STUDIES OF SOLUTIONS

OF

BORATES, ARSENITES AND TELLURATES

by

Wojciech Popiel.

A Thesis Presented for
the Degree of Doctor of Philosophy
in the University of London.

The Chemistry Research Laboratories
Battersea Polytechnic,
SUMMARY

The sorption of borate, arsenite and tellurate ions on a strongly basic anion-exchanger in the chloride form was investigated by means of a series of equilibrium experiments. From the results obtained, an attempt was made to determine the state of condensation of these anions under various conditions of concentration and pH.

The concentration ranges of boric, arsenious and telluric acid studied were 0.02-0.66M, 0.1-0.18M and 0.14-0.5M respectively, the pH value of these solutions being altered (in the approximate range 5-11) by addition of sodium hydroxide. The results have been interpreted in terms of sorption by the resin of the following ions:

(a) $B_5O_8^-$, $B_4O_7^-$ (or $HB_5O_9^-$) and $H_2B_3O_3^-$ from borate solutions.

(b) $As_3O_5^-$, $As_2O_4^-$, $H_2AsO_3^-$, $HAsO_2^-$ and $AsO_2^-$ from arsenite solutions.

(c) $Te_4O_{13}^-$, $Te_3O_{10}^-$, $H_5TeO_6^-$ and $H_4TeO_6^-$ from tellurate solutions.

The actual ion sorbed depending on the pH and concentration of the solution.

It appears that a decondensation of the polyanions can be brought about by dilution or by raising the pH of solution.

The ultra-violet absorption spectra of arsenite
and tellurate solutions were also studied, and evidence has been obtained that a correlation exists between the ions sorbed on the resin and the ionic state of the solution when the resin is absent.
PREFACE

The work described in this Thesis was carried out in the laboratories of the Chemistry Department, Battersea Polytechnic, under the general supervision of the Head of the Department, Dr. F.R. Goss.

I would like to express my gratitude to Dr. D.A. Everest for the interest he has shown in this work, and for his valuable discussion and encouragement during the course of these studies.

Thanks are also due to Mr. H. Godby, Chief Laboratory Technician, and his staff for their cooperation at all times.

W.J.P.
INDEX

Part I. General Introduction.

Reasons for undertaking the present work

Ion-exchangers, Introduction

Important properties of

Anion-exchangers in studies of complex systems

Simple anion systems

More complicated systems

Spectrophotometry, Introduction

Part II. Studies of Solutions of Borates.

Historical

Scope of the Work

Experimental

Ion-exchange Results

Strength of Boric Acid

Discussion:

(i) Relatively Weak Boric Acid Solutions

(ii) Borate Solutions of Higher Concentration

(iii) Other interpretations of the Work

(iv) Comparison with Solid Borates

(v) Conclusions and General Comments

Tabular Results for Part II.
Part III. Studies of Solutions of Arsenites.

Historical ............................................................... 61
Strength and Basicity of Arsenious Acid .................... 64
Scope of the Work .................................................... 69
Ion-exchange Studies .................................................. 71
Spectrophotometric Studies ....................................... 75
Discussion ............................................................... 77
Conclusions and General Comments ............................... 83
Comparison with Solid Arsenites ................................. 84
Tabular Results for Part III. ........................................ 85a-b

Part IV. Studies of Solutions of Tellurates.

Historical ............................................................... 86
Scope of the Work .................................................... 94
Ion-exchange Studies .................................................. 96
Spectrophotometric Studies ....................................... 103
Discussion ............................................................... 104
Other Interpretations ................................................ 107
Comparison with Solid Tellurates ............................... 112
Conclusions and General Comments ............................... 113
Tabular Results for Part IV. ........................................ 113a-c

Annex I. Washing the Resin ........................................ 114
Annex II. Calculation of Data for fig.8 ........................ 116
BIBLIOGRAPHY ........................................................... 118
PART I

GENERAL INTRODUCTION
Reasons for undertaking the present work.

The oxy-acids formed from the weakly electronegative and amphoteric elements are characterised by the ease with which they condense to form isopoly acids. These give rise to condensed anions which could be considered as derived from several molecules of the acid anhydride (1). Thus the formation of isopolymolybdates, tungstates and vanadates is well known and has received considerable attention in the literature.

Until recently the study of such condensed systems has been largely carried out using classical physico-chemical methods. A study of the rate of diffusion of ions (2) and the measure of the dialysis coefficient (3) were both attempted with the view to obtaining directly the ionic weights of the condensed species. Other methods of study will be referred to in later pages and include the following: cryoscopy and conductivity measurements, pH titration, solubility studies, distribution studies involving immiscible solvents, and absorption and Raman spectra (4).

But as most of these methods are subject to some limitation, it is not surprising that interpretation of results was not only difficult, but at times yielded conflicting conclusions. It is true to say that with the exception of the simplest systems, no condensed anion system has so far been adequately elucidated, and to what extent a particu-
lar weak oxyacid or its salt will yield condensed anions in solution is as yet not sufficiently clear. Nevertheless, from a review of literature it appears that the degree of condensation is dependent on two factors: the concentration of the solution and its pH value. So when dealing with solutions of weak acids which are thought to yield condensed anions, it is reasonable to anticipate that the degree of condensation will increase with a rise in concentration, and decrease with a rise in the pH of solution.

In recent years a new method of analysis of complex ions has been made possible by the development of ion-exchange resins (5). Everest and Salmon (6) were the first to adopt an anion-exchange technique in a study of the condensation of the germanate ion in alkaline solution, and due to the success of this method it was decided to extend it to the study of solutions of borates, arsenites and tellurites. The objects of the present work are therefore as follows:

(a) To attempt an elucidation of the ionic systems present in solutions of the above acids at various concentrations and pH values.

(b) To accumulate data on the sorption of these acids on strongly basic anion-exchange resins.

(c) With the use of a spectrophotometric method, to attempt a correlation between the anionic species sorbed on the resin, and those present in solution when the resin is absent.
ION EXCHANGERS .... An Introduction.

Historical.

The phenomenon of ion-exchange (7) was noticed as early as 1850 when Way and Thompson (8) discovered that certain salts (notably ammonium sulphate and potassium chloride) could not be easily leached out from the soil by the action of water. It appeared that certain ions were in some way held by the soil particles. The property of ion retention in minerals was eventually traced to some clays, alumina, apatites and especially the zeolites - a group of aluminium silicates of complex composition, but the discovery remained unnoticed until in 1905 R. Gans began attempts to utilise the ion-exchange power of natural and later synthetic zeolites for the purpose of water softening. The following year he put his researches on a commercial basis by taking out a patent for a fused alumino-silicate exchanger (9).

The water softening process involves percolation of hard water through a bed of zeolite in the sodium form, with a result that calcium ions are retained by the ion-exchanger and sodium ions are liberated into solution. The reaction is reversible:

\[
\begin{align*}
2 \text{Na-Zeolite} + \text{Ca}^{++} & \xrightarrow{\text{(sorption)}} 2 \text{Na}^{+} + \text{Ca-(Zeolite)}_2 \\
\text{zeolite in sodium form} & \xrightarrow{\text{(regeneration)}} \text{zeolite in calcium form}
\end{align*}
\]
The exhausted zeolite can be reconverted into the sodium form by treatment with a solution containing a high concentration of sodium ions.

The first analytical application of synthetic zeolite appears to have been made in 1917, when Folin and Bell (10) used an ion-exchange technique in the determination of ammonia in urine. By absorption on the zeolite, the ammonia was separated from interfering amino acids and later determined with Nessler’s reagent after displacement from the exchanger by means of sodium hydroxide. Nevertheless, purely inorganic ion-exchangers were found to have but a limited application as they are stable only in a narrow range of pH. They are easily decomposed in acid media and peptized in alkaline solution. Fortunately more stable organic materials such as cellulose (11) were also found to possess ion-exchange properties, attention was therefore focussed on the development of organic ion-exchangers which would have the necessary chemical inertness for the variety of uses in which an ion-exchange technique was indicated. These exchangers would have to satisfy the following requirements:

(a) complete insolubility in the medium in which they are to be used.

(b) a high power of exchange, i.e., a high "capacity" for ions.
Organic ion-exchangers by synthesis.

In 1935 a patent for a resin with suitable characteristics was taken out by B.A. Adams and E.L. Holmes (12), who condensed phenolsulphonic acids with formaldehyde, in this way obtaining a macromolecule with cation-exchange properties. Later the same workers produced an anion-exchange resin by condensing polyamines with formaldehyde. The reactions involved may be briefly represented as follows:

\[
\begin{align*}
\text{OH} & \quad \text{A} \quad \text{Phenol-} & \quad \text{SO}_3\text{H} \\
\text{condensation} \\
\text{CATION EXCHANGER:} & \\
\text{CH}_2 & \quad \text{SO}_3\text{H} & \quad \text{SO}_3\text{H} & \quad \text{SO}_3\text{H} & \quad \text{SO}_3\text{H} \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} \\
\end{align*}
\]

Exchange here is due to the \(-\text{SO}_3\text{H}\) groups.
In this way a long-chain resinous substance was obtained, each particle of which was a three-dimensioned crosslinked network making up a giant molecule. At intervals along the chain are found the "active sites", that is groups with ion-exchange properties. For cation-exchangers these groups are of the type: \(-\text{SO}_3\text{H}\) \(-\text{COOH}\) \(-\text{OH}\) etc., whereas for anion-exchangers these are \(-\text{NH}_2\) \(-\text{NHR}\) \(-\text{NR}_2\) and \(-\text{NR}_3^+\). Although attached to a complex hydrocarbon network, each of these groups was found to behave in the same way as in simpler organic compounds.
Effect of crosslinking.

As the effective capacity of the exchanger depends on the number of "active sites" present, it is clear that the greater the degree of crosslinking the higher the capacity per unit volume of the resin. A close molecular network nevertheless reduces the rate of diffusion of ions within it and seriously impairs the rate of exchange. On increasing the crosslinking, it is the change in affinity of the resin for various ions which is more noticeable, and not the increase in capacity. In practice a compromise is made so as to obtain a resin sufficiently crosslinked for a maximum capacity consistent with a reasonable exchange rate.

Modern exchangers.

Hitherto the main difference between cation and anion exchangers has been that the capacity of the latter was much more sensitive to pH, since the materials behaved as weak bases. Development of ion-exchange resins has led to the production of "monofunctional" exchangers, that is those which contain as far as possible only one type of exchange group, this gave rise to the possibility of a resin containing only strongly basic exchange sites. At present time, ion-exchange resins are known largely by their trade names and their chemical composition is often not disclosed. In recent years however, new anion-exchangers have appeared
on the market whose basic strength approaches that of sodium hydroxide. A typical synthesis of a strongly basic and monofunctional anion exchange resin based on polystyrene may be represented as follows:

\[
\text{STYRENE} \quad \text{DIVINYL BENZENE} \\
\text{(suspension polymerisation)} \\
\text{(chloromethylation followed by reaction with trimethylamine)} \\
\text{(CH}_3\text{)}_2\text{N.CH}_2
\]

**STRONGLY BASIC ANION-EXCHANGER (e.g., DOWEX 1 & 2)**

**Important properties of exchangers.**

It is well to recall the following characteristics of ion-exchange resins:
1) Both for cationic and anionic resins ion-exchange proceeds by equivalents. Thus the sorption of each gram equivalent of an ion is accompanied by a desorption of one gram equivalent of the ion originally on the resin.

Weakly basic resins may not at times be completely converted to a given ionic form, and may appear at first glance not to obey the above criterion. Thus if we consider a resin which has been incompletely converted to an anionic form X, it may be that on treatment with a solution containing the anionic species Y some of these Y ions will be sorbed in exchange for X, but an extra quantity will be sorbed by the so far unreacted sites. The net effect will be that one equivalent of X will be replaced by more than one equivalent of Y, and the proportion will depend on the quantity of the previously uninfluenced sites entering the reaction. This in turn will depend on the pH of the eluting solution and on the concentration of Y ions in it.

