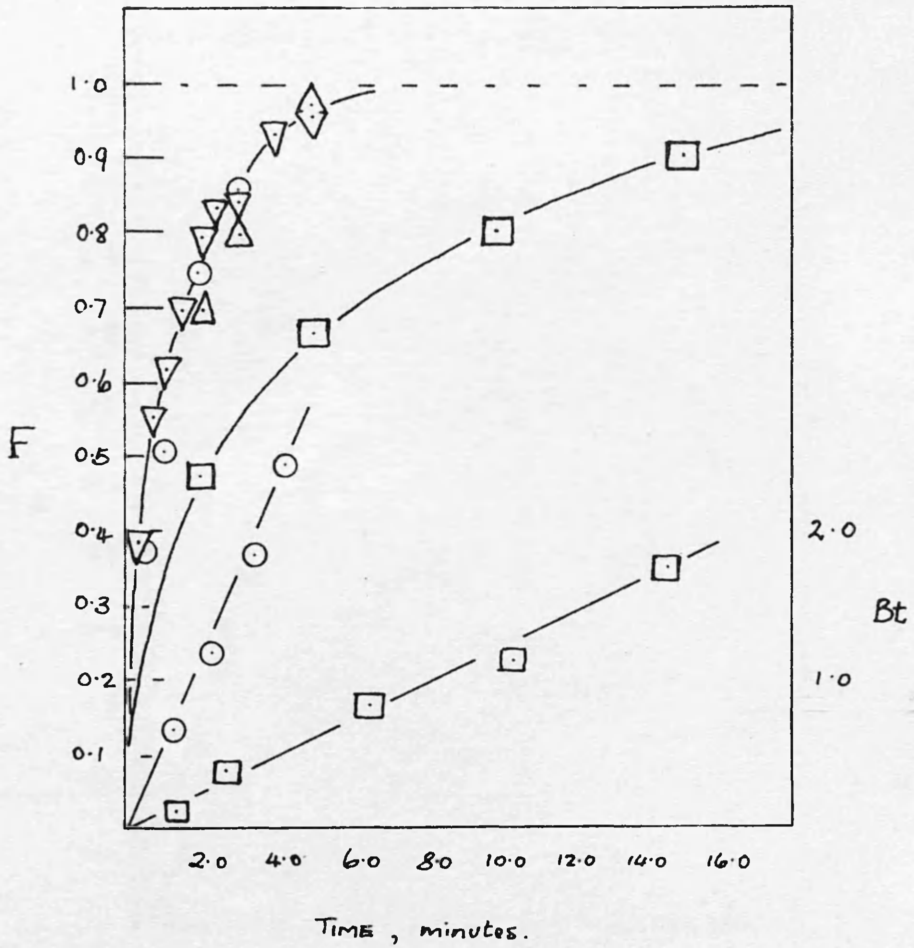
Infinite bath experiments. 5×10^{-5} M Caesium chloride
+ 0.1 M potassium chloride.

Experiment number	Sieve (B.S.S.)	Mean diameter (μ)	Radius from dye (Arbitrary)	B x 10^2 (min^{-1})
27	60-100	360	1.9	1.8
28	160-200	119	1.0	7.5



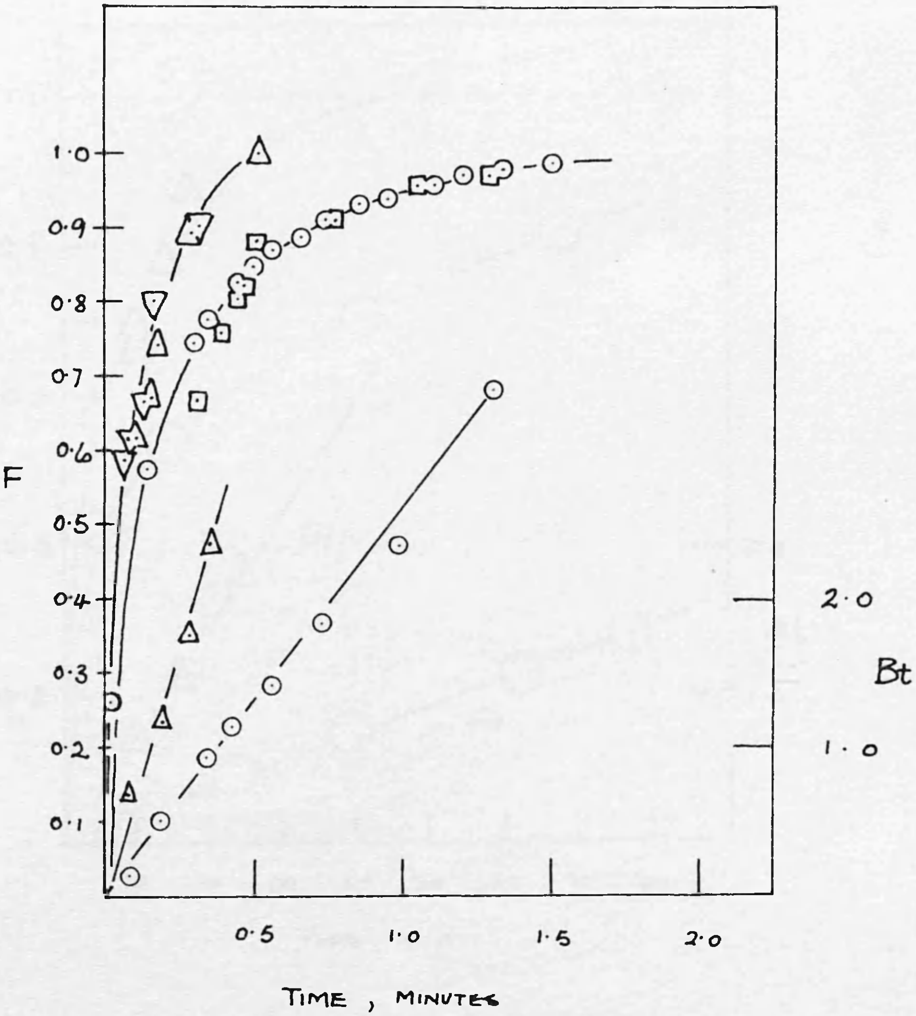
⊙ Expt. 5p ; △, 1T ; -¦- , 2T ; ⊡, 3T ; ▽, 4T.

FIGURE 10.



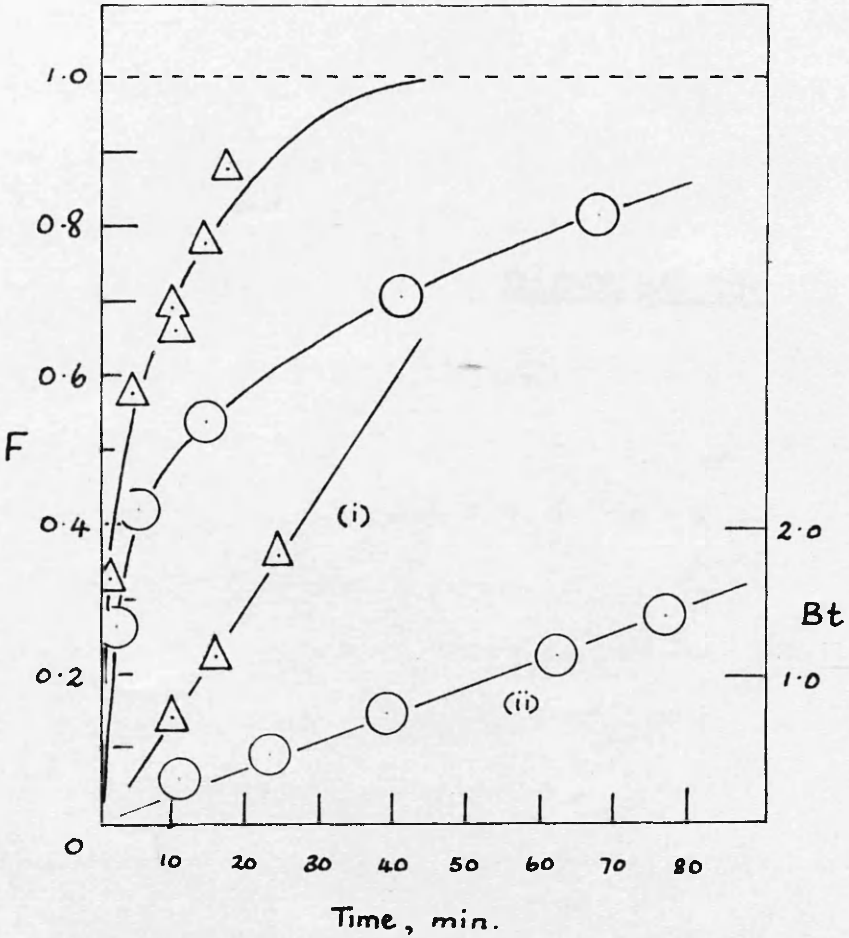
⊡, Expt. 11t; ·, 14t; ▽, 15p; △, 12t.

FIGURE 11.



⊡ , expt. 18 p ; ⊙, expt. 17 p ; △, expt. 25 p ; ▽, expt. 24 p.

FIGURE 12



○, expt. 27 ; △, expt. 28.

FIGURE 13.

PART III

DISCUSSION

THORIA:

Within experimental error, B_1 and B_2 showed the same exchange rates for sodium/hydrogen exchange, while B_3, prepared by equilibrating with organic resins, appeared to be considerably slower. On washing B_3 with acid, however, a rate approaching that for B_1 and B_2 was obtained. This is not easy to explain, but it may be due partly to absorption of organic material on the surface of the exchanger particles, although the concentration must be very small.

Good agreement is shown between titration and e.m.f. experiments, shown in figures (10) and (11). From these it is observed that rates of exchange are, within experimental error, independent of sodium ion concentration between 0.01 M and 1.0 M, and markedly dependent upon particle size. Furthermore, rotatory stirring in potentiometric, and mechanical shaking in titration experiments were without effect on the rate of exchange, pointing to particle diffusion as the rate determining mechanism. In analogous experiments, Conway, Reichenberg and Green(106) successfully applied the particle diffusion theory of Boyd et al.(91), describing diffusion into spherical particles of radius r, by the expression

$$F = 1 - 6/\pi^2 \sum_{n=1}^{n=\infty} \exp.(-n^2 Bt) / n^2 \qquad (1)$$

$$\text{where} \quad B = \pi^2 D_i / r^2 \qquad (2)$$

The main criterion of infinite bath conditions, for which equation (1) is strictly applicable is that the ionic composition of the surface of the exchanger should remain constant during the Kinetic experiment.(107) In this series of investigations, these conditions prevail, since the hydrogen ions emerging from the exchanger are neutralised by excess hydroxyl ions. Exchanger surface may then be considered saturated with sodium ions throughout the exchange process. The theory of Boyd, Adamson, and Myers was therefore applied.

Since F was a calculable function of Bt, as shown in equation (1), it was most convenient to obtain Bt for each value of F from Reichenberg's tables(108), and to plot this against experimental time. These curves included in figures (10) and (11) are linear, indicating that B is a constant for each particle size. From equation (2) it follows that Di is also independent of F.

The mean radius of the particles measured optically, was 134 μ for the smaller, and 250 μ for the larger sized fractions. The ratio of the squares of the radii is therefore 3.48, which agrees within experimental error with the inverse ratio of the respective B values as required by equation (2). Since many of the particles were irregular, dye absorption measurements provided an independent value of the ratio of surface areas. Assuming the particles to be spherical, the ratio of the squares of the radii was 3.2 ± 0.2, again in good agreement. Within experimental error therefore, the proportionality of B to r^{-2} is confirmed, and the effective diffusion coefficient may be calculated. Values are given in table (8). It is seen that D_i for B is greater than that for A, reflecting the difficulty of reproducing samples of thoria exchanger.

Effective diffusion coefficients of 4 to 15 x 10^{-8} cm^2/sec for Na^+/H^+ exchange on thoria may be compared with values from 10^{-6} to 10^{-5} cm^2/sec for sulphonic acid resins, and 4 x 10^{-9} cm^2/sec for the weak acid exchanger Amberlite IRC 50. It may be observed, therefore, that the effective diffusion coefficients of organic resin exchangers with comparable crosslinking decrease with falling strength of the acid exchange group. Conway, Reichenberg, and Green (106) have shown that this is due to incomplete dissociation of the hydrogen form, allowing fewer free hydrogen ions in the solid phase, and so reducing the effective concentration gradients. In such a classification, therefore, we may consider that thoria, in cation exchange, behaves as a weak acid exchanger, probably somewhat stronger than the carboxylic resins.