Even at present, some so called "monofunctional" strongly basic resins may contain a certain small proportion of weakly basic exchange groups (e.g. Dowex 1 & 2, ref.13 Wheaton and Bauman). This may lead to variation in capacity depending on the type of ion sorbed and the conditions of sorption, but this effect is considered to be very slight and in most analytical work it may be neglected.

The capacity of a given sample of resin for a particular ion is usually expressed in gram equivalents of the
ion per gram of resin, but the capacity is found to vary slightly between samples of equal weight, this being due to an inhomogeneity of crosslinking. Once the capacity of the sample has been found therefore, it is more usual to calculate the "equivalent of the resin" and subsequently to express any atomic species sorbed in terms of moles per equivalent of resin.

(2) For cationic and strongly basic resins, the exchange reaction is reversible and the final state of the system is independent of the direction from which the equilibrium is approached (Gregor, Belle and Marcus, ref. 13). But a considerable difference in the time taken to reach equilibrium from different directions may be observed, due to the different rates of diffusion of the ions.

(3) The affinity of a cation for the resin appears to depend both on its ionic charge and on its hydrated ionic radius. The selectivity of the resin leads to preferential sorption of ions of higher ionic charge from dilute solutions, but of ions of lower charge from concentrated solutions. For ions of similar ionic charge the affinity is inversely proportional to the hydrated ionic radius. From the latter it appears that the exchanger exerts an "ionic sieve" action, whereby ions of larger size will be liable to progressive exclusion by the dimensions of the resin lattice. It follows therefore that the higher the resin crosslinking, the stronger will be
the tendency for exclusion of ions of larger ionic radius.

The behaviour of anions is less predictable than that of cations and is yet uncertain, but Kunin and coworkers (14) have presented the following order of affinities of different anions:

\[
\text{SO}_4^{2-} > \text{CrO}_4^{2-} > \text{Citrate} > \text{Tartrate} > \text{NO}_3^- > \text{AsO}_4^{3-} > \text{PO}_4^{3-} > \text{Molybdate} > \text{Acetate} > I^- > \text{Br}^- > \text{Cl}^- > \text{F}^- 
\]

This is nevertheless only a qualitative estimation.

**Anion exchangers in studies of complex systems.**

If a solution containing an anionic species \( A^- \) is left in contact with a given quantity of a strong anion exchanger previously completely converted to the \( B \) form, then after a time the following equilibrium will result:

\[
A^- + \text{Resin-}B \rightleftharpoons \text{Resin-A} + B^- 
\]

The position of equilibrium will depend on the concentration of \( A^- \) originally in solution and on the quantity of resin used. Providing the ionic species \( B \) is univalent, the quantity of \( B \) desorbed will give us a direct measure of the number of "active sites" occupied on the resin by \( A \). At this stage we may discuss the two methods of using ion exchangers:

**Column technique.**

If in the above example the \( B^- \) ion is removed from the sphere of reaction, then the equilibrium will be displaced to the right in the usual manner and eventually the
resin will be converted to the A form. This is the basis of the "column technique" as used in ion-exchange chromatography. A quantity of resin-water slurry is introduced into a glass column containing a sintered glass disc or a glass wool plug, and the air bubbles adhering to the resin beads are displaced by backwashing with water. A schematic diagram of the apparatus is given overleaf. A certain swelling of the resin will take place due to hydration and must be allowed for. The column is now ready for use and the exchanger may be converted to a desired anionic form by slow passage of an acid of suitable concentration. The desorbed ions are removed by the stream of solution, and excess acid is then displaced by washing with distilled water.

The dimensions of the column will of course depend on the purpose of the experiment. Thus for a conversion of small quantities of strongly basic anion exchanger for subsequent laboratory use, it was found convenient to employ a column 25 cm. long and of 2 cm. internal diameter, holding appx. 30 g. of the resin. The exchanger was soaked overnight in a small quantity of concentrated acid, diluted with water and introduced into the column. Conversion was then completed by passage of 1 litre of 2M acid followed by washing with water.

**Batch technique.**

The column method has been found very suitable
Apparatus for Ion-Exchange column work

- Eluting Solution
- Solution level
- Resin bed
- Glass wool plug
- Eluate
- Polythene tubing
in many applications of ion-exchange, especially in preparative work and for separation of ions on the industrial scale, but in the study of complexes it is generally considered too cumbersome. The "batch technique" consists simply in allowing an ionic equilibrium to take place between the resin and solution phases. The resin and solution are then separated by filtration and retained for analysis. The attainment of equilibrium can be accelerated by mechanical shaking, and an advantage of the method is that smaller quantities of both the exchanger and the solution can be used. Furthermore the rate of exchange after a given time may easily be determined if necessary, by a rapid filtration of solution from the resin under suction and subsequent analysis of the two phases.

Other advantages of the batch technique include an easier interpretation of results, and the fact that by suitable regulation of the quantities of resin and solution a sorption of ions sufficient for analysis may be obtained without disturbing overmuch the ionic system present in solution.

The batch technique was used throughout the present study of the condensation of polyacids.
Batch technique results and the study of condensed anions.

An interpretation of the data obtained by the batch technique can now be considered. If a quantity of strong anion-exchanger in the chloride form is shaken up with a convenient volume of a solution of a weak acid HA, an equilibrium will be set up between the anions sorbed by the resin in exchange for chloride ions, and the anions still in solution. The number of chloride ions liberated into the solution phase will equal the number of "active sites" filled up by the anions of the weak acid. If we assume that the anions are univalent and non-condensed, i.e. that:

\[ \text{HA} \leftrightarrow \text{H}^+ + \text{A}^- \]

then for each A^- sorbed there will be one Cl^- desorbed. In other words, the ratio of the number of A^- ions sorbed to the number of Cl^- ions desorbed will be unity. If however the acid gives rise to bivalent non-condensed anions A'' then the ratio will be 0.5. For convenience we will refer to this ratio as the "R" value of the system, so that:

\[ R = \frac{\text{Moles of A sorbed on the resin}}{\text{Moles of Cl desorbed}} = \frac{\text{Number of atoms of A}}{\text{per ionic charge}}. \]

(NB. The symbol HA denotes a molecule of an oxyacid with A as the central atom of the anion. For the sake of brevity oxygen atoms have been excluded from the formula.)
A simple system involving condensed and non-condensed anions of like charges.

As has been stated before, it is reasonable to expect by analogy with systems already studied by other methods (1) that the degree of anionic condensation will increase if the solution is concentrated, and for a solution at a particular concentration a decondensation will take place with a rise in the pH value. Furthermore the condensed acid will normally be stronger than the non-condensed one.

If the acid HA gives rise to condensed anions, then assuming the simplest system to exist we will have:

\[ nHA \rightleftharpoons nH^+ + A_n^- \xrightarrow{\text{PH}} n\left( H^+ A^- \right) \]

unionised acid condensed anions uncondensed anions

The displacement of the equilibrium to the right will be brought about by dilution, or by increasing the pH. In the above example the R value of the condensed species would be n, and that of the uncondensed would be unity.

Having selected the concentration of an acid HA to be studied a series of batch experiments may be performed, the pH of the solution in each experiment being adjusted to a desired value by addition of alkali. After equilibrium has been attained and the resin filtered off, the quantity of A sorbed and the chloride desorbed per equivalent of resin at a particular pH value may be determined, and the results may then be conveniently expresses in graphical form.
The data which would be expected for the system assumed above is given on the diagram below:

Thus at the natural pH of the solution, the acid (even in its condensed state) is too weak to provide a sufficient concentration of ions for sorption of A to take place. But as the pH of solution is raised an increasing concentration of the condensed species \( A_n^- \) is produced and is sorbed on the resin in exchange for chloride ions. A measurement of the R value over this pH range will give \( n \), which is the degree of condensation of the anion. As the pH is further raised a transition from \( A_n^- \) to the non-condensed A\(^-\) (derived from a
weaker acid) is expected, so that the sorption of A will come to a maximum and then begin decreasing. Since the ionic charge in this transition is assumed to be unaltered, the "desorption of chloride" curve will also exhibit a maximum at the same pH value.

At a higher pH, when the ion A\(^-\) is the only one sorbed, the R value will become one. At yet higher pH values the "desorption of chloride" curve may show an increase due to the formation of A\(^--\), alternatively a similar effect may be noticed due to the competitive sorption of hydroxyl ions by the resin, if the concentration of these in solution is sufficiently high.

A system approximating to the one just described was actually found by Everest and Salmon (6) to exist in solutions of germanates. Here the condensed pentagermanate ion Ge\(_5\)O\(_{11}\) is slowly replaced on the resin by the non-condensed monogermanate ion GeO\(_3\)\(^--\), and since the ionic charge does not alter, the maximum sorption of germanium and desorption of chloride are found to occur at the same pH value. The existence of an intermediate species HGeO\(_3\)\(^--\) was suggested by the authors, but the concentration of this would have to be very slight if it is present at all since it does not affect the position of the maxima. Above pH 13 a sudden rise in desorption of chloride indicated a preferential sorption of hydroxyl ions by the resin.
More complicated systems. The "chloride shift".

When the decondensation process involves a successive production of several ionic forms of decreasing degree of condensation, then providing the ions are all of similar charge the only effect on the maxima will be that they will become flatter, but they will still coincide. If an intermediate condensed species occurs preferentially over a wide range of pH, then this will be shown by a flattening of the R value graph in that region.

We will now discuss an important possibility where the decondensation process gives rise progressively to a multivalent ion and then to the non-condensed ion. Consider the following transition:

\[ A_n^- \leftrightarrow A_{n-x}^- \leftrightarrow A^- \]

At the natural pH of the acid the sorption of A will be negligible as before, but as the pH is increased there will be gradually increasing sorption of \( A_n^- \) (as shown on the diagram below) and therefore a corresponding liberation of chloride into solution. Over the initial range of pH, the R value will be n if A is being sorbed exclusively. On further increase in pH, the ionic equilibrium in solution will change in favour of \( A_{n-x}^- \) and the sorption of A will be expected to come to a maximum and then decrease, since a condensed ion is being replaced on the resin by a less condensed one deri-
ved from a weaker acid. But as a univalent ion is being
replaced on the resin by a multivalent one, the net effect
is that the desorption of chloride will continue to increase,
and will come to a maximum only as the ionic concentration
in solution changes in favour of the non-condensed $A^-$.ion.

The expected $R$ value trend in the above transition would be a gradual decrease from $R:n$ to $R:1$, and the
value $R: \frac{n-x}{2}$ corresponding to the ion $A_{n-x}^-$ should fall at a
pH value somewhere between that of the maximum sorption of
$A$ and the maximum desorption of chloride. The discrepancy
between the pH values of the two maxima will be referred to
in later sections as the "chloride shift".

To sum up, we may derive two criteria from the above considerations:

1) If the maxima coincide at the same pH, then we would expect that the ionic charge of the various anions sorbed on the resin is the same throughout the pH range considered.

2) If a chloride shift is found, it is to be expected that one or more intermediate forms having a greater ionic charge exist at some stage of the decondensation process. The identity of the latter must then be inferred by study of the R value graph.

Limitations of the method.

The abovementioned theoretical treatment is of necessity very simplified. Among others, the assumption is made that only two ionic forms (derived from the acid HA) exist in equilibrium at any time, or if more species exist then their concentration is negligible. In practice if a yet more complex system exists in solution, this can only be inferred by circumstantial evidence derived from ion-exchange results and from data obtained by other methods.

The ion-exchange techniques described depend on the supposition that the ionic forms sorbed have a dissimilar affinity for the resin. If however a mixture of ions of similar charge and affinity (and whose degree of condensation
does not differ markedly) exists in the low pH region, then
their resolution by this method would be at best difficult
and in most cases impossible.