Zirconium phosphate:

Sodium/hydrogen exchange: The rate of exchange, is again independent of stirring, and of concentration of Na^+ ions between 0.01 and 0.10 M. It is therefore probable that the rate controlling mechanism is particle diffusion. Time plots of Bt in figure (12) agree very well at each ionic strength, the good linearity implying a constant effective diffusion coefficient over a range composition.

Although this theory is strictly for infinite bath experiments, its use in the present case is justified by the small change in external solution concentration (~ 10%) coupled with the high selectivity of zirconium phosphate for alkali metal ions.(109) Both effects tend to maintain surface exchange groups saturated with sodium ions. Furthermore, the implied constancy of D_i may be due to the similarity of the co-spheres of Na^+ and H^+ ions suggested by Gurney(110) in terms of viscosity measurements in electrolyte solutions. In support of this Soldano and Boyd(111) have also shown that self diffusion coefficients for sodium ions varied by only about 6% over a range of hydrogen ion compositions from 0 to 93%.

Caesium/potassium exchange: In this case an infinite bath technique was employed. Time plots of F and Bt are given in figure (13). The latter show good linearity and provide further evidence that particle diffusion is the rate controlling mechanism. Particle sizes, determined microscopically, are given in table (10). The ratio of the squares of the apparent radii, 9, differs widely from the inverse ratio of the B values, which for Cs^+/K^+ is 4 and for Na^+/H^+, approximately 2.5.

Each particle of exchanger produced by compression consists of a conglomeration of fine particles, the channels between which provide easy access to exchange sites. It is to be expected therefore, that the rates of exchange interpreted on the basis of solid diffusion will be relatively faster in the larger sized particles. Dye absorption measurements, therefore, were made to obtain a more realistic ratio of surface areas. Assuming spherical particles, the ratio of the squares of the radii became 3.6 in very good agreement with the inverse ratio of B values for Cs^+/K^+ exchange. Poor agreement with the Na^+/H^+ value is probably due to the uncertainty in B for the smaller sized fraction, in which the rate of exchange was very fast.

PART IV

EQUILIBRIUM STUDIES

Investigations by Amphlett(89), Krans(80), Gal and Gal(69), and Larsen and Vissers(109), have shown that the selectivity of zirconium phosphate for the alkali metal ions is: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. This is the same order as for polystyrene sulphonic acid resins(112). Cs^+ ion was chosen for equilibration studies in the hope that a deeper understanding of its exceptional affinity might be obtained. Since the studies on the hydrolysis of zirconium phosphate in aqueous solution, described in Part II, have shown it to be chemically stable in solutions of pH 3, Cs^+/H^+ exchange was chosen. In equilibrium studies on hydrous zirconia interest was centred upon exchange of anions, which occurred at low pH. Systems of monovalent and divalent ions were studied at constant ionic strength of 0.1 and 0.3 respectively. Amphlett(29) and Krans(80) showed anion capacity to be a function of pH, and hence in all determinations a hydrogen ion concentration was maintained, which was consistent with no cation exchange.

For comparison of equilibrium data, thermodynamic equilibrium constants were required. In their derivation it is usual to consider the exchange; $B^+ + AR \rightleftharpoons BR + A^+$, as a bimolecular reversible reaction. A^+, B^+; AR and BR being exchanging ions in solution and solid phases respectively, and

R referring to the univalent functional group of the ion exchanger. The thermodynamic constant K for this reaction is: $K = N_B\ m_A\ \gamma_A\ f_B / N_A\ m_B\ \gamma_B\ f_A$. N and m define concentrations in the solid and solution phases; γ_A, and γ_B are activity coefficients of the single ions in solution; while f_A, f_B refer to AR and BR in the exchanger. This approach combined with the use of the Gibbs Duhem equation was introduced independently by Ekedal, Hogfeldt and Sillen(113), and Argersinger, Davidson and Bonner(114). In the first investigations water activity and its variations were neglected. This problem was later treated by Hogfeldt(115), Gaines and Thomas(116) and Davidson and Argersinger.(117) Holm(118), in an excellent review article drew a comparison between these last three treatments, which will be numbered I, II and III respectively and are summarised in table (11).

<u>Table (11):</u>

Treatment	Components of the exchanger	Activity Coeff. of AR	$f_{AR} = 1$ at a solution concentration
I	AR, BR, H_2O	f^{I}_{AR}	molality of exchange
II	AR, BR, H_2O	f^{II}_{AR}	infinite dilution
III	$AR_{n_AH_2O}$ $BR_{n_BH_2O}$	$f^{III}_{AR_{n_AH_2O}}$	molality of exchange

The ion exchange equilibrium is formulated according to the various treatments: $B^+ + AR \rightleftharpoons BR + A^+$, in I and II, and $B^+ + AR_{n_AH_2O} \rightleftharpoons BR_{n_BH_2O} + A^+ + (n_A - n_B)H_2O$, in III. Owing to the different definitions of reference states, the values of f^{I}_{AR} are not comparable. $f^{III}_{AR_{n_AH_2O}}$ is less general than either f^{I}_{AR} or f^{II}_{AR}, since the choice of components rests on the assumption that the water sorption in an exchanger of given crosslinking saturated with two univalent ions is a linear function of the equivalent fraction of one of these ions. This relation for water content, $n_w = n_A + (n_B - n_A) N_B$ has been found experimentally only for NH_4^+/H^+(119) and Na^+/Cs^+(120) exchange on polystyrene sulphonic acid resins. The treatment II, of Gaines and Thomas(116) was therefore considered most useful, since it resulted in activity coefficients in the ion exchanger phase, which were independent of concentration of external solution. Pressure dependence of activity coefficients is common to all three methods, while both the pressure and composition (for III also the components n_A and n_B) of the reference states are changed by change in cross-linking. The activity coefficients of ions in solution, which enter equilibrium expressions are those of the single ions. They are not determinable separately, but only in the ratios in which they enter ionic compounds.

For an electrolyte dissociating in $\nu+$ cations and $\nu-$ anions, we may write a mean activity coefficient, $\gamma\pm$:

$\gamma\pm = \gamma_{+}^{\nu+} . \gamma_{-}^{\nu-}$, where $\nu = \nu+ + \nu-$,

$z+ . \nu+ = z- \nu-$ and $z+$ and $z-$ are the valencies of the ions. For two electrolytes AX and BX with a common ion X, the ratio of single ion activity coefficients reduces to:

$$\gamma_{B}^{z_A} / \gamma_{A}^{z_B} = \gamma_{BX}^{z_A} / \gamma_{AX}^{z_B} \, (\gamma_{BX} / \gamma_{AX})^{z_A \, z_B / z_X}$$

This becomes $\gamma_{B} / \gamma_{A} = (\gamma_{BX} / \gamma_{AX})^{2}$,

and $\gamma_{B} / \gamma_{A} = (\gamma_{BX} / \gamma_{AX})^{3}$ for 1:1, and 2:2 electrolytes respectively.

The treatment of Gaines and Thomas(116) was used to obtain equilibrium constants in the exchange systems, and the derivation is given below. The model used, considered the cation exchanger to have a fixed number of exchange sites per unit mass, capable of absorbing solvent, and incapable of absorbing anions. Symbols are given in table (2). For the exchange reaction $Z_a B^{I} + Z A^{II} \quad Z A^{I} + Z_a B^{II}$ in a closed system, the conditions of equilibrium are:

Constancy of energy, $\delta E^{I} + \delta E^{II} + \delta E^{III} = 0$,

" " A, $\delta n_a + \delta m_a = 0$,

" " B, $\delta n_b + \delta m_b = 0$,

electroneutrality, $Z_a \delta m_a + Z_b \delta m_b = 0$,

Constancy of solvent, $\delta n_s + \delta m_s + \delta \ell_s = 0$,

Table (12)

Phase$^{\mathrm{I}}$ exchanger	Phase$^{\mathrm{II}}$ external solution.	Phase$^{\mathrm{III}}$ solvent vapour.	
A^+ B^+ solvent(s)	A^+ B^+ solvent(s)	Solvent(s)	Components
μ'_A, μ'_B, μ'_s	μ''_A, μ''_B, μ''_S	μ'''_S	Chemical potentials
N (mole fraction)	M (molality)	–	concentration
n	m	l	moles of species
f_a, f_b (of components)	γ_a γ_b (of single ions)	–	activity coefficients
E^{I}	E^{II}	E^{III}	Energy terms

These include the term of constant exchange capacity $z_a \delta n_a + z_b \delta n_b = 0$. Applying the Gibbs theory to the equilibrium, we have

$$z_b \mu_a' - z_a \mu_b' = z_b \mu_a'' + z_a \mu_b'' \quad (1)$$

and $\mu_s' = \mu_s'' = \mu_s'''$

The chemical potentials μ_a' and μ_a'' may be written:

$$\mu_a' = \mu_a^{0\prime} + RT \ln N_a f_a \quad (2)$$

and $$\mu_a'' = \mu_a^{0} + RT \ln M_a \gamma_a \quad (3)$$

in which $\mu_a^{0\prime}$ and $\mu_a^{0\prime\prime}$ are the respective chemical potentials in the reference states, and

$$N_a = z_a n_a / (z_a n_a + z_b n_b) \quad (4).$$

The equilibrium constant for the reaction, K, is from equation (1);

$$K = N_a^{z_b} . M_b^{z_a} . \gamma_b^{z_a} . f_a^{z_b} / N_b^{z_a} . M_a^{z_b} . \gamma_a^{z_b} . f_b^{z_a}$$
$$= \exp. (z_a \mu_b^{\prime 0} - z_b \mu_a^{0\prime} + z_b \mu_a^{0\prime\prime} - z_a \mu_b^{0\prime\prime}) / RT.$$

The application of the Gibbs, Duhem equation to the exchanger phase enables the determination of activity coefficients in the exchanger phase and the calculation of K.

$$n_a \, d\mu_a' + n_b \, d\mu_b' + n_s' \, d\mu_s' = 0 \quad (5),$$

where $n_s' = n_s (z_a n_a + z_b n_b)$ and n_s is the solvent content of one exchange equivalent.

From equations (4) and (5)

$$N_a \, d\mu_a' / z_a + N_b \, d\mu_b' / z_b + n_s \, d\mu_s' = 0,$$

and so from (2) and (3),

$$N_a \, d\ln(f_a N_a/z_a) + N_b \, d\ln(f_b N_b/z_b) + n_s \, d\ln a_s = 0$$

and so,

$$N_a \, d\ln(N_a f_a)^{z_b} + N_b \, d\ln(N_b f_b)^{z_a} + z_a z_b n_s \, d\ln a_s \qquad (6)$$

Reference states must now be defined for the various components in order to allow integration of (6). The solvent reference states are chosen so that the activity of water in each phase is the same, i.e. for $\mu_s'' = \mu_s^{o''}$, $a_s'' = 1$, and $\mu_s^{o'} = \mu_s^{o''} = \mu_s^{o'''}$. Solid phase reference states are chosen as the mono-ion solid in equilibrium with an infinitely dilute solution of that ion, i.e., for $N_a = 1$, and $a_s = 1$, $f_a = 1$, etc. In the solution phase normal standard states are chosen, making a → m, as m → 0.

Kc, the selectivity coefficient, is defined by:-

$$\ln K = \ln K_c + \ln f_a^{z_b} - \ln f_b^{z_a}, \qquad (7)$$

and on differentiating,

$$d\ln K_c + d\ln f_a^{z_b} - d\ln f_b^{z_a} = 0 \qquad (8)$$

f_a and f_b are evaluated from (6) and (7) using the mathematical relation, $d\ln x/dx = 1/x$ So that;

$$z_b N_a \, d\ln N_a = z_b \, dN_a = -z_b \, dN_b$$
$$= z_b \, N_b \, d\ln N_b$$

i.e.

$$z_b N_a \, d\ln N_a + z_b N_b \, d\ln N_b = 0 \qquad (9).$$

The expansion of (6) is:

$$N_a z_b \, d\ln N_a + N_a z_b \, d\ln f_a + N_b z_a \, d\ln N_b + N_b z_a \, d\ln f_b + z_a z_b n_s \, d\ln a_s = 0 \qquad (6^1)$$

After subtraction of (6^1) and (9), and rearrangement,

$$-N_b \, d\ln f_b^{z_a} = (z_a - z_b)\, d\ln N_b + N_a \, d\ln f_a^{z_b} + z_a z_b n_s \, d\ln a_s \qquad (10).$$

Substitution of (10) into (8) gives,

$$d\ln K_c + d\ln f_a^{z_b}(1 + N_a/N_b) + (z_a - z_b)\, dN_b/N_b + z_a z_b n_s \, d\ln a_s / N_b = 0 \qquad (11$$

i.e. $d\ln f_a^{z_b} = -N_b \, d\ln K_c - (z_a - z_b)\, dN_b - z_a z_b n_s \, d\ln a_s$

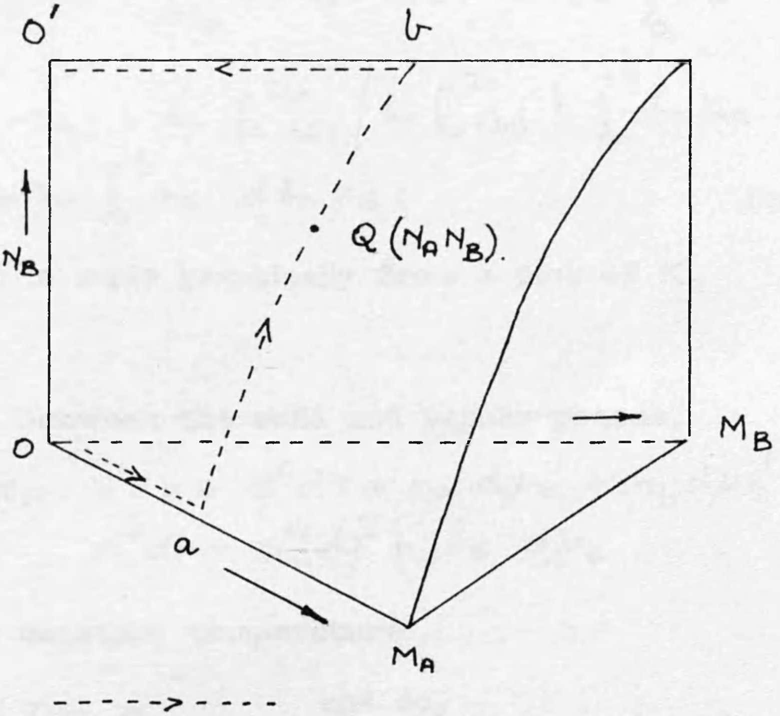
Integration of equation (10) is performed from pure A resin ($N_b = 0$), to $N_b = N_b$, noting that when $f_a = 0$, $N_a = 1$ and $N_b = 0$.

Since it is conducted on point functions of position on the isothermal surface, figure (14), the path between standard states may be chosen at convenience. Usually an isothermal line on this surface is measured at constant total molality in the solution, and is therefore conveniently taken as the curve a Q b . Integration of (11) along a Q b gives,

$$\left[\ln f_a^{z_b}\right]_a^Q = \int_{N_b=0}^{N_b} -N_b \, d\ln K_c - \int_{N_b=0}^{N_b} (z_a - z_b)\, dN_b - z_a z_b \int_a^Q n_s \, d\ln a_s .$$

i.e.

$$\ln f_{a(Q)}^{z_b} / \ln f_{a(a)}^{z_b} = -(z_a - z_b) N_b - N_b \ln K_c(Q) + \int_0^{N_b} \ln K_c \, dN_b - z_a z_b \int_a^Q n_s \, d\ln a_s .$$



PATH OF INTEGRATION ACROSS THE ISOTHERMAL SURFACE.

FIGURE 14

and similarly,

$$\ln f_{b}^{z_a}(a) \Big/ \ln f_{b(a)}^{z_a} = (z_a - z_b) N_a + N_a \ln K_c(a)$$

$$- \int_{N_b}^{1} \ln K_c \, dN_b + z_a z_b \int_{a}^{b} n_s \, d\ln a_s .$$

Hence we find,

$$\ln K = (z_b - z_a) + \ln f_{a\,(a)}^{z_b} \Big/ \ln f_{b\,(b)}^{z_a} + \int_0^1 \ln K_c \, dN_b$$

$$- z_a z_b \int_a^b n_s \, d\ln a_s . \qquad (7a)$$

The integration is made graphically from a plot of K_c against N_b.

For equilibrium between the solid and vapour phases,

dG = 0 so that, $V' dp = S' dT + n_a d\mu_a' + n_b d\mu_b' + n_s d\mu_s'$

and $V''' dp = S''' dT + l_s d\mu_s$

For pure A at constant temperature

$$d\mu_b' = dT = 0 \quad \text{and so,}$$

$$V' dp = n_a d\mu_a' + n_s d\mu_s \qquad (12)$$

and $V''' dp = l_s d\mu_s$ (13)

Combining (12) and (13),

$$(l_s V'/V''' - n_s) \, d\mu_s = n_a \, d\mu_a'$$

so that

$$RT (l_s V'/V''' - n_s) \, d\ln a_s = n_a RT \, d\ln N_a f_a .$$

Since $Z_a n_a = N_a$,

$$z_a (V'/\tau - n_s) \, d\ln a_s = N_a \, d\ln N_a f_a$$

Where l_s / V''' = τ the molar volume of pure vapour.

But Na = 1 so that,

$$z_a \left(V^1/\tau - n_s \right) d\ln a_s = d\ln f_a ,$$

On integration from $a_s = 1$ to $a_s = a$ we have,

$$\ln f_{a(a)}^{z_b} = z_a z_b \int_{a_s=1}^{a_s=a} \left(V^1/\tau - n_s \right) . \, d\ln a_s . \qquad (14).$$

Since V^1 is the molar volume of pure A resinate, V^1/τ is negligible compared with n_s and so equation (7a) becomes

$$\ln K = (z_b - z_a) + \int_0^1 \ln K_c \, dN_b - z_a z_b \left[\int_{a_s=1}^{a_s=a} n_s \, d\ln a_s - \int_{a_s=1}^{a_s=b} n_s \, d\ln a_s + \int_{a_s=a}^{a_s=b} n_s \, d\ln a_s \right].$$

For dilute solutions of symmetrical electrolytes $\ln a_s$ is almost independent of the mole fraction of the individual cations and so the term in the square brackets is zero.

$$\therefore \quad \ln K = (z_b - z_a) + \int_0^1 \ln K_c \, dN_b - z_a z_b (n_{s_a} - n_{s_b}) \qquad (15)$$

where n_{s_a} and n_{s_b} are the number of moles of water per equivalent of A and B resinates respectively. As is the mean solvent activity of the external electrolyte, and therefore for a univalent exchange equation (15) reduces to:

$$\ln K = \int_0^1 \ln K_c \, dN_b + (n_{s_b} - n_{s_a}) \ln a_s \qquad (16)$$

PART IV

EXPERIMENTAL

Caesium/hydrogen exchange on zirconium phosphate.

Equilibrations were carried out, using mixed solutions of HCl and CsCl, traced with Cs^{137}, at a total ionic strength of 0.1 M.

Analysis of Caesium: To measure the β activity of Cs^+ samples in solution, it was convenient to use a liquid immersion counter rather than to evaporate an aliquot and count as a solid. In counting with radioactive liquids the greatest losses occur by self absorption in the liquid itself: a few cm. of water are sufficient to absorb even very energetic β particles. In consequence, the absolute efficiency with liquid sources is small. Comparative measurements could, however, be made under similar conditions. To this end the thickness of liquid surrounding the counter should either be kept constant by a rigid annular sheath attached to the counter or should be sufficiently thick to be regarded as infinite. Similarly the depth of immersion should be constant. The activities of solution, however, are only strictly comparable when they are of the same density and hence of the same absorptive power for β particles.

In the determination of the caesium content of mixed caesium and hydrogen chloride solutions, at an ionic strength of 0.1 M, the β activity of the Cs^{137} was measured with an immersion Geiger-Muller counter. The liquid sample was contained in a rigid sheath around the counting tube as shown in figure (15). In order to reproduce the geometry of the sources 5 ml. samples were pipetted into the counter. The activities of stock dilutions, when corrected for coincidence and background errors, were plotted against caesium content. The curve obtained, figure (16), deviated only slightly from linearity probably due to the large counting losses incurred and to density changes of the solutions. Figure (16) gave a direct conversion of the corrected β activities into $[Cs^+]$ content. Activities were measured to 10^5 counts, reducing the counting error to ± 0.3%, page , and the overall error in the determination of caesium to approximately ± 0.5%. After each experiment, the counting tube was rinsed with distilled water and dried with acetone. Background counts on a 5 ml. sample of distilled water taken before and after a series of measurements remained constant, indicative that no Cs^{137} was absorbed on the glass walls of the counting tube.

Analysis of Hydrogen ion: HCl solutions were determined, using sodium hydroxide solution, which was prepared, and standardised by the method described on page .

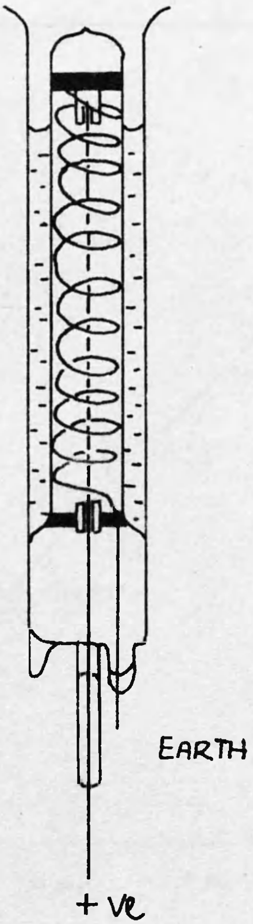


FIGURE 15

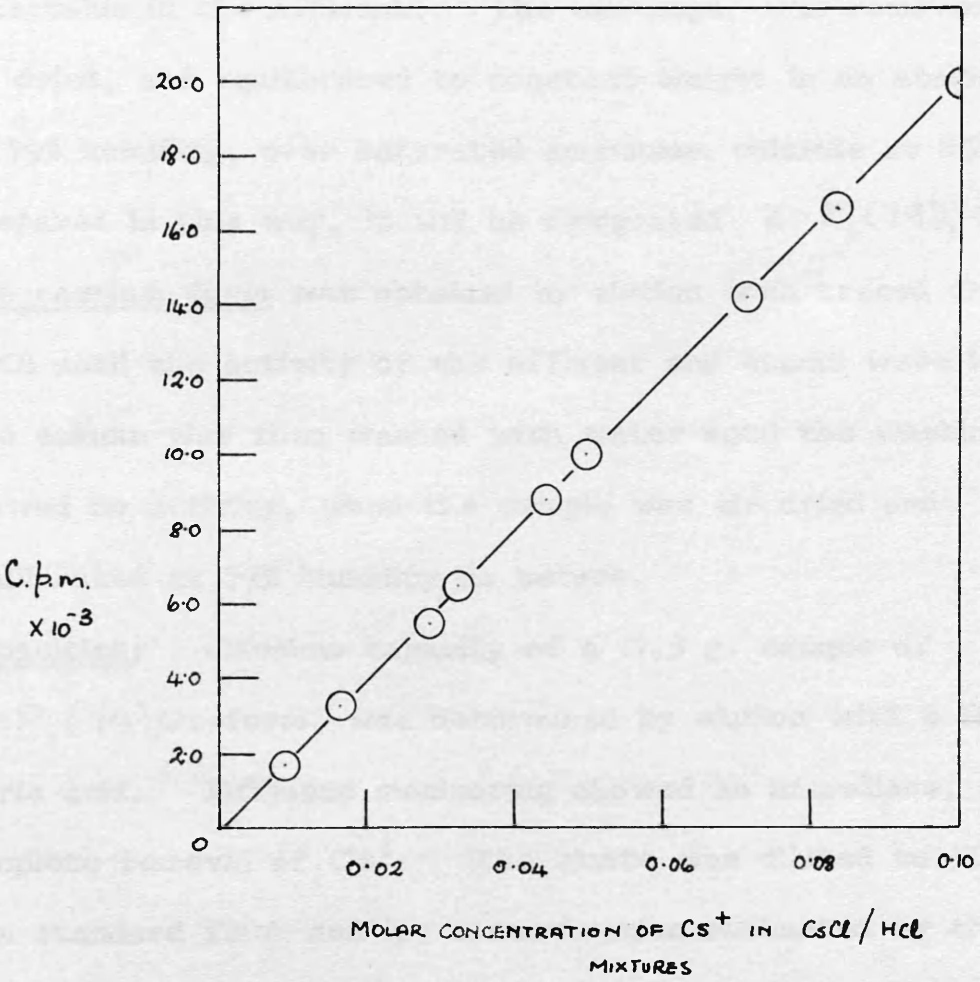

20·0
18·0
16·0
14·0
12·0
10·0
8·0
6·0
4·0
2·0
0
C.p.m. x 10^{-3}
0·02
0·04
0·06
0·08
0·10
MOLAR CONCENTRATION OF Cs^+ IN CsCl / HCl MIXTURES

FIGURE 16.