Furthermore, as the R value at a particular pH
is itself obtained from the ratio of two separate determinat-
ions, it is clear that any inaccuracy in the latter will be
magnified in the former. The most interesting region, i.e.
that of low pH, is unfortunately the one where the sorption
and desorption of ions is very small compared to the concen-
tration of the acid in solution. An inaccuracy in these
determinations may therefore lead to serious errors in the
R value. For example it would be impossible to differentiate
by this method between the existence of a species such as
X_{10}^{-3} (R: 3.3) and X_{11}^{-3} (R: 3.7). Theoretically however it
would be possible to obtain an improved resolution in this
case by using resins of different degrees of crosslinking.
In this way the "ionic sieve" action of the resin lattice
may under the right conditions favour the sorption of one or
other of the species, depending on their hydrated ionic
radius.

Again, if the ionic transition brought about
by decondensation involves the presence of several intermedi-
ates, as in the following example:

\[ A_n^- \rightarrow A_{n-x}^- \rightarrow A_{n-y}^- \rightarrow A^- \]

it would be impossible to resolve the ions of intermediate
condensation, unless their concentration was appreciable and reasonably constant over a relatively large region of pH. their presence could then be inferred from a constancy or near-constancy of the R value in that region.

Ion competition.

An interesting attempt at improving resolution of ions in the batch method involves creating increased competition for the resin. For example if two ionic forms A and B compete for the chloride form of the resin, then the sorption of both can be depressed by increasing the chloride concentration of the solution phase, in this way enhancing the role of chloride ions in the competition for the resin.

If the relative affinities of A and B for the resin are sufficiently dissimilar, the addition of chloride will depress sorption of the ion with the weaker affinity for the resin to a greater extent, and the value of R will alter in such a way as to indicate the ion with the greater affinity.

A method which involves increasing the ion competition was utilised in the study of germanate solutions already referred to (6), and was successful in demonstrating the differential sorption of Ge$\text{O}_{11}^-$ and Ge$\text{O}_3^-$ on the resin. Addition of a known quantity of chloride tended to increase the R value to 2.5, and indicated the sorption of the pentagermanate ion.
Condensation and decondensation of an oxyacid, brought about by change in pH or concentration of solution, will result in an alteration of electronic configuration and therefore in the formation of compounds in different states of electric polarisation. It would be reasonable to suppose therefore that a decondensation reaction may be studied by light absorption and light refraction methods.

For example the well known colour change from orange to yellow brought about by addition of alkali to a dichromate solution, may be followed visually and is due to a decondensation to the chromate. The value of a spectrophotometric method in the study of this system was realised some years ago by Viterbi and Krausz (15) who investigated the equilibrium

\[ 2 \text{CrO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{Cr}_2\text{O}_7^{3-} + 2\text{OH}^- \]

and the effect on the visible and ultra-violet spectrum of adding large quantities of alkali in order to displace the equilibrium to the left.

Déribéré (16) studied the effect of the pH on the transmission of near infra-red rays through a number of solutions likely to give condensed anions. He found that although the effect on the visible and ultra-violet light was often considerable, there was little difference in the infra-red transmission of these solutions at various pH values.
From these results we may conclude that the most fruitful data will be obtained by examination of the ultra-violet absorption spectrum, unless the solution to be investigated is coloured in which case the visible light range may also be studied.

Method of "continuous variations"

A quantitative treatment for identification of compounds formed in solution by reaction of two components has been suggested by Job (17). This method of "continuous variations" has been extended and made applicable to the study of complex ions by Warren, Vosburgh and Cooper (18). Briefly, the formation of many complex ions can be represented by:

\[ A + nB \rightleftharpoons AB_n \]

where \( A \) is a metallic ion and \( B \) is the anion of the condensing acid. To determine \( n \), solutions of \( A \) and \( B \) of the same molar concentrations are mixed together in varying proportions and a suitable property of the resulting mixture is measured, e.g. light absorption or refractive index. The difference "\( D \)" is then determined between the value found, and the value calculated for \( A \) and \( B \) assuming no interaction between them. \( D \) is then plotted against the composition of the solution, a curve being obtained which should have a maximum (or minimum) if the property measured has a larger (or smaller) value.
for the complex ion than for the unreacted A and B.

Job has shown that the composition at which D is a maximum (or minimum) bears a simple relation to "n", and is independent of the equilibrium constant provided the molar concentrations of A and B are the same.

The method of continuous variations has nevertheless several disappointing limitations:

(1) When only one compound is formed (as in \( \text{Cr}_2\text{O}_7^{2-}\rightarrow\text{CrO}_4^{2-} \)) the results of spectrophotometry are independent of the wavelength. But when more than one compound is formed, as is more usual, the wavelengths for the investigation have to be judiciously selected because each ionic species will absorb in a different region of the spectrum. This leads to questionable results unless the conclusions can be adequately confirmed by other methods.

(2) In order for the results to be independent of the equilibrium constant, the molarity of solutions A and B must be the same. This results in a gradual dilution of B as a mixture of increasing A content is formed, and prevents use of the method as it stands for the investigation of systems which are not only dependent on pH but also on concentration.

Thus Warren and coworkers were able to use the method of continuous variations in demonstrating the chromate-dichromate transition, but could throw no light on the
species of higher degree of condensation whose existence has been shown by diffusion work (19). A method utilising the change in refractive index was also used recently by Plsko and Liska (20) in a very limited study of the condensation of molybdate ions. The variation in refractive index was nevertheless so small that it had to be measured by interferometry.

From these considerations it becomes clear that the method of continuous variations without modification is of little value in the present study. Rather than undertake a quantitative investigation of questionable value, it was decided to attempt a correlation between ion-exchange results and those of spectrophotometry on a qualitative level. To this end, the effect of pH on the ultra-violet absorption spectrum of the oxyacid was determined using solutions whose acid concentration was maintained constant throughout. The pH was regulated by addition of alkali, while the total volume of the mixture was kept constant by addition of a suitable quantity of water. In this way, the spectrophotometric results obtained depend on the equilibrium constants of the various reactions brought about by decondensation. As these constants are unknown, the data cannot be interpreted quantitatively.
PART II

STUDIES OF SOLUTIONS OF BORATES
Early work.

The chemical constitution of boric acid has been much studied in the last half-century. As early as 1903, Auerbach concluded from distribution experiments (21) that borate ions unite with excess boric acid in solution to form polyborate ions, the tendency for the formation of such ions being appreciable. He stated that the type of polyborate ion depends on the concentration of boric acid in solution and suggested that in presence of the saturated acid at 25°C the condensed anions contain an average five atoms of boron for each negative charge. Auerbach allowed boric acid and another weak acid (arsenious) to compete for a quantity of sodium hydroxide insufficient for complete neutralisation, and stated that his results suggest that polyboric acids are stronger than the non-condensed boric and arsenious acids.

One of the first extensive investigations was due to Kolthoff (22) who in 1926 examined the conductivities of boric acid solutions from 0.1 to 1.0 molar and found that the acid does not obey Ostwald's dilution law. The almost hundredfold rise in the dissociation constant observed was explained by suggesting the formation of a tetraboric acid whose dissociation constant was calculated to be $6 \times 10^{-8}$. Later Kolthoff and Bosch (22) examined a series
of borax and boric acid-sodium metaborate solutions. They explained the abnormal pH trend observed on dilution by applying the law of mass action and assuming the formation of condensed anions, especially those derived from a stronger penta-boric acid which was thought to be formed in solutions of high boric acid concentration. At concentrations below 0.1M no condensed ions could be detected. These results are claimed to be of a qualitative nature only, but their interpretation agrees with the conclusions reached by Auerbach. The dissociation constant of monomeric boric acid was calculated by Kolthoff and Bosch to be $5.5 \times 10^{-10}$ at $18^\circ C$.

Kolthoff's reasoning was soon to receive the support of a cryoscopic study of borate solutions due to Menzel (23), who examined solutions of the alkali metal mono-, di- and penta-borates at various concentrations. Menzel concluded that monoborate ($B_2O_2^{-}$), tetraborate ($B_4O_7^{-}$) and pentaborate ($B_5O_5^{-}$aq.) ions were all present in the respective solutions, but the pentaborate was extensively dissociated into the lower polyborates, as shown by the Van't Hoff "i" factor being only 3.0-4.5 in the most concentrated pentaborate solutions studied.

Menzel also attempted conductimetric measurements, but the data obtained gave somewhat ambiguous results. These studies were some years later extended by Thygesen (24) who measured the conductivities of boric acid solutions of
various concentrations, and found that in the 0.028-0.125 M range the overall dissociation constant was almost stable, hence he concluded that up to ca. 0.1M solutions, boric acid behaves as a weak monobasic and monomeric acid. Thygesen found that the curve of molecular conductivity versus molarity shows a sharp minimum when the molarity is appx. 0.1, from which he deduced that above this concentration there is increasing formation of polyboric acids of a higher order. He calculated the various possible dissociation constants of boric acid at concentrations 0.25-0.6M, assuming degrees of condensation from unity (uncondensed) to five (pentaboric acid). It was found that $K_3$ showed the greatest constancy, from which the predominance of the univalent triborate may be inferred, but Thygesen thought it more probable that a mixture of univalent and bivalent tetraborate exists in this concentration range.

In 1943 Menzel and Schultz (25) reexamined sodium monoborate solutions cryoscopically, confirming previous results by this method (23), and found that even with borate concentrations as high as 2M no deviation attributable to polymerisation could be detected. From this it can be inferred that at high pH values boric acid-alkali solutions are non-condensed irrespective of their concentration. This is confirmed by a Raman spectra study of sodium borate performed by Edwards, Morrison, Ross and Schultz (46).
Recent work.

At this stage, the study of boric acid entered increasingly into the field of polemic, chiefly due to the work of Souchay and of Carpeni. In a joint publication (26), Carpeni and Souchay described studies of the neutralisation curves of solutions of boric acid at concentrations between 0.03 and 0.26 M. They found that the curves obtained all intersected at one point irrespective of the concentration of the acid. This was later to be termed the "isohydric point" (point of equal hydrogen ion concentration) by Carpeni (27). Following the previous theoretical treatment by Bye (28) Carpeni and Souchay interpreted their studies on the basis of the existence of the ions $\text{B}_5\text{O}_3^-$, $\text{HB}_4\text{O}_7^-$ and $\text{BO}_2^-$, which they said were formed successively during the neutralisation process. They emphasised that the condensation of boric acid would be affected by two separate factors: the total boron concentration and the pH, the importance of which had not been fully appreciated by previous workers.

Subsequently Carpeni reconsidered these conclusions, and in particular he has put a different interpretation on the significance of the isohydric point (29). He considers that if an isohydric point is obtained for an acid undergoing a condensation-degradation reaction, its very presence is a result of the existence of a unique ionic equilibrium in solution. He postulates that this equilibrium
is between two (and only two) ionic species such that one species is simple and the other condensed. The existence of the simple species is favoured by high pH and by low concentration.

In the case of boric acid, Carpeni maintains (30) that the only two ions involved in the equilibrium are the monoborate $H_2BO_3^-$ and the bivalent pentaborate $HB_5O_9^-$ . Furthermore he attempts to assign structures to all solid borates and explain anomalies in their behaviour on the basis of the existence of these two ionic forms only (31).

Recently, in a more detailed study of borate solutions, Carpeni has found that the position of the isohydric point is unchanged on varying the boron concentration from 0.01M to saturation, or on varying the temperature from 5 to 95°C . Also, at room temperature $KB_5O_8$ is the borate salt in equilibrium with the isohydric solution, whereas at 85-95°C this salt is $K_2HB_5O_9$ . He again emphasised his view that only $HB_5O_9^-$ and $H_2BO_3^-$ ions occur in borate solutions (32).

Carpeni's revised conclusions have been strongly criticised by Souchay and others (33) on theoretical grounds involving principally the interpretation of the isohydric point.

The concentration dependence of the condensation of boric acid is again illustrated by the work of Stetten (34). He showed by means of pH measurements that in the concentration
range 0.1 to 0.6M a polyboric acid exists in solution, with an average composition of 3.2 atoms of boron per molecule. The presence of this acid could not be detected in < 0.1M solutions. Stetten's work was extended by Edwards (35) who explains his results on the basis of a trimer, and suggests two possible structures of the latter. Above 0.6M solutions of boric acid, the presence of a hexamer is suggested by Edwards but no reasonable structure can be found for it.

The views of Souchay on the nature of borate solutions have been recently summarised and amplified by Lourijsen-Teyssedre (36), who used pH measurements, partition coefficient data on the distribution of boric acid between water and pentyl alcohol, and cryoscopic methods based on the depression of the transition point between sodium sulphate decahydrate and the anhydrous salt. Lourijsen-Teyssedre concluded that in boric acid solutions unionised HBO₂ molecules were largely present, but on addition of alkali their concentration decreased being offset by an increased concentration of B₅O₈⁻, B₄O₇⁻, and BO₂⁻ ions in solution. Initially it was the B₅O₈⁻ ions which were the most quickly formed, their concentration reaching a maximum at an alkali-boron ratio of ca. 0.2:1 (for 0.25M boric acid solutions), when about one third of the total boron was present as B₅O₈⁻ ions. Further additions of alkali caused a rapid decondensation of these ions, which had entirely disappeared from
solution at an alkali:boron ratio of ca. 0.4:1. The concentration of \( \text{B}_4\text{O}_7^{--} \) reached a maximum at an alkali:boron ratio of ca. 0.5:1, about 50% of the boron then being present as this ion. At higher ratios the concentration of \( \text{B}_4\text{O}_7^{--} \) decreased smoothly until it reached zero at a ratio of 1:1.

The concentration of \( \text{BO}_2^- \) ions increased only slowly on initial addition of alkali, but at high alkali ratios it became the predominant ion in solution. Lourijsen-Teyssedre's diagram to illustrate the above transition is reproduced below.

![Diagram showing the proportion of ions or molecules in solutions of alkali:boron ratios](image)

Lourijsen-Teyssedre also pointed out that the condensation of boric acid was concentration dependent, an increase in boron concentration causing an increase in the proportion of condensed borate ions present. Below a boric acid concentration of ca. 0.1M no \( \text{B}_5\text{O}_8^- \) ions could be detected in solution whilst the quantity of \( \text{B}_4\text{O}_7^{--} \) ions was greatly reduced.

A later potentiometric study by Lefebvre (37)
agrees in general with the above, but the existence of $\text{H}_4\text{O}_7^-$ is included in the interpretation. Lefebvre's results appear to prove that a tricondensed ionic form does not exist.
SCOPE OF THE PRESENT WORK

An examination of the previous section indicates that condensation of boric acid is indeed dependent both on the concentration of solution and on the pH. A high proportion of published work suggests that the most condensed ionic species formed is the pentaborate, whereas opinion is divided as to the nature of the ions of intermediate condensation. Conductivity, potentiometric and pH measurements seem unable to distinguish between the presence of either $\text{B}_4\text{O}_7^{--}$ or $\text{HB}_4\text{O}_7^-$ or mixtures of both these forms as the intermediates, but most workers are agreed that at high pH and below 0.1M concentration the $\text{BO}_2^-$ ion is present as the sole anionic species.

In the work to be described, an attempt will be made

(a) to define the most condensed species formed in an almost saturated boric acid solution at room temperature.

(b) to investigate the effect of concentration on sorption of boron on the resin under varying conditions of pH.

(c) to suggest the species of intermediate condensation present in solution at various stages of neutralisation.

(d) to test the validity of Carpeni's postulate, whereby the ionic equilibrium is due solely to the two species $\text{H}_2\text{BO}_3^-$ and $\text{HB}_5\text{O}_9^-$. 
EXPERIMENTAL

I. Preliminary

Anion exchanger.

Preliminary studies indicated that boric acid is sorbed by the strong base anion-exchanger Amberlite IRA 400 in the chloride form. This is a benzyl trimethylammonium type resin manufactured by Rohm and Haas Co. The exchanger was prepared from the hydroxide form by leaving this to stand for some hours in contact with approximately 5M hydrochloric acid, then washing into a suitable column (cf. p. 12) containing a sintered glass disc, and completing the conversion by treatment with ca. 2N hydrochloric acid. The resin in the column was then washed free of excess acid by passage of de-ionised water until the washings were neutral to methyl orange and gave negligible cloudiness with silver nitrate. The resin was air-dried and sieved to constant mesh size before use.

Washing water.

Throughout these studies, all water used for washing the resin was previously distilled, and immediately before use it was passed through a column of Bio-deminrolit (a mixed-bed resin manufactured by the Permutit Co.) to complete the de-ionisation process.
Preparation of solutions.

Stock solutions (ca. 0.9, 0.6, 0.3 and 0.03M) were prepared by dissolving analytical grade orthoboric acid in boiled-out distilled water. Samples of the above solutions were pipetted out (50 ml.) and their pH was altered by addition of various quantities of sodium hydroxide solution, the total volume of the mixture being adjusted to 75 ml. by addition of water. Graphs of the quantity of NaOH added versus the pH of solution obtained could then be plotted. By using such graphs, solutions of any desired pH could be made up, the boric acid concentration of the final solutions obtained being 0.6, 0.4, 0.2 or 0.02M depending on the molarity of stock solution used.

It was found necessary to measure out samples of the 0.9M solution at a temperature of 30°C, since its boric acid content exceeds that of saturated solutions at room temperature. At 15°C the solubility of boric acid is approximately 41 g. per 1000 g. of water, which gives a 0.66M solution (39). The following procedure was therefore found more convenient in investigating almost saturated boric acid solutions: a stock saturated solution was prepared at 15°C, the temperature being chosen as that just below the lowest laboratory temperature. The solution was then filtered to remove any undissolved boric acid, and was next divided into two - one part being adjusted to a convenient high pH by
addition of solid sodium hydroxide. Measurements of pH were then made on mixtures made up of various proportions of the two solutions, and the results were expressed graphically as before, so that solutions of any desired pH value could be subsequently formulated.

Glassware etc.

All glass apparatus used was previously treated with a sulphuric acid-potassium dichromate cleaning mixture, and rinsed out with distilled water. The rubber bungs used on flasks were previously boiled in a weak solution of sodium carbonate, followed by boiling in dilute hydrochloric acid and then in several quantities of distilled water.

II. Equilibrium experiments using the batch technique.

Suitable quantities (0.5 or 1.0 g.) of the resin were weighed out into a series of dry 150 ml. conical flasks and 75 ml. samples of a boric acid solution (adjusted in pH as described above) were added to the resin. The resin-solution mixtures were stoppered with rubber bungs. Nine days were allowed for equilibrium to be established between solution and resin phases, each flask being mechanically shaken for at least 2 hrs. each day. Experiments for longer times showed these periods to be adequate.

Each solution was then separated from the resin
by filtration through a small dry column (1 cm. internal diameter, 10 cm. long) containing a glass wool plug. The filtrate was retained for analysis of the boron content and for pH measurements.

The resin was then flushed into the column and rapidly washed with a stream of water (ca. 50 ml.) under suction, to prevent interaction between the resin phase and the partially diluted solution. A further 300 ml. of water were then passed slowly through the column to complete the washing. All washings were rejected. The chloride still sorbed on the resin was then eluted with 300 ml. of 2N nitric acid, the rate of elution being adjusted to take appx. 8 hrs. The concentration of chloride in the eluate was then determined. (NB. Annex I. describes expts. on washing the resin).

To find the capacity of the resin sample, it was completely converted to the chloride form by treatment with 300 ml. of 2N hydrochloric acid, and washed free of excess of acid. The chloride was then eluted with 300 ml. of 2N nitric acid as before, and determined in the eluate. The capacity was found to vary from sample to sample (see p. 9-10) and the results have been expressed in moles of chloride sorbed per equivalent of resin.

Since the quantity of chloride desorbed by the borate ions was found to be small, it could not be determined accurately in the solution phase and was therefore calculated
by difference as follows:

\[
\text{chloride desorbed} = \left( \text{capacity of resin} \right) - \left( \text{chloride still sorbed} \right)
\]

III. Analytical methods.

Boron was determined in solution as boric acid. Aliquot portions (10 ml.) of the filtrate were first neutralised to methyl-red by dilute hydrochloric acid, then a slight excess of glycerol or mannitol was added and the solutions were titrated to phenolphthalein with standard sodium hydroxide. It was found that sharper end-points were obtained using mannitol, since mannitoboric acids are stronger than glyceroboric (40), but satisfactory results were also obtained with glycerol provided this was neutralised to phenolphthalein before use. In titration of 10 ml. portions of 0.66M boric acid, an addition of appx. 4 g. of mannitol or 25 mls of glycerol proved sufficient.

The quantity of boron sorbed on the resin was obtained by difference from the boric acid concentration of the filtrate, and the initial concentration of the solution phase before addition of the resin.

Chloride was determined gravimetrically as silver chloride. Measurements of pH were made with a commercial-type pH
meter incorporating a glass electrode and a saturated calomel electrode. For strongly alkaline solutions an "Alki" glass electrode was used (Cambridge Instrument Co.).

IV. Spectrophotometric experiments.

A "Unicam" single beam spectrophotometer incorporating a hydrogen lamp was used, and the fused silica cells were 1 cm. in crosssection.

Preliminary studies showed however that in the concentration range studied, boric acid solutions do not absorb in the wavelength region 2000-3200 Å.
ION-EXCHANGE RESULTS

The five concentrations of boric acid-sodium borate solutions studied were 0.66, 0.6, 0.4, 0.2 and 0.02M, and 75 ml. samples of these solutions contained 50, 45, 30, 15 and 1.5 millimoles of boron respectively.

The resin chloride from 1.0 and 0.5 g. of the exchanger was approximately 3 and 1.5 milliequivalents respectively.

Choice of the quantity of exchanger used

Preliminary batch experiments were made using only 0.25 g. of the resin. However the quantities of boron sorbed on the resin were found to be inconveniently low, and the experiments were abandoned in favour of those using 0.5 g. of the resin. For later work, 1.0 g. samples were used in the interest of yet greater accuracy. Nevertheless, as can be expected from the law of mass action, doubling the quantity of resin used (while keeping the volume of solution constant) does not double the amount of boron sorbed, although it appreciably increases the sorption. Also, the use of larger quantities of exchanger increases the manipulation difficulties and requires larger volumes of eluting solutions. A compromise has therefore to be found between the quantity of resin used and the total sorption of boron obtained.

Thus in later work on boric acid, and subsequent
on solutions of arsenites and tellurates, it was found more convenient to use 1.0 g. resin samples.

Presentation of results.

Results for the various concentrations of boric acid studied are shown in graphical form in figures 1-7, and also in tables 1-6. The boron sorbed and chloride desorbed at a particular pH value are expressed in moles per equivalent of resin. The ratio of boron sorbed to chloride desorbed at a particular pH value gives the R value as described previously (p.14).

Unless specifically stated, all pH values reported in this work are those of the equilibrated solutions. But it was found that although the pH of boric acid solutions changed slightly on attaining equilibrium with the resin, nevertheless this change was not greater than ca. 0.3 of a pH unit compared with the initial value. The greatest pH change occurred in the very low and very high pH regions.

In the 0.66 and 0.6M solutions the sorption of boron reached a maximum at pH 7.6, and the maximum chloride desorption occurred at pH 8.5. For 0.4 and 0.2M solutions this boron maximum came at pH 8.0 and 8.5; whereas the chloride maximum occurred at pH 8.7 and 9.1 respectively. There was therefore a divergence between the positions of the maxima, i.e. a "chloride shift" (cf. p.18) which increased with
increasing boron concentration of solution. The results appear to be independent of the quantity of exchanger used. The chloride shift for boric acid is shown in graphical form in fig.1 below. It appears to reach a steady value when the concentration of boric acid in solution becomes ca. 0.6M.