Ionic forms of zirconium phosphate:

The hydrogen form was obtained by elution with 0.1 M HCl and washing with distilled water until no chloride ion was detectable in the effluent. The exchanger was removed, air dried, and equilibrated to constant weight in an atmosphere of 79% humidity, over saturated ammonium chloride at 25°. Prepared in this way, it will be designated $ZrP_1(79)_1$ H-form.

The caesium form was obtained by elution with traced 0.1 M. CsCl until the activity of the effluent and eluant were identical. The column was then washed with water until the washings showed no activity, when the sample was air dried and equilibrated at 79% humidity as before.

Capacities: Caesium capacity of a 0.5 g. sample of $ZrP_1(79)$Cs-form, was determined by elution with 6 M nitric acid. Effluent monitoring showed an immediate, and complete removal of Cs^+. The eluate was diluted to 50 ml. in a standard flask and its concentration estimated by the standard counting technique.

The capacity of a sample of ZrP (79) H - form was determined similarly, after first converting to the caesium form.

To determine possible anion capacity, ZrP, (79), H-form, was eluted with 0.1 M. nitric acid and the total eluate analysed for chloride ion, which was shown to be absent.

Displacement Studies: 1 g samples of Z P (79), H-form were placed in density bottles and their displacements measured at 25°, in water, n - heptane and carbontetrachloride.

Exchange experiment: Stock solutions of O.1 M. HCl and CsCl, containing Cs^{137}, were mixed in various proportions to give a series of solutions of total ionic strength O.1. O.2 g. samples of Z P (79) in the caesium or hydrogen forms were equilibrated with 10 ml. portions of these solutions at 25°. Sfter 48 hours, when the system was in equilibrium, 5 ml. samples were withdrawn and counted. From the activities, the caesium concentration was determined, using the calibration curve shown in figure (16). The equilibrium batches, containing O.2 g. of exchanger, in the mixed Cs and H-forms, were filtered through small columns, of dimensions 2 x 30 mm. The solid was washed free from active solution and the caesium content determined, as before, by elution with 6 M. nitric acid.

To test for reversibility, O.2 g. samples of Z P, (79), H-form were equilibrated at 25° with 10 ml. portions of solution, O.O33, and O.O67 M. in caesium and hydrogen chlorides respectively. Each sample of the resultant, mixed exchanger was filtered, washed, dried, and equilibrated with mixed CsCl and HCl solutions as before.

Equilibria of monovalent anions on hydrous zirconia:

The pairs of ions studied in this series of equilibrium experiments were chloride/nitrate, chloride/thiocyanate, and thiocyanate/nitrate.

Analysis for Chloride: Chloride ion was analysed using Mohr's method, in which chloride in solution was titrated using silver chromate as indicator (121a).

Analysis for nitrate: Since no suitable method for nitrate analysis was available, solutions were determined by an ion exchange technique. The polystyrene sulphonic acid cation exchanger, Amberlite IRA 120, was prepared in the hydrogen form by elution with 2 M. HCl and washed free from chloride with distilled water. Sodium nitrate solution containing approximately 1 meq. of salt was pipetted on to a column, and washed slowly through with distilled water, until no acid was detectable in the effluent. The total washings, which then contained an equivalent amount of nitric acid were titrated against standard sodium hydroxide.

Analysis for thiocyanate: The method consisted in the titration of thiocyanate ion, in dilute nitric acid, with a standard solution of mercuric nitrate, using a little iron alum solution as indicator. Immediately the thiocyanate was converted into the mercuric salt, the solution became water clear, giving a sharp end point.(121b)

Thiocyanic acid: A solution of 0.1 M. thiocyanic acid was prepared by slowly washing 50 meq. of KCNS stock solution through a column of Amberlite IRA 120, in the hydrogen form. The washings were collected in a 500 ml. standard flask until no acid was detectable in the effluent, and made up to the mark. Analysis with sodium hydroxide showed agreement within ± 0.2%.

Analysis of thiocyanate/chloride mixtures: The method suggested by Vogel(121c), in which chloride was separated as bismuth oxychloride, was found to be unsuitable. A conductimetric method was evolved based upon the relative solubilities of silver chloride and silver thiocyanate:

$$S_{AgCl} / S_{AgCNS} = 1{\cdot}2 \times 10^{-10} / 7{\cdot}1 \times 10^{-13}$$
$$= 170.$$

On the addition of A_gNO_3 to a neutral solution containing mixed CNS^- and Cl^- one would expect the precipitation of A_gCNS to be complete before A_gCl precipitation occurred; this was found to be the case.

Conductivity titration: This was carried out in a flask, similar to that shown in figure (5a), containing a pair of platinum conductivity electrodes, (Phillips, PR 95/10), in the central opening. The solution was freed from carbon dioxide by nitrogen bubbling, and the conductivities measured, using a transformer ratio arm bridge. When a constant reading was obtained, additions of standard A_gNO_3 were made, and the solution thoroughly mixed. Conductivities were corrected for the increase in volume during the titration, and plotted against the volume of silver nitrate added. A typical curve for such a titration is shown in figure (17). The 'end points' of these curves correspond to complete precipitation of A_gCNS, and of A_gCNS and A_gCl respectively. The estimated accuracy of this determination was ± 1%.

Ionic Forms: Samples of the hydrous zirconia exchanger were eluted with mixed solutions of NaA and HA of total ionic strength 0.1, and of acid concentration 0.01 M, (where A represents a monovalent anion). When no further exchange occurred, the samples were filtered, and quickly washed under suction, to prevent undue removal of A^- ion by hydrolysis. The exchanger was then allowed to equilibrate to constant weight over saturated ammonium chloride at 25°.

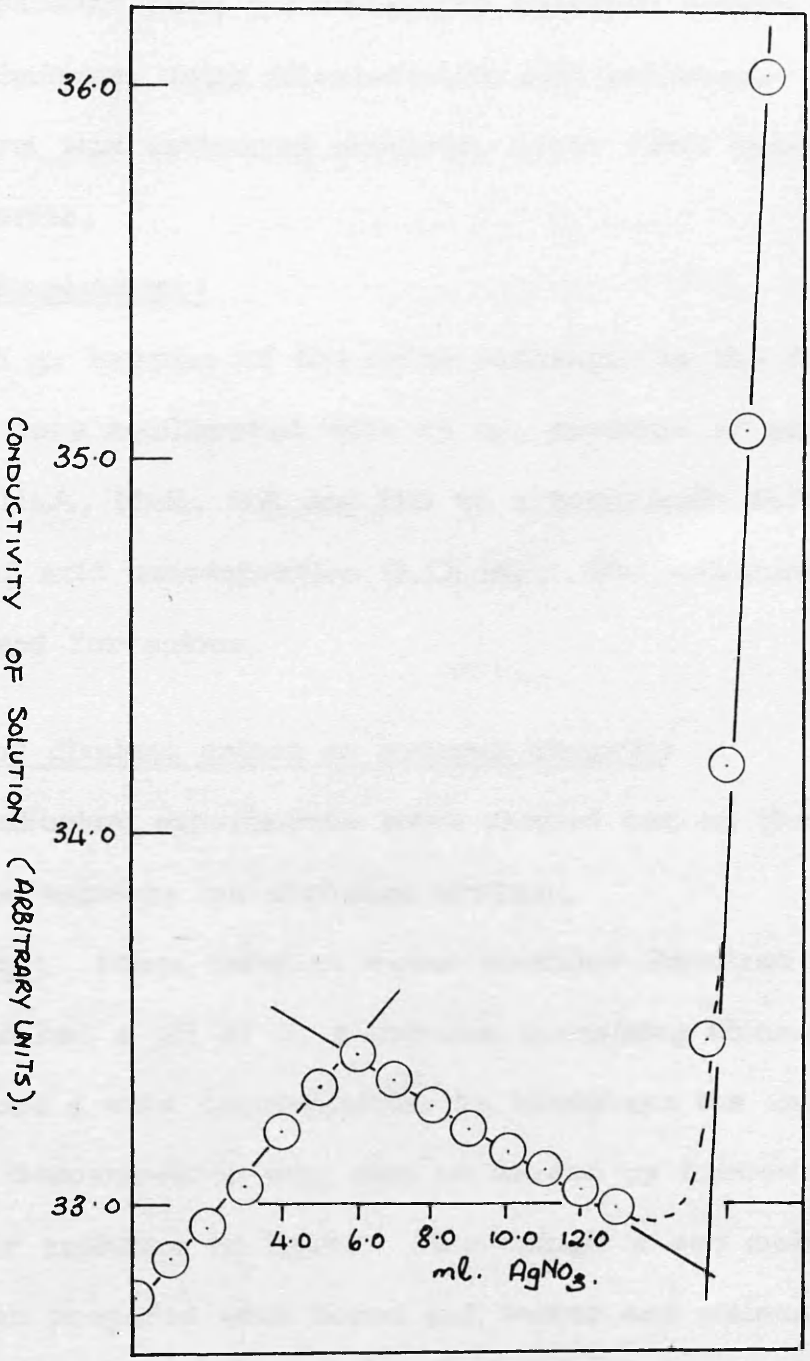

CONDUCTIVITY OF SOLUTION (ARBITRARY UNITS).
36·0
35·0
34·0
33·0
4·0
6·0
8·0
10·0
12·0
ml. AgNO3.

FIGURE 17.

Capacities were determined by standard column elution techniques, using nitrate/nitric acid solutions. The nitrate form was estimated similarly, after first converting to the chloride.

Exchange Experiment:

0.5 g. samples of the dried exchanger in the A^- or B^- forms were equilibrated with 25 ml. portions of solution containing NaA, NaB, HA and HB to a total ionic strength 0.1, and of acid concentration 0.01 M. The solutions were then analysed for anions.

Equilibria of divalent anions on hydrous zirconia:

Equilibrium experiments were carried out on the thiosulphate/sulphate ion exchange system.

Thiosulphate: Since distilled water contains dissolved carbon dioxide, and has a pH of 5, a solution containing thiosulphate ion undergoes a slow decomposition to bisulphate ion and sulphur. Moreover, decomposition may also be caused by bacterial action or hastened by exposure to light. Accordingly a one molar solution was prepared with boiled out water and maintained in the dark in an atmosphere of nitrogen.

Thiosulphate solutions were standardised by iodine titration against KIO_3 in acidic KI solution.(121d)

Sulphate: Since the sulphate solutions were used together with thiosulphate in exchange studies, care was taken to exclude carbon dioxide during preparation.

Sulphate was determined by precipitation as $BaSO_4$ which was ignited to constant weight at 600°.(121e)

Ionic forms: Exchanger in the sulphate, and thiosulphate forms was prepared by elution of hydrous zirconia with the carbonate-free 0.1 M. solutions. It was then washed and dried at 79% humidity as before, care being taken to exclude carbon dioxide.

Capacities were determined by elution with 0.3 M. sodium nitrate solution. Since the solutions of sulphate and thiosulphate were maintained carbonate free, their pH was approximately 6. Under these conditions there is some possibility of cation uptake on zirconia. To test for this 0.5 g. samples of hydrous zirconia in the chloride form were equilibrated with carbonate free solutions 0.05 M. in traced CsCl. 5 ml. samples of these solutions, analysed for Cs^+ showed no cation uptake.

Furthermore the pH of 6 ensured that the ionic species HSO_4^- and $HS_2O_3^-$ were present to negligible extent.

Exchange Experiment: O.5 g. of exchanger in the sulphate or thiosulphate form were equilibrated with 25 ml. portions of solutions containing varying proportions of each anion, and of total ionic strength O.3. The equilibration was carried out in 100 ml. round-bottomed flasks, which were flushed with nitrogen and sealed before being placed in a thermostat at 25°. The batches were equilibrated for two days with intermittent shaking. Concentrations of the equilibrium solutions were determined by back titration of standard iodine using O.1 M. sodium thiosulphate.

PART IV

RESULTS

Zirconium Phosphate: The results, which were derived from capacity determinations, are shown in table (13). These indicate that 2.5 m. moles of water, per meg. of exchange capacity, are lost in the conversion from hydrogen to caesium forms.

Table (13).