For 0.02M solutions the desorption of chloride did not reach a maximum, for reasons which will be discussed later, and the chloride shift for this concentration was taken to be zero since the R value graph (fig.4) indicates no condensed species.

The following data have been collected from batch
experiments using 0.5 g. of resin and 75 ml. of solution:

(a) Fig. 2 shows the relation between the concentration of solution and the maximum quantity of boron sorbed. This appears to follow an approximately straight-line relationship for concentrations above 0.1M, but occurs at different pH values depending on the concentration of solution, as will be apparent on examination of figures 4-7.

(b) The relation between concentration of boric acid and the maximum quantity of chloride desorbed is also given in fig. 2. It appears that this maximum tends to reach an almost steady value as the concentration of boric acid becomes high.
The maximum amount of boron sorbed from solution by 0.5 g. of the resin was 9%, 11%, and 12% for the 0.6, 0.4 and 0.2M solutions. For 0.02 and 0.66M solutions, where 1.0 g. of resin was used, this figure was 13% and 12% respectively.

(c) The pH value at which boron is first sorbed from solution varies with the concentration, and is given in fig. 3. The values are only approximate as they have been obtained by extrapolation. Direct determination in this range of pH is difficult and inaccurate due to the small quantities of boron sorbed on the resin.

![Fig. 3](image-url)
It may be seen that as the concentration of boric acid is increased to saturation, the pH at which boron is first sorbed tends towards a steady value in the region of pH 4.9.

**THE STRENGTH OF BORIC ACID**

The dissociation constant of boric acid has been determined by several workers, but its value is so small that the results are of doubtful accuracy.

Thus $K_1$ is quoted variously as $5.7 - 6.4 \times 10^{-10}$ which makes the uncondensed orthoboric acid approximately equal in strength to p-chlorophenol and weaker than hydrocyanic acid. The second dissociation constant $K_2$ is estimated as $1.8 \times 10^{-13}$ and $K_3$ as $3 \times 10^{-14}$ which is of the order of the acid strength of glucose and mannitol respectively. (42,43)

Nevertheless boric acid is well known to form chelate complexes with certain cis-polyhydroxy compounds, with a consequent decrease in the firmness of the bonding of its acid hydrogen. This permits the titration of boric acid as a relatively strong acid (44), (cf. p.40).
Fig. 4

0.02 M Boric acid
(1.0 g of resin)

Moles per equiv. of resin

- ○ boron sorbed
- △ chloride desorbed
- ⋄ R value (calculated from the boron & chloride graphs)

pH
Fig. 5

0.2 M Boric Acid
($\frac{3}{4}$ gm resin samples)

Moles per Equivalent of Resin vs pH

- O Boron sorbed
- △ Chloride desorbed
- ◇ "R" value
Fig. 6
0.4 M Boric Acid
(0.5 g resin samples)

N moles per equiv. of resin

\[ R^n \]

- ○ sorption of boron
- △ desorption of chloride
- ◊ R value.
in Boric Acid.

sorption of boron

desorption of chloride

"R" value

(0.5g. resin samples)
DISCUSSION

From the present study it appears that boric acid is not strong enough to be sorbed on the resin at its natural pH, under the conditions of an equilibrium experiment. The pH must first be raised by addition of alkali, e.g. to form sodium borate which dissociates giving a higher quantity of borate ions than does free boric acid. The sorption of borate ions therefore occurs at a higher pH value, at which the boric acid-sodium borate mixture provides a sufficient quantity of borate ions.

For example in an equilibrium experiment using 1.0 g. of resin in the chloride form, and 75 ml. of 0.66M boric acid, the pH of solution would have to be altered from 3.9 to ca. 4.7 before sorption could be detected.

Nevertheless, as shown in fig.3 p.46, the higher the boric acid concentration of solution, the lower is the pH value at which borate ions begin to be sorbed.

I. Relatively weak borate solutions

0.02M Boric acid experiments. (fig.4 and table 1)

The R value obtained in the pH region 7.5-8.0 is unity, which indicates sorption of monoborate ions $\text{H}_2\text{BO}_3^-$. Monoborate must also be the predominant form existing in solution at this concentration, as one would expect any ions deri-
ved from the stronger polyboric acids to be more readily sorbed on the resin. At higher pH values R steadily decreases, which may be due to sorption of small amounts of HBO\(_3^-\) (R: 0.5) or B\(\text{O}_3\)\(^{-}\) (R: 0.33). Sorption of a species with a higher ionic charge is indicated by the fact that whereas sorption of boron comes to a maximum at pH 9.5, the chloride desorbed continues to increase throughout the whole pH range studied.

However, overmuch significance cannot be attributed to the variations observed at higher pH, as the results cannot be calculated with great accuracy owing to the small amount of boron sorbed from 0.02M solutions. The possibility of sorption of small quantities of carbonate or hydroxide ions, to give fractional R value, cannot be completely discounted although the concentration of hydroxide ions only becomes appreciable above pH ca. 11.

It is of interest that no boron sorption by 0.25 g. quantities of resin could be detected from 0.002M solutions (75 ml. samples).

II. Borate solutions of higher concentration.

Introduction.
The R values (figs. 5-7, tables 2-5) obtained with 0.66-0.2M boric acid solutions indicate that condensed borate ions are being sorbed by the resin at pH values below ca. 10. The degree of condensation is greater at lower pH
and at higher boron concentrations of solution. Table 6 shows the maximum R value obtained for each of the concentrations studied.

Table 6.

<table>
<thead>
<tr>
<th>Concentr. (M)</th>
<th>Maximum &quot;R&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.66</td>
<td>5.0</td>
</tr>
<tr>
<td>0.6</td>
<td>5.0</td>
</tr>
<tr>
<td>0.4</td>
<td>ca4.0</td>
</tr>
<tr>
<td>0.2</td>
<td>ca3.0</td>
</tr>
<tr>
<td>0.02</td>
<td>1.0</td>
</tr>
</tbody>
</table>

At pH values greater than ca. 10, R tends towards unity irrespective of the boron concentration of solution, indicating the progressive sorption of a univalent monoborate ion. This would agree with the views of Carpeni (30-32), Souchay (33) and Lourijsen-Teyssedre (36) all of whom consider that monoborate ions are the chief species existing in solution in this pH region at all boron concentrations.

That monoborate ions are the sole species present in sodium borate solutions (which possess a pH greater than ca. 10) over a wide range of concentrations, has been shown by other workers using cryoscopy (25,45) and Raman spectra (46) methods.
The chloride shift obtained with all 0.2-0.66M solutions indicates the existence of an intermediate polyvalent condensed species, whose R value would be less than five (cf. p.18 seq.). An interpretation of the present results can be given on the basis of the equilibrium:

\[ \text{B}_5\text{O}_8^{-} \rightleftharpoons \text{B}_4\text{O}_7^{-} \rightleftharpoons \text{H}_2\text{B}_3\text{O}_3^{-} \]

existing in solution, in such a way that dilution or a rise in pH displaces the equilibrium to the right. These are in fact the conclusions reached by Lourijsen-Teyssedre (36) who states further that the formation of penta-, tetra- and monoborate ions overlaps to some extent.

0.6M boric acid experiments. (fig.7 and table 4)

Let us consider the data obtained for 0.6M solutions in the light of the above equilibrium. The maximum R value obtained is five, and remains unaltered on increasing the concentration to near-saturation (i.e. 0.66M boric acid solution, see table 5). This indicates sorption of \( \text{B}_5\text{O}_8^{-} \) and it seems probable that in this region of pH the concentration of ions other than the pentaborate is negligible in solution. A decondensation to \( \text{B}_4\text{O}_7^{-} \) on increasing the pH will explain the chloride shift, since the peak in boron sorption at pH 7.6 will be due to the replacement of pentaborate ions by those of a slightly weaker and less condensed acid, whereas desorption of chloride continues to increase due to replacement of
a univalent ion on the resin by a bivalent one. Sorption of chloride then comes to a maximum at pH 8.5, due to an increasing sorption of the much weaker singly charged monoborate ion $\text{H}_2\text{BO}_3^-$. 

Which of the polyborate ions will be sorbed on the resin under given circumstances, is governed by the following three factors:

(i) The degree of dissociation of a particular polyboric acid, i.e. the concentration of the respective polyborate ion in solution.

(ii) The charge on the ion, and the overall boron concentration of solution.

(iii) The hydrated ionic radius of the anion.

The first two factors may at times reinforce, or work in opposition depending on the conditions.

If the bivalent tetraborate ions existed predominantly in a certain pH range, this would be indicated by a near-constancy in the R value curve in this region. Furthermore, $R: 2$ would occur somewhere between pH 7.6 and 8.5, the values for the boron and chloride peaks (see p.19). This is not obtained in practice, and it is probable that the $\text{B}_4\text{O}_7^{2-}$ ion (when it exists) is always present with a relatively large quantity of $\text{B}_5\text{O}_8^-$ or $\text{H}_2\text{BO}_3^-$ or both, depending on the pH. This is in agreement with the data obtained by Lourijsen-Teyssedre, and already referred to on p.33.
The interpretation given above can be briefly summarised as follows:

(a) Up to ca. pH 6.2, \( B_5O_8^- \) ions are sorbed on the resin almost exclusively.

(b) As the pH rises, the sorption of \( B_5O_8^- \) increases, along with progressively greater quantities of \( B_4O_7^- \), giving rise to a steady decline of the \( R \) value.

(c) The concentration of \( B_4O_7^- \) should reach a maximum somewhere between pH 7.6 and 8.5, but the \( R \) value in this region is well above 2 which shows that appreciable quantities of the pentaborate are still sorbed on the resin.

(d) A small quantity of \( H_2BO_3^- \) is possibly present in solution even at low pH. The sorption of the monoboriate becomes significant at ca. pH 8.5, and is responsible for
the decline in chloride desorption at higher pH values. Nevertheless, the sorption of $B_5O_8^-$ and $B_4O_7^{--}$ is still appreciable in the pH region 7-10, although that of the pentaborate is on the decline.

(e) Sorption of the monoborate becomes exclusive at pH ca. 11 where the R value approaches unity.

In this way it is probable that all the three species referred to are capable of existing together over a relatively large pH range, which tends to disagree with the postulate put forward by Carpeni (30) that an equilibrium exists due to two ionic species only, one of which is the $HB_5O_9^{--}$ ion.

From the results for 0.6M solutions, an attempt has been made to calculate the proportion of each ionic species sorbed on the resin at various pH values. Of necessity, for the purpose of calculation, it had to be assumed that only two different ionic species were present at any particular pH value, but the results are thought to be sufficiently of value to be included in the present description (fig.8). The method used in calculating the data for fig.8 is described in Annex II in the final pages of this work.

At pH values above ca. 8.9 a salt crystallises from the equilibrium solution on standing. On analysis, this salt was found to have a Na:B ratio of 1:2, probably corres-
Fig. 8

Sorption of Penta-, Tetra-, and Monoborate ions, calculated assuming only two species to be present at a time.

Calculated sorption of boron:
- as $B_5O_8^-$ ions
- as $B_4O_7^{2-}$
- as $H_2BO_3^-$
ponding to Na₂B₄O₇. It is significant that this is the pH region at which the results in fig. 8 indicate that the concentration of B₄O₇⁻⁻ sorbed on the resin approaches a maximum.

0.4 and 0.2 M boric acid experiments. (figs. 5-6, tables 2-3)

As the boron concentration in solution is diminished, the trend in R values indicates that progressively less pentaborate ions are sorbed on the resin relative to the bivalent tetraborate ions. Thus at pH values corresponding to those of the chloride shift (8.0-8.7 for 0.4 M, and 8.5-9.1 for 0.2 M solutions) the R values tend increasingly towards two. Furthermore, the decrease in the chloride shift observed on decreasing the boron concentration (fig. 1, p. 44) is due to the decrease in concentration of both the pentaborate and the tetraborate ions in solution, and therefore a smaller pH range in which the former decondenses into the latter.

Strength of the polyboric acids, and the relative affinity of the polyborate ions for the resin.

So far it has been assumed that the affinities of the pentaborate and the tetraborate ions for the resin do not differ widely, but that the strength of pentaboric acid is nevertheless slightly higher than that of tetraboric. That this assumption is reasonable can be deduced from the work of Kolthoff (22), Thygesen (24) and Stetten (34) who
showed that the polyboric acids are all of comparable strength although considerably stronger than monoboric acid.

A series of "chloride competition" batch experiments were performed on 0.2M solutions in an attempt to find a definite change in the R value, which would indicate the ion with the stronger affinity for the resin (cf. p.22). Although 1.0 g. resin samples were used and the chloride concentration of solution was 1.0 mmoles per 75 ml. (added as sodium chloride), only a slight increase in the value of R was observed, which implies that the affinity of the pentaborate ions for the resin is not much greater than that of the tetraborate at this concentration. It may be, however, that the pentaborate is not present in sufficient quantity for any marked difference in sorption to be obtained. The results are given in table 7.

III. Other interpretations of the present work.

Although the results described can be completely interpreted on the basis of the conclusions of Lourijsen-Toyssedre, i.e. the presence in solution of the penta-, tetra- and monoborate ions, nevertheless other interpretations could be advanced.

The chloride shift could likewise be explained by assuming the ion HB5O9− (R: 2.5) postulated by Carpeni (32)
to be sorbed over the middle pH range either in place of, or as well as the bivalent tetraborate ion. It is also possible and logical that the ion HB₄O⁷⁻ (R: 4) (37) occurs as an intermediate between the B₅O₇³⁻ and B₄O₇⁴⁻ ions.

At this stage it would be unwise, by consideration of ion-exchange results alone, to favour any one of these interpretations in particular. Nevertheless, it must be pointed out that (i) during the course of experiments on 0.6M boric acid solutions, a salt thought to be Na₂B₄O₇ did in fact crystallise out in the pH range at which from ion-exchange work the concentration of B₄O₇⁴⁻ is thought to approach a maximum; (ii) Lourijsen-Teyssedre's interpretation is in agreement with our present knowledge of solid borates. A short review of these is given below.

IV. Comparison with solid borates.

Polyborates, which exist in unknown quantities in solution, are known to be plentiful in the solid state and various degrees of condensation have been attributed to them (4, 47). Although the complex species which exist in the solid state are not necessarily the same as those which exist in solution, it is interesting at this stage to compare the data so far considered with the results of investigations of solid borates.

An early study (48) of the system M₂O-B₂O₃-H₂O
reveals that the following salts will separate from solution at 30\(^\circ\)C.

- \( LiBO_2 \)
- \( Li_2B_4O_7 \times \text{aq.} \)
- \( LiB_5O_8 \ 5 \text{aq.} \)
- \( NaBO_2 \)
- \( Na_2B_4O_7 \ 10 \text{aq.} \)
- \( NaB_5O_8 \ 5 \text{aq.} \)
- \( KBO_2 \)
- \( K_2B_4O_7 \ 4 \text{aq.} \)
- \( KB_5O_8 \ 4 \text{aq.} \)

A later study (49) of the system \( Na_2O-B_2O_3-H_2O \) at 60\(^\circ\)C shows presence of the following salts:

- \( Na_2O.5B_2O_3.10H_2O \) pentaborate decahydrate (\( NaB_5O_8 \ 5H_2O \))
- \( Na_2O.2B_2O_3.5H_2O \) borate pentahydrate (\( Na_2B_4O_7 \ 5H_2O \))
- \( Na_2O.B_2O_3.4H_2O \) metaborate tetrahydrate (\( NaBO_2 \ 2H_2O \))
- \( Na_2O.B_2O_3.H_2O \) metaborate monohydrate
- \( 2Na_2O.B_2O_3.H_2O \) hemihydrate.

In the study of ammonium borates, the tetaborate and the pentaborate were also found.

It is clear therefore that the solid alkali borate systems tend to support the claim for the existence of the penta-, tetra- and monoborate ions in solution. However other borates are known which do not fit this classification:

- e.g., \( Ca_2B_6O_{11} \ 5H_2O \) Colemanite.
- \( 2Mg_3B_8O_{15}.MgCl_2 \) Boracite.
- \( Na_2B_4O_7.Ca_2B_6O_{11} \ 16H_2O \)

Also, phase studies of the system \( B_2O_3-H_2O \) are claimed to
indicate that the only stable hydrates are HBO₂ (metaboric acid) and H₃BO₃ (orthoboric acid). The hemihydrate H₂B₄O₇ (tetraboric acid) although reported in the older literature apparently has no stable existence (50). Other vapour pressure studies of boric acid (51) appear to show that it is present in the solid state as nB₂O₃.H₂O where n has values from 1 to 8. Similarly Michel (52) describes a series of solid borates which give B₂nO₃n+1 where n is 1-6.

From X-ray diffraction work, Zachariasen (53) has shown that crystalline boric acid consists of a vast network of B(OH)₃ groups held together by hydrogen bonds, and Raman spectra studies tend to support this conclusion (54). It may be therefore, that on dissolving a quantity of boric acid in water, the hydrogen bonds between boric acid molecules are progressively broken down and replaced by bonds between boric acid and water molecules. In this way a large number of ionic species may be formed whose degree of condensation gradually decreases with dilution. Of the various borate species formed, only some may exist in sufficient quantity to be detected - or be stable enough to form solid salts.

V. Conclusions and general comments

The following outstanding points can be drawn from this work:
(a) No condensed borate ions appear to exist in 0.02M solutions of boric acid.
(b) The most condensed species sorbed on the resin from concentrated solutions is the univalent pentaborate, which agrees well with the conclusions reached by the majority of previous workers.

(c) It is apparent that a bivalent condensed species exists as an intermediate.

(d) Results can be interpreted if it is assumed that an equilibrium exists in solution (above 0.02M) between the univalent pentaborate, bivalent tetraborate and the univalent monoborate, although other ionic species may also be present.

(e) Decondensation of polyborate ions is achieved by dilution or by raising the pH of the solution.

(f) The results appear to exclude the existence of a unique equilibrium in borate solutions between $\text{HB}_5\text{O}_9^-$ (R: 2.5) and $\text{H}_2\text{B}_3\text{O}_3^-$ ions over the whole pH range, as postulated by Carpeni. But such an equilibrium could exist in more concentrated boric acid solutions above pH ca.9.

Below pH 9 the R values found are too large for the sorption of $\text{HB}_5\text{O}_9^-$ as the only condensed species, and the results clearly point to the sorption of more than one polyborate ion.

In conclusion, it is probable that the boric acid system is far more complex than hitherto assumed. Intermediate condensed species certainly cannot be resolved adequately by the use of ion-exchange methods, just as they cannot be resolved using the classical methods described by previous workers.
TABLE 1.
(Data for fig. 4)

Ig. Amberlite IRA 400-Cl
75 ml. of solution (0.02 M Boric Acid)

<table>
<thead>
<tr>
<th>pH</th>
<th>moles per eq. resin</th>
<th>B sorbed</th>
<th>Cl desorbed</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.73</td>
<td></td>
<td>0.0132</td>
<td>0.0191</td>
<td>0.69</td>
</tr>
<tr>
<td>8.01</td>
<td></td>
<td>0.0358</td>
<td>0.0370</td>
<td>0.97</td>
</tr>
<tr>
<td>8.17</td>
<td></td>
<td>0.0359</td>
<td>0.0633</td>
<td>0.59</td>
</tr>
<tr>
<td>8.85</td>
<td></td>
<td>0.0597</td>
<td>0.0751</td>
<td>0.80</td>
</tr>
<tr>
<td>9.39</td>
<td></td>
<td>0.0770</td>
<td>0.0940</td>
<td>0.82</td>
</tr>
<tr>
<td>9.43</td>
<td></td>
<td>0.0701</td>
<td>0.0977</td>
<td>0.72</td>
</tr>
<tr>
<td>9.49</td>
<td></td>
<td>0.0740</td>
<td>0.0953</td>
<td>0.78</td>
</tr>
<tr>
<td>9.78</td>
<td></td>
<td>0.0743</td>
<td>0.1071</td>
<td>0.69</td>
</tr>
<tr>
<td>9.84</td>
<td></td>
<td>0.0678</td>
<td>0.1139</td>
<td>0.60</td>
</tr>
<tr>
<td>10.26</td>
<td></td>
<td>0.0612</td>
<td>0.1180</td>
<td>0.52</td>
</tr>
<tr>
<td>11.40</td>
<td></td>
<td>0.0418</td>
<td>0.1465</td>
<td>0.29</td>
</tr>
</tbody>
</table>

R values calculated from the boron sorption and chloride desorption graphs (fig. 4)

<table>
<thead>
<tr>
<th>pH</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5-7.9</td>
<td>1.0</td>
</tr>
<tr>
<td>8.1</td>
<td>0.90</td>
</tr>
<tr>
<td>8.5</td>
<td>0.85</td>
</tr>
<tr>
<td>9.0</td>
<td>0.81</td>
</tr>
<tr>
<td>9.5</td>
<td>0.73</td>
</tr>
<tr>
<td>10.0</td>
<td>0.58</td>
</tr>
<tr>
<td>10.8</td>
<td>0.39</td>
</tr>
<tr>
<td>11.4</td>
<td>0.29</td>
</tr>
</tbody>
</table>
TABLE 2
(Data for fig. 5)

0.5g. Amberlite IRA 400-C1
75 ml. of solution (0.2M Boric Acid)

<table>
<thead>
<tr>
<th>pH</th>
<th>moles per equiv. of resin</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B absorbed</td>
<td>Cl desorbed</td>
</tr>
<tr>
<td>5.68</td>
<td>0.07</td>
<td>0.02</td>
</tr>
<tr>
<td>6.06</td>
<td>0.19</td>
<td>0.06</td>
</tr>
<tr>
<td>6.15</td>
<td>0.195</td>
<td>0.06</td>
</tr>
<tr>
<td>6.25</td>
<td>0.31</td>
<td>0.08</td>
</tr>
<tr>
<td>6.47</td>
<td>0.29</td>
<td>0.08</td>
</tr>
<tr>
<td>6.95</td>
<td>0.64</td>
<td>0.18</td>
</tr>
<tr>
<td>6.96</td>
<td>0.61</td>
<td>0.21</td>
</tr>
<tr>
<td>7.39</td>
<td>0.79</td>
<td>0.25</td>
</tr>
<tr>
<td>7.46</td>
<td>0.85</td>
<td>0.28</td>
</tr>
<tr>
<td>7.76</td>
<td>1.02</td>
<td>0.36</td>
</tr>
<tr>
<td>8.02</td>
<td>1.11</td>
<td>0.38</td>
</tr>
<tr>
<td>8.05</td>
<td>1.11</td>
<td>0.39</td>
</tr>
<tr>
<td>8.11</td>
<td>1.15</td>
<td>0.41</td>
</tr>
<tr>
<td>8.50</td>
<td>1.16</td>
<td>0.46</td>
</tr>
<tr>
<td>8.52</td>
<td>1.19</td>
<td>0.46</td>
</tr>
<tr>
<td>8.53</td>
<td>1.19</td>
<td>0.47</td>
</tr>
<tr>
<td>8.57</td>
<td>1.13</td>
<td>0.46</td>
</tr>
<tr>
<td>8.62</td>
<td>1.15</td>
<td>0.46</td>
</tr>
<tr>
<td>8.69</td>
<td>1.17</td>
<td>0.47</td>
</tr>
<tr>
<td>8.90</td>
<td>1.14</td>
<td>0.49</td>
</tr>
<tr>
<td>9.23</td>
<td>0.99</td>
<td>0.48</td>
</tr>
<tr>
<td>9.45</td>
<td>0.90</td>
<td>0.48</td>
</tr>
<tr>
<td>9.73</td>
<td>0.64</td>
<td>0.46</td>
</tr>
<tr>
<td>10.03</td>
<td>0.61</td>
<td>0.42</td>
</tr>
<tr>
<td>10.80</td>
<td>0.17</td>
<td>0.36</td>
</tr>
</tbody>
</table>
TABLE 3
(Data for fig. 6)