ZrP (79)

Form	Weight g.	Capacity meq.	Wt. matrix. + water
H	0.950	0.554	0.9495
Cs	0.997	0.554	0.9234

Since it was shown from thermobalance studies (Part II), that on heating to 250° interstitial water was completely removed from the zirconium phosphate matrix, weighed amounts of ZP (79) in the caesium and hydrogen forms were heated to this temperature, and the water contents in table (14) calculated.

Table (14).

Exchanger Form	Sample weights ZP (79)	250°	Capacity meq.	M. moles H_2O per meq. capacity
H	0.6942	0.6119	0.405	11
Cs	0.4619	0.4240	0.265	8

Once again the water lost in conversion was about three m. moles per exchange equivalent.

Zirconia: The results of these determinations, table (15), indicate no difference in water contents with ionic form.

Table (15)

Exchanger Form.	Wt. ZrO_2 (79) cap. 1 meq. (g.)	Wt. 1 meq. of ion (g.)	Wt. matrix + water
Cl	0.517	0.035	0.482
NO_3	0.545	0.062	0.483
CNS	0.542	0.058	0.484
S_2O_3	1.30	0.114	1.191
SO_4	1.29	0.096	1.198

Displacement Studies:

Since n - heptane and carbontetrachloride may be regarded as inert media, the constancy of displacements, table (16), implies a close similarity between ZrP, (79), H-form and material equilibrated with water. We may therefore assume that differences in water contents between ionic forms of an exchanger at 79% humidity are equal to those in pure water.

Table (16).

Medium	Wt. ZrP (79) H-form to displace 1 ml. (g).
Water	2.43
n - heptane	2.40
carbontetrachloride	2.41

A possible Structure for ZrP: Assuming that the displacement of ZrP (79), H-form gives approximately the density of ZrP (anhydrous), it is possible to obtain a rough estimate of the apparent distance between exchanging sites. The density of ZrP H-form is 2.4 g. 1 ml. and the capacity, 0.583 meq./g., so that the number of exchange sites/ml. is No. $0.583.2.4/10^3 = 8.4 \times 10^{20}$ (where No is Avogadro's number). Assuming a cubic lattice, in which there are n sites/cm. of side, then, $n^3 = 8.4 \times 10^{20}$, and therefore the distance between sites would be about 10 A.

ZrP has been shown in Part II to correspond to diphosphatozirconic acid, $ZrO(H_2PO_4)_2$, M.W., 301. Since only one site, per phosphate grouping, will dissociate in acid solution, 0.301 g. of the anhydrous exchanger would have an expected capacity of 2 meq. The observed capacity for such a sample is shown to be 0.20 meq./m.mole, from table (14), so that only one in ten phosphate groups are available for exchange purposes.

Equilibrium Studies:

Caesium/hydrogen exchange on zirconium phosphate: Caesium contents of equilibrium solutions, and the capacity of exchanger batches, allowed the calculation of a series of selectivity coefficients for both the forward and reverse reactions. The results are shown in tables (17a) and (17b), in which $K_{H}^{Cs} = \bar{Cs}\left[H^{+}\right]/\bar{H}\left[Cs^{+}\right]$, and $K_{Cs}^{H} = \bar{H}\left[Cs^{+}\right]/\bar{Cs}\left[H^{+}\right]$ respectively. To investigate the validity of this method of calculation, samples of equilibrated solid were analused by elution. Results, table (18), show that calculated and observed mole fractions in the exchanger phase are in experimental agreement. Since, however, solution analysis was subject to fewer errors, these values were used.

Table (18).

Solution	Original Form	Meq. Cs^{+} / 0.2 g. sample obs.	calc.
5	Cs	0.092	0.089
9	Cs	0.071	0.061
11	Cs	0.043	0.047
1	H	0.077	0.078
6	H	0.047	0.052

Reversibility: A plot of mole fraction in solution against exchanger composition, figure (18), showed marked hysteresis. The results of reversibility tests demonstrated that when a

Table 17a:

Caesium ion exchange on to H-form ZrP (79).
Samples 0.200 g. ZrP (79) H-form.
Capacity, 0.117 meq., equilibrated with 10 ml. portions of Solution.

Solution	Cs^+ contents of solution.		$[H^+]/[Cs^+]$	$\bar{Cs}^+/\bar{H}^+$	K_c
	original (M)	Equilibrium (M)	Solution A	Solid B	= A x B
1	0.1000	0.0922	0.0846	2.02	0.171
2	0.0909	0.0837	0.195	1.61	0.314
3	0.0833	0.0767	0.303	1.30	0.395
4	0.0714	0.0657	0.522	0.966	0.504
5	0.0500	0.0447	1.237	0.833	1.03
6	0.0444	0.0392	1.55	0.816	1.27
7	0.0333	0.0286	2.50	0.683	1.70
9	0.0166	0.0139	6.19	0.310	1.92

Table (17b) ~~(18)~~:

Hydrogen ion exchange on to Cs - form ZrP (79).
Samples 0.200 g.
Capacity 0.142 meq., equilibrated with 10 ml. portions of Solution.

Solution	Cs^+ contents of solution.		$[Cs^+]/[H^+]$	$\bar{H}^+/\bar{Cs}^+$	Kc^1
	original (M.)	Equilibrium (M.)	Solution A^1	Solid B^1	$A^1 \times B^1$
5	0.0500	0.0553	1.23	0.588	0.725
7	0.0333	0.0396	0.654	0.794	0.520
9	0.0167u	0.0248	0.330	1.00	0.330
10	0.0091	0.0173	0.209	1.37	0.288
11	0.0000	0.0094	0.103	2.00	0.206

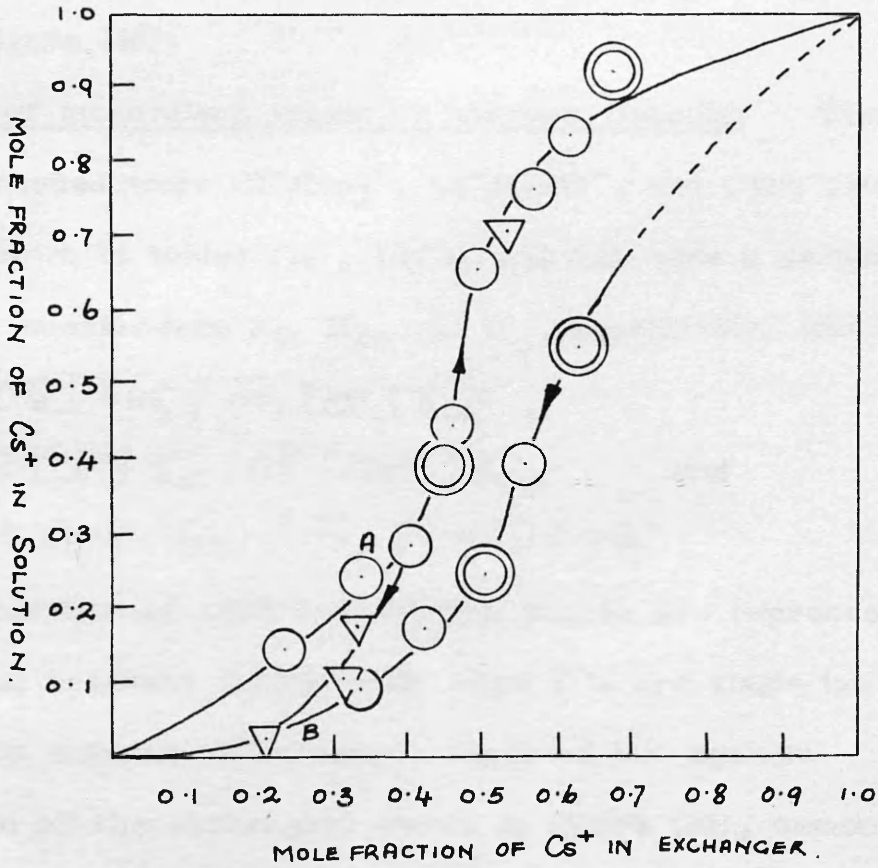

1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
MOLE FRACTION OF Cs+ IN SOLUTION.
A
B
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
MOLE FRACTION OF Cs+ IN EXCHANGER.

FIGURE 18.

mixed exchanger was equilibrated with solutions of increasing caesium content, the equilibrium point was on the upper curve: it was, therefore, the same as if equilibration were carried out in one stage. When, however, the mixed exchanger form was equilibrated with solutions of decreasing caesium content, the equilibrium points lay on a tie-line AB joining the two curves, figure (18).

Equilibria of monovalent anions on hydrous zirconia: The systems studied were Cl^-/No_3^-, Cl^-/CNS^-, and CNS^-/No_3^-. Results shown in tables (19), (20), and (21) give a series of selectivity coefficients K_1, K_2, and K_3 respectively, where

$K_1 = \overline{Cl}\,[NO_3^-]\,\gamma_{NO_3^-} / \overline{NO_3}\,[Cl^-]\,\gamma_{Cl^-}$,

$K_2 = \overline{CNS}\,[Cl^-]\,\gamma_{Cl^-} / \overline{Cl}\,[CNS^-]\,\gamma_{CNS^-}$ and

$K_3 = \overline{CNS}\,[NO_3^-]\,\gamma_{NO_3^-} / \overline{NO_3}\,[CNS^-]\,\gamma_{CNS^-}$

The compositions of solid and solution phases are represented by bars and brackets respectively while γ's are single ion activities in solution as before. Plots of lnK against composition of the exchanger, shown in figure (19), demonstrate reversibility and allow calculation of thermodynamic equilibrium constants by the method of Gaines and Thomas, (page 81). Since the water contents of each form of the exchanger was constant, the equation (16) reduced to:

$$\ln K = \int_0^1 \ln K_c \, dH .$$

The thermodynamic equilibrium constants, K^{o}'s, obtained from graphical integration of the $\ln K^{*}$ plots were $K_1^{o} = 1.04 \pm 0.1$, $K_2^{o} = 1.54 \pm 0.1$, and $K_3^{o} = 1.94 \pm 0.2$. Since this series of exchanges represents a system, in which each ion is separately paired with the other two, $K_1^{o} = K_3^{o} / K_2^{o} = 1.25 \pm 0.2$, while $K^{o}_{1\,\text{obs.}} = {}^{\text{calc.}}\,1.04 \pm 0.1$. Agreement between calculated and observed values of K_1^{o} was within the experimental error of ± 10%.

<u>Equilibria of divalent anions on hydrous zirconia:</u> Selectivity coefficients for sulphate/thiosulphate exchange on hydrous zirconia were calculated for both forward and reverse exchanges, table (22), in which

$$K_c = \overline{SO_4}\,[S_2O_3^{=}]\,\gamma_{S_2O_3^{=}} \Big/ \overline{S_2O_3}\,[SO_4^{=}]\,\gamma_{SO_4^{=}}$$

Since the water contents of the sulphate, and thiosulphate exchangers were equal, the thermodynamic equilibrium constant, K_c^{o} was obtained graphically from figure (20), from which K_c^{o} was 2.1.

* THE RATIOS OF THE ACTIVITY COEFFICIENTS IN SOLUTION WERE CALCULATED FROM THE DEBYE – HÜCKEL EQUATION, AND SO, $\gamma_{NO_3^-}/\gamma_{Cl^-} = \gamma_{Cl^-}/\gamma_{CNS^-} = \gamma_{NO_3}/\gamma_{CNS} = 1$.

Table (19): I NO_3^- on to Cl^- - form of zirconia; capacity 1.74 meq./g.

II Cl^- on to NO_3^- - form of zirconia; capacity 1.89 meq./g.

	Solution	Cl^- content of solution original	Cl^- content of solution equilibrium	$[NO_3^-]/[Cl^-]$ Solution	Cl^-/NO_3^- Solid	K_1
I	1	0.100	0.0998	-	-	-
	2	0.0909	0.0936	0.068	11.89	0.813
	3	0.0833	0.0881	0.136	6.25	0.849
	4	0.0714	0.0793	0.261	3.52	0.920
	5	0.0500	0.0632	0.582	1.64	0.952
	6	0.0444	0.0593	0.686	1.37	0.937
	7	0.0333	0.0509	0.963	0.977	0.941
	8	0.0286	0.0467	1.14	0.928	1.05
	9	0.0167	0.0383	1.61	0.611	0.985
II	3	0.0833	0.0590	0.694	1.36	0.944
	5	0.0500	0.0321	2.12	0.490	1.038
	10	0.0091	0.0057	16.29	0.082	1.35

The symbols of reactions I and II are ◇ and -◇- respectively; figure (19).

Table (20): I Cl^- on to CNS^- - form of zirconia; capacity 2.016 meq./g.
II SCN^- on to Cl^- - form of zirconia; capacity 2.16 meq./g.