0.5g. Amberlite IRA 400-Cl
75ml. of solution (0.4M Boric Acid)

<table>
<thead>
<tr>
<th>pH</th>
<th>moles per equiv. of resin</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B sorbed</td>
<td>Cl desorbed</td>
<td>R</td>
</tr>
<tr>
<td>4.13</td>
<td>negl.</td>
<td>0.0117</td>
<td></td>
</tr>
<tr>
<td>5.81</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.02</td>
<td>0.728</td>
<td>0.184</td>
<td>3.95</td>
</tr>
<tr>
<td>6.98</td>
<td>1.57</td>
<td>0.424</td>
<td>3.69</td>
</tr>
<tr>
<td>7.40</td>
<td>1.86</td>
<td>0.530</td>
<td>3.51</td>
</tr>
<tr>
<td>7.48</td>
<td>1.88</td>
<td>0.543</td>
<td>3.46</td>
</tr>
<tr>
<td>7.97</td>
<td>1.93</td>
<td>0.600</td>
<td>3.21</td>
</tr>
<tr>
<td>7.98</td>
<td>2.00</td>
<td>0.606</td>
<td>3.30</td>
</tr>
<tr>
<td>8.41</td>
<td>1.80</td>
<td>0.635</td>
<td>2.84</td>
</tr>
<tr>
<td>8.78</td>
<td>1.75</td>
<td>0.639</td>
<td>2.74</td>
</tr>
<tr>
<td>9.06</td>
<td>1.47</td>
<td>0.629</td>
<td>2.33</td>
</tr>
<tr>
<td>9.62</td>
<td>1.19</td>
<td>0.633</td>
<td>1.88</td>
</tr>
<tr>
<td>9.98</td>
<td>0.754</td>
<td>0.552</td>
<td>1.37</td>
</tr>
</tbody>
</table>
TABLE 4
(Data for fig.7)

0.5g. Amberlite IRA 400-Cl
75ml. of solution (0.6M Boric Acid)

<table>
<thead>
<tr>
<th>pH</th>
<th>moles per equiv. of resin</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B sorbed</td>
<td>Cl desorbed</td>
</tr>
<tr>
<td>4.50</td>
<td>0.202</td>
<td>0.0215</td>
</tr>
<tr>
<td>5.68</td>
<td>1.40</td>
<td>0.244</td>
</tr>
<tr>
<td>6.21</td>
<td>2.10</td>
<td>0.421</td>
</tr>
<tr>
<td>6.47</td>
<td>2.15</td>
<td>0.454</td>
</tr>
<tr>
<td>7.08</td>
<td>2.70</td>
<td>0.605</td>
</tr>
<tr>
<td>7.42</td>
<td>2.79</td>
<td>0.661</td>
</tr>
<tr>
<td>7.69</td>
<td>2.68</td>
<td>0.687</td>
</tr>
<tr>
<td>7.95</td>
<td>2.73</td>
<td>0.682</td>
</tr>
<tr>
<td>8.07</td>
<td>2.70</td>
<td>0.705</td>
</tr>
<tr>
<td>8.58</td>
<td>2.50</td>
<td>0.698</td>
</tr>
<tr>
<td>8.93</td>
<td>2.20</td>
<td>0.688</td>
</tr>
<tr>
<td>9.32</td>
<td>1.93</td>
<td>0.662</td>
</tr>
<tr>
<td>9.64</td>
<td>1.61</td>
<td>0.646</td>
</tr>
<tr>
<td>10.04</td>
<td>1.34</td>
<td>0.588</td>
</tr>
</tbody>
</table>

Results using 1.0g. of resin:

<table>
<thead>
<tr>
<th>pH</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.63</td>
<td>5.25</td>
</tr>
<tr>
<td>5.79</td>
<td>4.88</td>
</tr>
<tr>
<td>5.90</td>
<td>4.98</td>
</tr>
<tr>
<td>6.00</td>
<td>(4.43)</td>
</tr>
</tbody>
</table>
### TABLE 5

(see p.37 of text)

1.0g. Amberlite IRA 400-Cl

75ml. of solution (0.66M Boric acid)

<table>
<thead>
<tr>
<th>pH</th>
<th>moles per equiv. of resin</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B sorbed</td>
<td>Cl desorbed</td>
<td>R</td>
</tr>
<tr>
<td>4.94</td>
<td>0.422</td>
<td>0.0798</td>
<td>5.29</td>
</tr>
<tr>
<td>5.17</td>
<td>0.709</td>
<td>0.140</td>
<td>5.05</td>
</tr>
<tr>
<td>6.16</td>
<td>1.58</td>
<td>0.365</td>
<td>4.33</td>
</tr>
<tr>
<td>7.22</td>
<td>2.09</td>
<td>0.579</td>
<td>3.61</td>
</tr>
<tr>
<td>7.96</td>
<td>2.07</td>
<td>0.629</td>
<td>3.30</td>
</tr>
<tr>
<td>9.02</td>
<td>1.43</td>
<td>0.601</td>
<td>2.38</td>
</tr>
<tr>
<td>9.63</td>
<td>0.822</td>
<td>0.582</td>
<td>1.41</td>
</tr>
</tbody>
</table>

### TABLE 7

1.0g. Amberlite IRA 400-Cl

75ml. solution (0.2M Boric Acid)

1.0 mmole of chloride (in form of NaCl) added to each sample of solution.

<table>
<thead>
<tr>
<th>pH</th>
<th>moles per equiv. of resin</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B sorbed</td>
<td>Cl desorbed</td>
<td>R</td>
</tr>
<tr>
<td>7.17</td>
<td>0.17</td>
<td>0.02</td>
<td>(7.92)</td>
</tr>
<tr>
<td>7.64</td>
<td>0.31</td>
<td>0.08</td>
<td>3.71</td>
</tr>
<tr>
<td>8.41</td>
<td>0.53</td>
<td>0.17</td>
<td>3.10</td>
</tr>
<tr>
<td>8.71</td>
<td>0.56</td>
<td>0.21</td>
<td>2.73</td>
</tr>
<tr>
<td>9.05</td>
<td>0.53</td>
<td>0.23</td>
<td>2.27</td>
</tr>
<tr>
<td>9.38</td>
<td>0.42</td>
<td>0.235</td>
<td>1.80</td>
</tr>
<tr>
<td>9.76</td>
<td>0.32</td>
<td>0.21</td>
<td>1.49</td>
</tr>
<tr>
<td>10.60</td>
<td>0.21</td>
<td>0.19</td>
<td>1.10</td>
</tr>
<tr>
<td>11.48</td>
<td>0.16</td>
<td>0.18</td>
<td>0.89</td>
</tr>
</tbody>
</table>
PART III

STUDIES OF SOLUTIONS OF ARSENITES
In 1903, Auerbach (21) noticed that boric and arsenious acids have a similar tendency to undergo condensation in neutral and weakly alkaline solutions. He investigated 0.03-0.23M arsenious acid solutions by means of partition experiments between pentyl alcohol and water, and by competition with boric acid for limited quantities of a base. In addition to the presence of simple monocarnenite ions, he inferred also the existence of diarsenite, and possibly also more complex ions in solutions of higher concentration. But the concentration of these condensed forms was thought to be low in dilute solutions.

Some years later Garret, Holmes and Laube (55) determined the solubility of arsenious oxide in solutions containing increasing quantities of sodium hydroxide. They found the solubility to be greater than that which would be expected on the basis of formation of NaAsO₂ alone, and concluded that salts derived from condensed arsenious acids were also present. Solutions containing 0.2-1.2 gm atoms of arsenic and up to 1 mole of sodium hydroxide per litre were studied, and the presence of the univalent di- and tri-arsenite ions was inferred.

In work with more dilute solutions of arsenious acid, condensed ions could not be detected. Thus Roth and Schwartz (56) from freezing point measurements on 0.008-0.06M
arsenious acid, concluded that the acid was entirely in the monomeric form. Similarly Carpeni and Souchay (26) could not obtain an Isohydric Point by titration of arsenious acid solutions (up to 0.2M) with sodium hydroxide, which implied to them an absence of condensed species in this concentration range.

In strongly alkaline solutions arsenious acid appears to be present in the monomeric form, even in relatively high concentrations. A determination of ionic weight of the arsenite ion was performed by Brintzinger and Ratanarat (57), who from dialysis experiments on 0.1M potassium arsenite in 2M KOH concluded that the arsenite ion was present as $\text{As(OH)}_6^{3-}$.

The ultra-violet absorption spectrum of arsenious acid (up to 0.1M) was studied by Goldfinger and von Schweinitz (58). An absorption line was found at 2680 $\text{Å}$ in molar potassium hydroxide, which was attributed to $\text{H}_2\text{AsO}_3^-$. On increasing the alkali concentration to 12M another line was found at 2800 $\text{Å}$ which was thought to be due to $\text{HAsO}_3^{2-}$, and complete dissociation into $\text{HAsO}_3^{2-}$ was assumed at this concentration. It was suggested that these solutions might also contain small amounts of the $\text{AsO}_3^{3-}$ ion, and the maximum concentration of $\text{H}_2\text{AsO}_3^-$ was thought to occur at pH 11.6.

More recently Souchay (59) repeated the solubility measurements of Garret, Holmes and Laube, working with 0.3-0.8M arsenious oxide solutions in sodium hydroxide.
In order not to alter the activity coefficient of arsenious acid by varying the total concentration of ions present, he maintained the ionic strength constant by addition of sodium nitrate. Souchay also repeated Auerbach's partition work but used octyl alcohol. He inferred that in arsenious acid solutions up to 0.1M, the simple ions $\text{AsO}_2^-\text{ exists exclusively, but the condensed form As}_2\text{O}_5^-\text{ appears at higher concentrations (60). The monovalent diarsenite ion HAs}_2\text{O}_4^-\text{ reported by previous workers was thought not to exist.}

Recently, on examination of more concentrated arsenious oxide solutions (0.2-0.8M) Lourijsen-Teyssedre (61) succeeded in obtaining an Isohydric Point (cf. Carpeni and Souchay, 26). From the pH changes produced on diluting aqueous solutions of $\text{As}_2\text{O}_3$, the Isohydric Point, and an interpretation of Souchay's solubility and partition experiments, Lourijsen-Teyssedre concluded yet again that polyarsenites are present wholly as $\text{As}_3\text{O}_5^-\text{ and that the ion HAs}_2\text{O}_4^-\text{ either does not exist or is present in undetectable quantity. In a critical survey of past work she states that the reason why Auerbach could not obtain an equilibrium constant without postulating at least two condensed species was due to working with insufficiently concentrated solutions, which accentuated the errors involved in the technique used. The reason why Carpeni and Souchay did not obtain an Isohydric Point was also due to the concentration of the test solutions being so low that the
formation of polyarsenites was only slight.

Lourijsen-Teyssedre calculated that in 0.2M solutions of arsenious acid the maximum quantity of arsenic present as $\text{As}_2\text{O}_5^-$ is only approximately 10% of the total and is undetectable by the techniques described by her, whereas in 0.8M solutions this quantity approaches 50% of the total.

**THE STRENGTH AND BASICITY OF ARSENOUS ACID.**

An aqueous solution of arsenious oxide gives an acid reaction, and the customary formulation of the non-condensed arsenious acid thus formed is the ortho form $\text{H}_3\text{AsO}_3$ or $\text{As(OH)}_3$, nevertheless the acid cannot be isolated in the free state. The formula assigned to arsenious acid has not yet been settled, and one must consider other possibilities such as a meta acid $\text{HAsO}_2$ or $\text{AsO(OH)}$, or a hexahydro acid $\text{H}_3\text{As(OH)}_6$. Furthermore, the compound is stated to dissociate not only as an acid but also as a base (62).