	Solution	CNS^- content of solution original (M)	equilibrium (M)	$[Cl^-]/[SCN^-]$ Solution	$\overline{SCN}/\overline{Cl}$ Solid	K_2
I	9	0.0167	0.0377	0.165	9.26	1.53
	8	0.0286	0.0474	1.11	1.15	1.28
	3	0.0833	0.0885	0.130	7.01	0.91
	3	0.0833	0.0563	0.764	1.68	1.28
II	4	0.0714	0.0480	1.082	1.18	1.26
	6	0.0444	0.0285	2.516	0.586	1.48
	8	0.0286	0.0170	4.88	0.403	1.96
	10	0.0048	0.048	19.97	0.144.	2.88

The symbols for reactions I and II are ⊙ and -⊙- respectively; figure (19).

Table (21): I CNS^- on to NO_3^- - form of zirconia; capacity 1.98 meq./g.

II NO_3 on to CNS^- - form of zirconia; capacity 2.04 meq./g.

	Solution	CNS^- content of solution original (M)	equilibrium (M)	$[NO_3^-]/[CNS^-]$ Solution	$\overline{CNS}/\overline{NO_3}$ Solid	K_3
I	2	0.0091	0.0046	20.7	0.127	2.63
	3	0.0167	0.0091	10.0	0.234	2.34
	4	0.0286	0.0167	4.99	0.431	2.15
	5	0.0500	0.0312	2.21	0.905	2.00
	6	0.0556	0.0352	1.84	1.06	1.95
	8	0.0714	0.0467	1.14	1.66	1.89
	9	0.0833	0.0554	0.81	2.40	1.93
II	1	0.000	0.0234	3.12	0.675	2.11
	2	0.0091	0.0305	2.28	0.901	2.05
	3	0.0167	0.0361	1.77	1.09	1.93
	4	0.0286	0.0450	1.22	1.49	1.82
	5	0.0500	0.0609	0.642	2.73	1.75
	6	0.0556	0.0649	0.538	3.33	1.80
	9	0.0833	0.0869	0.151	10.43	1.57
	10	0.0909	0.0929	0.0763	19.33	1.48

The symbols for reaction I and II are ⊡ and -⊡- respectively; figure (19).

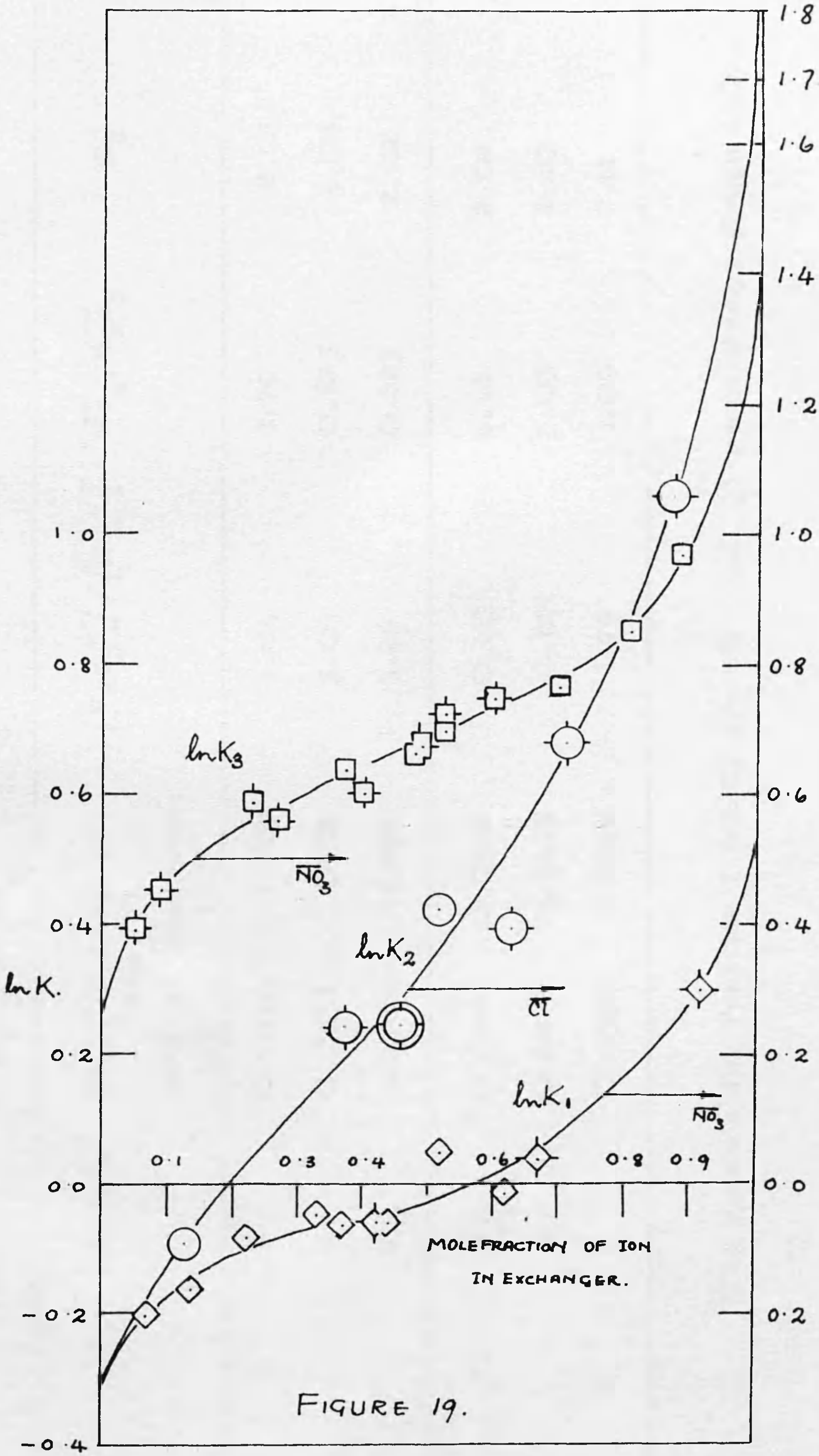

1·8
1·7
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0·0
0·2
-0·2
-0·4
ln K.
ln K3
$\overline{NO_3}$
ln K2
$\overline{Cl}$
ln K1
$\overline{NO_3}$
0·1
0·3
0·4
0·6
0·8
0·9
MOLEFRACTION OF ION
IN EXCHANGER.

FIGURE 19.

Table (22): I $S_2O_3^=$ on to $SO_4^=$ - form of zirconia; capacity 0.66 m.m./g.

II $SO_4^=$ on to $S_2O_3^=$ - form of zirconia; capacity 0.77 m.m./g.

$S_2O_3^= / SO_4^= = 1.09$.

	Solution	$S_2O_3^=$ content of solution		$[S_2O_3^=] / [SO_4^=]$	$\overline{SO_4}/\overline{S_2O_3}$	K_c
		original (M)	equilibrium (M)			
I	6	0.0556	0.0509	1.04	1.79	2.04
	9	0.0833	0.0752	3.03	0.625	2.08
	11	0.1000	0.0892	8.26	0.223	2.02
II	3	0.0167	0.0292	0.413	4.46	2.02
	4	0.0286	0.0401	0.671	3.03	2.20
	6	0.0556	0.0636	1.75	1.09	2.12

The symbols for reaction I and II are ⊙ and ⦶ respectively; figure (20).

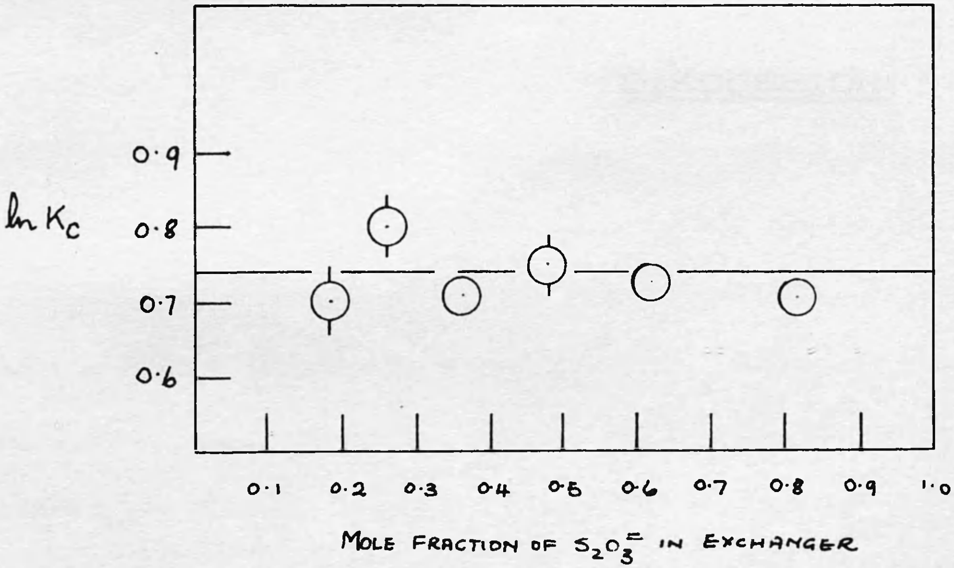

ln Kc
0·9
0·8
0·7
0·6
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
Mole fraction of $S_2O_3^=$ in exchanger

FIGURE 20.

PART IV

DISCUSSION

Zirconium phosphate:

Hysteresis: Barrer and Falconer$^{(122)}$ discussed reversible exchange isotherms for interactions of similar ions bound to adjacent sites on a crystalline exchanger matrix. The final expression for the thermodynamic equilibrium constant for exchange was equivalent to that of Kielland$^{(123)}$, in which it was shown that for the reaction,

$A^+_{soln} + \bar{B}_{cryst} \rightleftharpoons \bar{A}_{cryst} + B^+_{soln}$, log $f_a = CN_B^2$, and log $f_b = CN_A^2$. f_a and f_b are the activity coefficients of the ions A^+ and B^+ in the exchanger, and C is a constant. The expression derived for the equilibrium constant was, therefore, $\log K_0 = \log m_b N_a / m_a N_b + C(1 - 2N_a)$, where m and N represent concentrations in the solution and solid phases respectively. Barrer and Falconer, however, related C to the interaction energy w between B^+ ions occupying adjacent sites on the crystalline matrix. When w was positive the B^+ ions showed no tendency to occupy adjacent sites and the exchange isotherm observed was sigmoidal. If, however, w was negative the B^+ ions showed a tendency to aggregate on adjacent sites, giving an isotherm in the shape of an ogee curve. (The terms sigmoid and ogee both signify S-shaped. In the present work these terms will be used to describe curves of the types shown in figures (18) and (19) respectively.) Barrer claimed that such aggregation might be associated with a difficulty of nucleating a growing phase in or on the parent phase of the exchanger crystal. This would involve extra free energy terms corresponding to surface tension and strain, and so delay spontaneous growth of crystal germs into crystallites well past the point of true thermodynamic equilibrium. In the reverse reaction, similar effects would occur, and since the work done against strain and surface tension would be positive in each case, the resultant isotherms would be irreversible and show hysteresis.

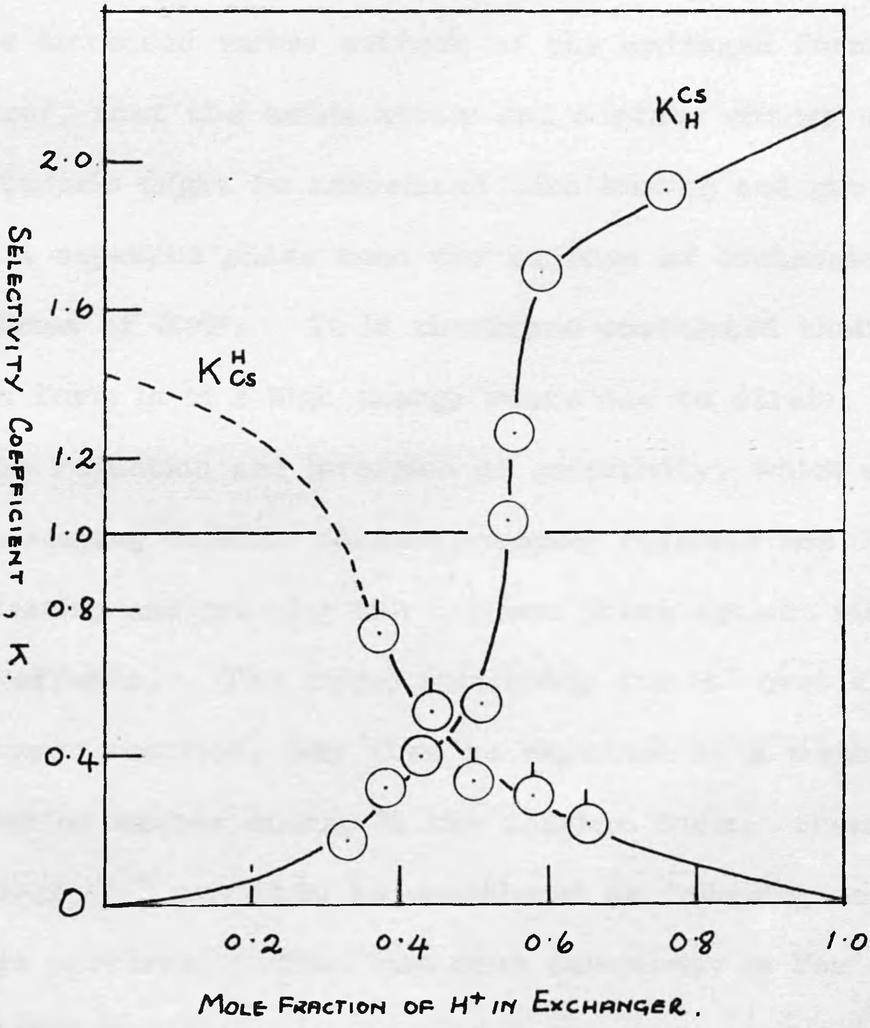
Barrer and Hinds(124) in equilibrium studies on aluminosilicate materials have observed hysteresis in several exchange systems, Na^+/K^+ exchange on analcite, and Na^+/Ag^+, Li^+/Ag^+ on basic cancrinite. In each case the isotherms were basically of the ogee type and the existence of two mutually insoluble solid phases was demonstrated in the partially exchanged materials. A striking example was, however, reported by Barrer and Falconer(122), in which the hysteresis loops were sigmoidal, while no conclusive evidence of the coexistence of two mutual solid phase could be detected by optical or X-ray methods. This latter case was analogous to that observed for Cs^+/H^+ exchange on zirconium phosphate.

Although the presence of sigmoidal rather than ogee curves, in these examples, might be explained in terms additional energy considerations, the qualitative application of Barrer's ideas must involve the concepts of nucleation and phase separation within the exchanger.

Capacity data on the caesium and hydrogen forms of ZrP indicated that only one in ten of the possible sites in the solid matrix are capable of exchange. Only this fraction of sites may therefore be considered to be adjacent to intercrystalline channels, along which exchange occurs. The picture of ZrP is therefore one in which we have crystallites of diphosphatozirconic acid permeated by intercrystalline water, such that only surface phosphate groups may exchange cations. The replacement of hydrogen for caesium ions on surface sites might therefore cause the requisite surface and strain effects required for hysteresis, while even complete conversion to the caesium form would leave the X-ray powder photographs substantially unaltered.

Gregor Belle and Marcus (125) have attempted to explain selectivity coefficients in quaternary ammonium exchange resins in terms of ion association between exchanger groups and counter ions. In order to explain more complex exchange isotherms they postulated further association of the ion pairs to form clusters. An isotherm corresponding to that for Cs^+/H^+ exchange on ZrP would then correspond to a system, in which one of the exchanging counter ions formed random ion pairs throughout the exchanger matrix, while the other formed clusters. The possibility of hysteresis, which is purely a crystalline phenomenon, could not be considered in such elastic organic resins.

Selectivity: The most striking property of zirconium phosphate is its high affinity for caesium and the alkali metal cations. Amphlett(38) and Gal and Gal(59) have measured mass distribution coefficients $K_D = ($ meq./g. of exchanger $\div$ meq./ml. of solution at equilibrium$)$ for alkali metal salt solutions in contact with the hydrogen form of zirconium phosphate. The results indicated that the affinities fell in the series $Cs^+ > K^+ > Na^+ > Li^+$, which was confirmed by Kraus(80) who has also noted similar high selectivities when the exchanger was largely in the hydrogen form. Selectivity coefficients for the Cs^+/H^+ equilibrium on ZrP (79) in figure (21) indicate that the exchanger indeed showed high selectivity for Cs^+ when largely in the hydrogen form. However, as exchange proceeded and the caesium content was appreciable, loading became progressively more difficult and inversion of selectivity occurred.



Selectivity Coefficient, K.
2·0
1·6
1·2
1·0
0·8
0·4
0
0·2
0·4
0·6
0·8
1·0
K_{H}^{Cs}
K_{Cs}^{H}
Mole Fraction of H^+ in Exchanger.

FIGURE 21.

The features of the reverse reaction were exactly similar. The presence of hysteresis and the selectivity patterns in these exchanges lead, in the absence of further data to the following postulate for the exchange mechanism. We may suppose, from the large size of the unhydrated caesium ion and the increased water content of the hydrogen form of the exchanger, that the extra strain and surface energy effects of hysteresis might be associated with loading and growth of Cs^+ in a separate phase upon the surface of exchanging crystallites of ZrP. It is therefore postulated that the caesium form is in a high energy state due to strain, and that the reduction and inversion of selectivity, which occurred with increasing caesium content, merely reflects the difficulty of nucleating and growing the caesium phase against increasing energy effects. The initial selectivity for H^+ over Cs^+, in the reverse reaction, may then be explained as a mechanism of reduction of excess energy in the caesium form. Subsequent removal of Cs^+ may then be considered as following normal exchange patterns. That the true selectivity is for Cs^+ over H^+ is suggested from the data of Larsen and Vissers(109) which showed that reversible exchange of Li^+, Na^+, and K^+ ions on the hydrogen form of zirconium phosphate followed the normal affinity series, $K^+ > Na^+ > Li^+$.

Energy considerations for the reaction $Cs^+ + \bar{H} \longrightarrow \bar{Cs} + H^+$, to proceed from left to right spontaneously, demand that there must be an overall loss in the Gibbs free energy, i.e. $-\Delta G$ must be positive. If the caesium form of ZrP, ($\bar{Cs}$), is a high energy species, the energy change for the reaction would be positive, and in order that ΔG be negative a net increase in entropy would be required. The process of Cs^+ loading from solution would reduce, and the displacement of H^+ from the matrix would increase the entropy. The overall entropy change must therefore depend upon the relative magnitudes of these effects.

Theories of Selectivity: The affinity series, $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, is assumed as the natural order of chemical affinities on zirconium phosphate. It is in agreement with that for polystyrenesulphonic acid exchangers(112) but exactly the opposite for polycarboxylic acid exchangers.(126) Bregman(126), has explained the behaviour of the alkali metal ions on weak acid cation exchangers by the use of Robinson-Harned-Stokes hypothesis of "localised hydrolysis".(127) This stated that the protons of nearby water molecules repelled by a positive ion possessed a certain tendency to form bonds with proton acceptors, such as hydroxyl or acetate ions present in solution. The strengths of such bonds would then depend upon the intensity of the electric field around the cation and therefore increase from Cs^+ to Li^+. The affinity for a carboxylic acid exchanger should therefore decrease in the series, $Li^+ > Na^+ > K^+ > Cs^+$.

Gurney (110), however, introduced a theory of electrolytes based on the conception of order producing and order destroying ions, which may be used in the present case. He postulated semi-empirically that there was a certain degree of order among molecules of water at room temperature. Morgan and Warren (128) have also suggested that the average number of nearest neighbours of a water molecule is about 4, arranged tetrahedrally, in a configuration of the lowest electrostatic energy. An ion introduced into the water will interfere with this structure in a way which is dependent upon its charge and size. Around each ion in solution there is a co-sphere of solvent, containing all the molecules of solvent giving a measurable contribution to the property being studied. If an ion of high field strength, e.g. Li^+, is introduced into water, it will have a strong ordering effect upon the water dipoles in its co-sphere, resulting in a higher degree of order such an ion is order producing. If, on the other hand, the ion is so large as to disturb the water structure due to geometrical reasons, the result is a breakdown of the water structure in the co-sphere. The weaker electrostatic field is incapable of ordering the water dipoles to any appreciable extent and so the ion, e.g. Cs^+, is order destroying. In connection with ion exchange selectivity, the treatment of more concentrated solutions is of special interest.

A concentrated solution may be regarded as one in which the co-spheres of the ions are forced to overlap. When this occurs, short range forces develop, and are superimposed upon existing electrostatic interactions. These forces are attractive, or repulsive for ion pairs of the same, or different order producing characteristics respectively. The ordering characteristics of the alkali metal ions range from Li^+, which is strongly order producing to Cs^+, which is order destroying. Consequently the interaction between these and any one of the order destroying halide ions increases from Li^+ to Cs^+. Generalising, the activity coefficient of a salt decreases when we go from ions of dissimilar order-disorder character to those of similar character due to the presence of these short range forces. Without the necessity of any special hypotheses, therefore, it follows that the activity coefficients of salts of the alkali metals with order producing anions, e.g. OH^- and F^-, decrease, in agreement with the experimental results of Stokes and Robinson(129). It is not possible to apply this theory to salts of the transition metals, because, in this case, strong quantum-mechanical forces are superimposed.

In the application of the theory to ion exchanger equilibria, it is of fundamental interest to know whether the functional exchange group is order producing or destroying. The anion of a weak acid would be expected to be order producing while that of a strong acid, order destroying. In agreement with this, the perchlorate ion is strongly order destroying due to the large size of the perchlorate ion and the even charge distribution, by resonance over the four oxygen atoms. While the order producing character of the acetate ion, which is shown by the decrease in activity coefficients of the alkali acetates from Cs^+ to Li^+ (129), is probably due to the localisation of charge on one of the oxygens of the carboxyl group. On this basis we may regard the sulphonate group of the strong acid exchangers as order destroying, and hence, the selectivity for alkali metal ions to be, $Cs^+ > K^+ > Na^+ > Li^+$, as observed(112). The order producing carboxyl group of the methacrylic acid exchangers will therefore favour an inversion of the above selectivities (126).

We may now discuss the selectivity of ZrP in terms of Gurney's theory. Chemical evidence, Part II, suggests that phosphate is present as, $ZrO(H_2PO_4)_2$, so that there are, at least in theory, two dissociable hydrogen ions corresponding to the first and second dissociations of phosphoric acid. Activity data, however, shows that $\gamma_\pm$ $KH_2PO_4 < \gamma_\pm$ NaH_2PO_4, and $\gamma_\pm$ $K_2HPO_4 > \gamma_\pm$ Na_2HPO_4, where $\gamma_\pm$ represents mean activity coefficients of the species. It is possible that $H_2PO_4^-$ is order destroying, so that if only one hydrogen ion dissociates from ZrP the functional group obtained, $ZrO - HPO_4^-$, will be order destroying. If, however, both hydrogen ions dissociate, e.g. in alkaline solution, the resulting function group, corresponding to $HPO_4^{=}$, would be order producing. In acidic solutions, therefore, ZrP would be expected to have the affinity series described by Amphlett (39), in which Cs^+ is most strongly held, while in alkaline solutions Li^+ would be preferred.

Unfortunately, the extensive hydrolysis of ZrP in alkaline solution prevents determinations of selectivities in this medium. A suitable model system, however, is available in the phosphonic acid resins described by Bregman(126). The phosphonic exchanger, Nalcite x - 219, contained an exchange group similar to phosphate, and may be represented by $R.PO(OH)_2$, where R represents the resin matrix. It was shown to be stable in acids and bases, and to have two dissociable hydrogen ions. Bregman found, in plotting selectivity coefficients for Na^+/H^+ exchange against pH, that at pH ~ 6 an inversion of selectivity occurred, so that at high pH Na^+, and at low pH, K^+ ions were selected. This is in agreement with Gurney's theory, supporting the postulate that, in acid solutions, the selectivity of ZrP for alkali metal ions can only be accounted in terms of monofunctionality of the exchanger.

Hydrous Zirconia: It is seen from tables (19), (20), and (21), that the affinity of hydrous zirconia, for the monovalent anions, lies in the series: $CNS^- > NO_3^- \sim Cl^-$. Activity data for the potassium salts showed the following trend of the mean activity coefficients,

$\gamma_{\pm} KNo_3 \ll \gamma_{\pm} KCNS \simeq \gamma_{\pm} KCl$, indicating, in terms of Gurney's theory (110) that the order destroying properties of the ions lie in the series, $No_3^- \gg CNS^- \simeq Cl^-$. Although there was a reversal of order between CNS^- and Cl^- ions, the selectivities showed that No_3^-, which had the greatest order destroying properties, was only weakly held, indicating an order producing exchange site.

For the divalent exchange of $SO_4^{=}$ and $S_2O_3^{=}$, the order of affinity was, $SO_4^{=} > S_2O_3^{=}$. Activity data for the sulphates of the alkali metals showed no consistent trend, and yielded no information regarding the ordering properties of the ions. However, since $S_2O_3^{=}$ could be regarded as an $SO_4^{=}$ ion in which one oxygen atom was replaced by a larger and more polarisable sulphur atom, it would be reasonable to suppose that the order destroying nature of $S_2O_3^{=}$, would be greater than that of $SO_4^{=}$. The observed selectivity for $SO_4^{=}$, then suggests that the exchange site on hydrous zirconia is once again order destroying.

The physical picture of hydrous zirconia postulated in Part II, suggests that zirconia acts as a protonated oxide in solutions of low pH. Such protonated sites would be expected to be strongly order producing, and so favour the selectivities observed.

1. THOMPSON, J.Roy.Agr. Soc. (Engl.) (1850), 11, 68.
2. WAY, J. Roy. Agr. Soc. (Engl.) (1850), 11, 303.
3. WAY, ibid. (1852), 13, 123.
4. LEMBERG, Z.deut. geol. Ges. (1870), 22, 335.
5. LEMBERG, ibid. (1876), 28, 519.
6. GANS, German patent, 197, 111, (1906).
7. GANS, Centr. Mineral. Geol. (1913), 22, 728.
8. PAULING, J.Amer.Chem.Soc. (1927), 49, 765.
9. PAULING, Proc. Nat. Acad. U.S. (1930), 16, 123, 453.
10. BRAGG, 'Atomic Structure of Minerals' Cornell Univ. Press, (1937).
11. MATISON, Soil. Sci. (1950) 49, 109.
12. MATISON, Ann. Agr. Coll. (Sweden), (1942), 10, 56.
13. BARRER, (Review), Proc. Chem. Soc. (1958), 99.
14. THOMAS, J. Chem. Phys. (1954), 22, 258.
15. THOMAS, ibid. (1956), 24, 993.
16. THOMAS, J. Phys. Chem. (1960), 64, 224.
17. ADAMS & HOLMS, J. Soc. Chem. Ind. (1935), 54, 1-6T.
18. D'ALELIO, U.S. Patents (1944), 2,340, 111; 2,366, 007; and 2,366, 008.
19. U. S. Patent (1952) 2,591, 573.
20. OGBORN, 'Synthetic Ion Exchangers', Chapman & Hall Limited, London, (1961).

21. VERWEY & KRUYT, Z. Phys. Chem. (1933), A167, 137, 149, 312.

22. AMPHLETT, Proceedings of Second International Conf. on Peaceful Uses of Atomic Energy, Geneva, (1958), Vol.28, p.17, U.N.

23. SCHWAB & DATTLER, Z. Angew Chem. (1937), 50, 691.

24. SCHWAB & DATTLER, ibid. (1939), 52, 666.

25. GRAHAM & THOMAS, J. Amer. Chem. Soc. (1947), 69, 816.

26. SACCONI, Discuss. Faraday Soc., (1949), 7, 173.

27. KRAUSE & CIOKOWNA, Z. Anorg. Chem. (1932), 204, 20.

28. KURBATOV & WOOD, J. Phys. Chem. (1951), 55, 1170.

29. AMPHLETT, McDONALD & REDMAN, J. Inorg. Nucl. Chem. (1958) 6, 236.

30. KRAUS, PHILLIPS, CARLSON & JOHNSON, Proc. of Second International Conf. on Peaceful uses of Atomic Energy, Geneva, 1958, Vol. 28, p.3, U.N.

31. KRAUS & PHILLIPS, J. Amer. Chem. Soc. (1956), 78, 249.

32. AMPHLETT, McDONALD & REDMAN, J. Soc. Chem. Ind. (1957), 365.

33. NANCOLLAS & HARKIN, unpublished results.

34. AHRLAND, Acta. Chem. Scand. (1960) 14, 1059.

35. KOZAWA, J. Inorg. Nucl. Chem. (1961), 21, 315.

36. TEWARI, Kolloid Z. (1956), 149, 65.

37. MERTZ, Z. Electrochem., (1959), 63, 288.

38. ZHABROVA & EGOROV, Russ. Chem. Rev. (1961), 338.

39. AMPHLETT, McDONALD & REDMAN, J. Inorg. Nucl. Chem. (1958) 6, 220.

40. KRAUS, J. Amer. Chem. Soc., (1956) 78, 694.

41. PROSPERT & KIKINDAI, Compt. rend. (1962) 254, 860.

42. KRAUS, O.R.N.L., 2159: 41, (1956) Oak Ridge. Nat. Laboritory.

43. CABRAL, J. Chromatog., (1960), 4, 86.

44. NUNES, De COSTAS & JERONIMO, J. Chromatog., (1961), 5, 546.

45. KRAUS, Nature (1956), 177, 1128.

46. CROUCH, CORBETT & WILLIS, A.E.R.E., C/R - 2325, (1957).

47. BRESLER, Radiokhymiya (1959), 1, 507.

48. THIS THESIS, part II page 37

49. MALIK & ALI, Kolloid Z., (1961), 175, 139.

50. KHAN, RAHMAN & HAIDER, Chem. Abs. (1962), 56, 8040, h.

51. SMIT, ROBB & JACOBS, J. Inorg. Nucl. Chem. (1959), 12, 104.

52. BROADBANK, Analyst, (196o) 85, 365.

53. BROADBANK, J. Inorg. Nucl. Chem. (1961), 23, 311.

54. KRTIL, J. Inorg. Nucl. Chem. (1960), 12, 367.

55. KRTIL, ibid. (1961), 19, 298.

56. BRITTON, J. Chem. Soc. (1925), 2120.

57. LARSEN, FERNILIUS & QUILL, Ind.Eng.Chem. (1949) 15, 512.

58. HAHN & WILLARD, Anal. Chem. (1949) 21, 293.

59. GAL & GAL, Proc. of Second International Conf. on Peaceful uses of Atomic Energy, Geneva, (1958) Vol. 28, p. 24, U.N.

60. BLUMENTAL, The Chemical Behaviour of Zirconium, D. Van Nostrand Coy. Inc., N.Y., (1958).

61. BRIGGS, J. Chem. Soc. (1929), 242.

62. LUNGREN, Arkiv Kemi (1958) 13, 59.

63. LUNGREN & SILLEN, ibid (1949), 1, 277.

64. ABERTI & CONTE, J. Chromatog (1961) 5, 224.

65. MICHELSON, Anal. Chem. (1957), 29, 60.

66. THAMER & VOIGT, J. Amer. Chem. Soc. (1951) 13, 3197.

67. BRIT. STAND., 1647, (1950).

68. D'EYE & WAIT, 'X-ray Powder Photography in Inorganic Chemistry'
Butterworth Scientific Publ., London, (1960), p. 50.

69. MONTIGNIE, Bull. Soc. Chim. (1946), 13, 176.

70. HABER, Monatsch. (1897), 18, 687.

71. PAYKULL, oefvers. Vet. Akad. For., 22, 1873.

72. BEMMELIN, Z. Anorg. Chem. (1905), 45, 83.

73. SIMON & FISCHER, Z. Anorg. Chem. (1929) 185, 130.

74. LARSEN & GAMMILL, J. Amer. Chem. Soc. (1950), 72, 3615.

75. FREUNDLICH, Ber, (1928), 61B, 2219.

76. Russ. J. Inorg. Chem. (1960), 5, 687.

77. KRAUS & HOLMBERG, J. Phys. Chem. (1954), 58, 325.

78. HEITMAN, Acta. Chem. Scand, (1954), 8, 1626.

79. DOBRY, GUINARD & MATHIEU-SICAUD, J. Chim.Phys. (1953) 50, 501.

80. LUNGREN, Arkiv Kemi, (1950), 2, 535.

81. WEISER, 'Inorganic Colloid Chemistry' Vol.II, p.18, J. Wiley &
Sons Inc. (1935).

82. GAYER & LEIDER, J. Amer. Chem. Soc. (1954), 76, 5938.

83. HEVESY & KIMURA, J. Amer. Chem. Soc. (1925), 47, 2540.

84. LARSEN & VISSERS, J. Phys. Chem. (1960), 64, 1732.

85. BLUMENTAL, Ind. Eng. Chem., (1954), 46, 528.

86. WEIGNER, Trans. 3rd International Congress of Soil Sci.
(1936) 3, 5.

87. NACHOD & WOOD, J. Amer. Chem. Soc. (1944) 66, 1380.

88. THOMAS, ibid. (1944), 66, 1664.

89. JUDA & CARRON, ibid. (1948), 70, 3295.

90. TURSE & RIEMAN, J. Phys. Chem., (1961), 65, 1821.

91. BOYD, ADAMSON & MYERS, J. Amer. Chem. Soc., (1947), 69, 2836.

92. NERNST, Z. physik. Chem. (1904), 47, 52.

93. NERNST, ibid. (1905), 53, 235.

94. LEVICH, Discuss. Faraday Soc. (1947), 1, 37.

95. EDESKUTY & AMUNDSON, J. Phys. Chem. (1952), 56, 148.

96. ADAMSON & GROSSMAN, J. Chem. Phys. (1949), 17, 1002.

97. ADAMSON & GROSSMAN, J. Phys. Chem. (1952), 56, 97.

98. KRESSMAN & KITCHENER, Discuss. Faraday Soc. (1949), 7, 90.

99. CARSLAW & TAEGER, 'Conduction of Heat in Solid', Oxford Univ.
Press, (1947), p.83.

100. PATERSON, Proc. Physic. Soc. (1947), 59, 50.

101. SCHOGL & HELFFERICH, J. Chem. Phys. (1957), 26. 5.

102. HELFFERICH, J. Chim. Phys. (1958), 55, 157.

103. HELFFERICH, J. Chem. Phys. (1958), 58, 418.

104. HELFFERICH, J. Phys. Chem. (1962), 66, 39.

105. KOLTHOFF, & O'BRIEN, J. Amer. Chem. Soc. (1939), 61, 3409.

106. CONWAY, GREEN & REICHENBERG, Trans. Farad. Soc. (1954) 50, 511.

107. REICHENBERG, Private communication, (1961).

108. REICHENBERG, J. Amer. Chem. Soc. (1953), 75, 589.

109. LARSEN & VISSERS, J. Phys. Chem. (1960), 64, 1732.

110. GURNEY, 'Ionic Processes in Solution' McGraw Hill Book Coy.1953.

111. SOLDANO & BOYD, J. Amer. Chem. Soc., (1953), 75, 6107.

112. REICHENBERG & MCAULEY, J. Chem. Soc. (1955), 2741.

113. EKEDAL, HOGFELDT & SILLEN, Acta, Chem. Scand., (1950), 4, 556, 828.

114. ARGERSINGER, DAVIDSON & BONNER, Trans. Kansas Acad. Sci., (1950), 53, 404.

115. HOGFELDT, Arkiv Kemi, (1952) 5, 147.

116. GAINES & THOMAS, J. Chem. Phys. (1953), 21, 714.

117. DAVIDSON & ARGERSINGER, Ann. N. Y. Acad. Sci. (1953) 57, 105.

118. HOLM, (Review), Arkiv Kemi, (1956), 10, 151.

119. BONNER, ARGERSINGER & DAVIDSON, J. Amer. Chem. Soc. (1952) 74, 1044.

120. SOLDANO, LARSEN & MYERS, J. Amer. Chem. Soc., (1955), 77, 1339.

121. VOGEL, 'A Textbook of Quantitative Inorganic Analysis', Longmans, Green & Co. Ltd., (1960) pages, (a) 251, (b) 266, (c) 266, (d) 334, & (e) 401.

122. BARRER & FALCONER, Proc. Roy. Soc. (1956), 2364, 227.

123. KIELLAND, J. Soc. Chem. Ind., (1935), 54, 232.

124. BARRER & HINDS, J. Chem. Soc. (1953), 1879.

125. GREGOR, MARCUS & BELLE, J. Amer. Chem. Soc. (1955), 77, 2713.

126. GREGMAN, Ann. N.Y. Acad. Sci. (1953), 57, 125.

127. HARNED & OWEN, 'Physical Chemistry of Electrolyte Solutions'
Reihold Publ. Corp. N.Y., (1950).

128. MORGAN & WARREN, J. Chem. Phys. (1938), 6, 670.

129. STOKES & ROBINSON, Trans. Farad. Soc. (1949), 45, 612.