The strength of arsenious acid is of the same order as that of boric acid. Its first dissociation constant $K_1$ has been determined by Goldfinger and von Schweinitz (58) from a pH titration curve obtained by use of several different indicators, and is quoted as $2.8 \times 10^{-10}$. For the purpose of calculation, the acid was assumed to exist in monomeric form. Later determinations using the glass electrode are in good agreement with the above, and a value of $8 \times 10^{-10}$ at $25^\circ$C
is reported (63).

The question now arising is whether or not a second dissociation constant exists for arsenious acid. From the customary formulation $H_3AsO_3$ one would expect not only a second but also a third dissociation step, and we find that $K_2$ has actually been determined spectrophotometrically by Goldfinger and von Schweinitz and found to be $1.6 \times 10^{-14}$. But this evaluation is based on the tacit assumption that the ultra-violet absorption lines obtained (58) were indeed those of $H_2AsO_3^-$ and $HAsO_3^{2-}$, which has been disputed by later workers (68).

The above value for $K_2$ is in reasonable agreement with recent cryoscopic work of Souchay and Hessaby (64) who find the second dissociation constant to be between $10^{-14}$ and $10^{-15}$ (such that the average value is $1.7 \times 10^{-14}$) and state that since $K_3$ cannot be measured by this method it must be considerably inferior to $10^{-15}$.

It is well known that alkali trimetallic salts of arsenious acid cannot be prepared except in alcoholic medium (65), and although a series of esters of the type $As(OR)_3$ are known they are obtained indirectly (62). On the other hand, as already stated, Brintzinger has found from dialysis work in strongly alkaline solutions that the ionic weight of the arsenite ion observed corresponds to the formula $As(OH)_6^{3-}$ which would be derived from a hexahydro acid $H_2[As(OH)_6]$. They therefore suggest that the formation of the
tri-potassium salt is due to:

\[ 3\text{KOH} + \text{As(OH)}_3 = \text{K}_3\text{[As(OH)}_3] \]

and not to:

\[ 3\text{KOH} + \text{H}_3\text{AsO}_3 = \text{K}_3\text{[AsO}_3] + 3\text{H}_2\text{O} \]

A great many salts of arsenious acid correspond to the type \( M\text{IAsO}_2 \) and a number of observations would appear to indicate that the acid is present in solution not in the ortho- but in the meta-form \( \text{HAsO}_2 \). Thus J.K. Wood (66), from the measurement of electrical conductivity and the catalytical influence on saponification of the methyl esters of acetic acid, suggests that arsenious acid is only monobasic. This view is shared by Britton and Jackson, Ishikawa and Aoki, and others (67) as a result of measurements using a glass electrode.

Recent evidence for the monobasicity of arsenious acid has been provided by osmotic measurements due to Stehlik (68), who noticed that hydroxy compounds have in general a tendency to form a loose association with certain monohydric alcohols. Thus if a measurement is made of the rate of osmosis of mixtures containing various proportions of the hydroxy compound under test and a suitable alcohol, it is found that the rate is at a minimum at a particular stoichiometrical ratio of the two compounds. The number of molecules of monohydric alcohol present at this point for each molecule of the compound under test is termed the "rush number", and is taken to denote the number of -OH groups the compound
possesses, or a simple multiple of it.

Thus the "rush number" for boric acid was found to be 3, showing that the acid is $\text{B(OH)}_3$. Similarly the value for telluric acid was found to be 12 or 18 depending on the alcohol used, thus the acid is shown to be $\text{Te(OH)}_6$. (cf. part IV of the present work). For arsenious acid, the graph of the rate of osmosis versus composition did not show a minimum, and therefore the rush number was inferred to be zero. This has been taken by Stehlik to signify that the ortho-form $\text{As(OH)}_3$ does not exist, and the only alternative was considered to be $\text{HAsO}_2$, whose structure was suggested to be a chelate ring:

$$\text{As} \leftrightarrow \begin{array}{c} 0 \end{array} \text{H}$$

In this way a structure devoid of $-\text{OH}$ groups would be obtained and therefore there would be no possibility of adding on a monohydric alcohol molecule by forming a hydrogen bond between the two hydroxyl groups.

From the data of other workers Stehlik has given evidence that the chelate ring suggested by him is sterically possible. Since in chelate rings it is generally necessary to suppose an equilibrium between the closed cis-form and the open trans-form (69), which is partially dissociated, Stehlik suggests the following:

$$\text{As} \leftrightarrow \begin{array}{c} 0 \end{array} \text{H} \leftrightarrow \begin{array}{c} \text{As} \end{array} \begin{array}{c} 0 \end{array} \text{H} \leftrightarrow \text{AsO}_2^- + \text{H}^+$$
in such a way that the transform only exists in very small quantity and does not come into account when the rush number is measured.

It must be stressed that in his investigations of boric, arsenious and telluric acid, Stehlik used relatively dilute solutions, hence the effect of polyacid formation must have been insufficient to influence his results in any way. The arsenious and telluric acid stock solutions used were both 0.1M, and although the concentration of stock boric acid was 0.5M all the three acids were further diluted by addition of various quantities of 0.5-1.0M aqueous alcohol solutions.
SCOPE OF THE PRESENT WORK

The maximum solubility of arsenious oxide at 25°C is 0.1035 moles per 1000 g. of water (55) which gives an appx. 0.2M solution of arsenious acid.

A literature survey shows that no condensed arsenite species are thought to exist in solutions up to 0.1M. At concentrations in the range 0.1-0.2M, it is generally accepted by recent workers that the concentration of condensed species is not very large and that the most condensed species is the univalent triarsenite (As$_3$O$_5^-$ or H$_2$As$_3$O$_6^-$), but there seems to exist a disagreement as to the possible existence of a species of intermediate condensation. As in the case of boric acid, arsenious acid is found to decondense both on dilution and on raising the pH value of the solution by addition of alkali.

The object of the present work was therefore as follows:

(a) To find if the concentration of condensed arsenite ions in approximately 0.2M solutions is sufficient for these ions to be sorbed in quantity on a strongly basic ion-exchanger under the conditions of an equilibrium experiment.

(b) To ascertain that the maximum degree of condensation of the polyarsenite ions is indeed threefold, giving rise to As$_3$O$_5^-$.

(c) To find whether a species of intermediate condensation
(such as $\text{HAs}_2\text{O}_4^-$) is really either absent or only present in negligible quantities, as suggested by Lourijsen-Teyssedre.

(d) To trace the process of decondensation on increasing the pH of solution.

(e) In view of the conflicting evidence regarding the basicity of arsenious acid, to investigate the possible presence of polyvalent non-condensed ions ($\text{HAsO}_3^{--}$ and $\text{AsO}_3^{---}$) which would indicate that an ortho-form of the acid exists.

(f) By means of spectrophotometry, to find if there is any simple relation between the ions sorbed on the resin and those actually present in solution when the resin is absent.
Anion Exchanger. Preliminary studies showed that arsenious acid is sorbed by the strong base anion-exchanger Amberlite IRA 400 in the chloride form, as in the case of boric acid. The exchanger was prepared as described previously (p. 36).

Preparation of solutions.

As previously stated (p. 69) a saturated solution of arsenious acid is approximately 0.2M at 25°C, but it was found that more concentrated solutions could be prepared. The supersaturated solutions thus obtained were stable at room temperature for ca. 2 days.

Arsenious oxide is wetted by water only with difficulty, so stock solutions containing ca. 0.27 and 0.15 g. atoms of arsenic were prepared by dissolving analytical grade arsenious oxide in the minimum quantity of boiling water and then diluting to the required volume. This was found to be more convenient than using large quantities of water at once, and is in agreement with the observations of Margulis and Ganc (70). These showed that the arsenious oxide already dissolved in water seems to promote the further dissolution of solid As₂O₃ and that extraction by small quantities of water will dissolve much more As₂O₃ than the same amount of water applied in a single extraction.
In a preliminary experiment samples (50 ml.) of stock solution were diluted to 75 ml. by addition of various quantities of sodium hydroxide solution and water. The pH values of these solutions were determined, and a graph of the pH against the quantity of sodium hydroxide added was plotted. This enabled 75 ml. samples of arsenious acid (0.18 and 0.1M) to be formulated subsequently at any desired pH.

II. Equilibrium experiments.

These were carried out in a similar manner to that described for boric acid (p.38). One gram quantities of the resin were weighed out into a series of dry 150 ml. conical flasks, and 75 ml. samples of arsenious acid suitably adjusted in pH were added to the resin. After stoppering with rubber bungs the batches were mechanically shaken for approximately 2 hours daily for seven days, to enable an equilibrium to be established between the solution and resin phases. Experiments extending for longer times showed this period to be adequate.

Each solution was then filtered from the resin using a small dry column containing a glass wool plug, and subsequent treatment of the resin was exactly as described for boric acid (p.39).
III. Analytical methods.

Arsenic was determined in the filtrate by titration with standard iodine, the procedure being as follows:

10 ml. portions of the solution were acidified with hydrochloric acid to methyl red, and an excess of sodium bicarbonate (ca. 1 g.) was added. The mixture could then be titrated with N/10 iodine solution (standardised by means of As₂O₃) to a starch end-point:

\[
\text{H}_3\text{AsO}_3 + \text{I}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{I}^-
\]

Chloride determinations and pH measurements were performed as described on page 40.
IV. Results of Ion-Exchange studies.

The two concentrations of arsenious acid studied were 0.18 and 0.1M, and therefore 75 ml. samples of these solutions contained 13.5 and 7.5 millimoles of arsenic respectively. The higher concentration was chosen as 0.1M in order to be as close as possible to a saturated solution of arsenious acid at room temperature without having to thermostat the experiment. In view of the necessity of shaking each batch experiment, thermostatting would be a cumbersome process.

The results of ion-exchange experiments are shown in graphical form in figures 9-10, and also in tables 8-9. These include sorption of arsenic on 1.0 g. resin samples, the desorption of chloride and the R value at various values of pH, the pH being (as before) those of the equilibrated solutions.

The maximum sorption of arsenic from solution was ca. 12% of the total in both the concentrations studied. The maximum R value obtained approaches 3 at low pH in the more concentrated solutions, but remains steadily at unity in the 0.1M solutions.
Fig. 9

0.1 M Arsenious acid-
(1.0 g resin: IRA 400 CI)

Mole per equiv. of resin

Arsenic sorbed

Chloride desorbed

"R" value
Fig. 10

0.18 M Arsenious acid
(1.0 g of resin)
Experimental.

A "Unicam" SP 500 single beam spectrophotometer, incorporating a hydrogen lamp, was used throughout. The cells were of fused silica, and 1 cm. in crossection.

The arseneous acid solutions used wore of the same concentration and in the same pH range as those for the ion-exchange experiments. As sodium hydroxide itself was found to absorb appreciably in the wavelength range studied (ultra-violet: 2200-3200 Å), the reference solutions wore made to contain the same concentration of sodium hydroxide as the solutions under test.

Results.

The ultra-violet spectrograms obtained show sharp absorption edges, which move to longer wavelengths as the pH of solution is increased (fig. 11-12). It appears therefore that arseneous acid behaves like an inorganic indicator acid whose colour change takes place in the ultra-violet range of light. Similar behaviour has been noticed in solutions of telluric acid by Jander and coworkers (71) and is analogous to the colour change observed in dichromato solutions on decondensation to chromato (15)

The extent of shift of the spectrograms for arseneous acid as the pH is altered is shown on figs. 13-14,
where the wavelength corresponding to 50% absorption is plotted against the corresponding pH of solution. In this way we may find the pH region corresponding to the greatest shift of the absorption edge.
Fig. 11

0.1 M Arsenious acid –
Absorption spectrograms

pH of solution

- a - 5.70
- b - 8.00
- c - 8.32
- d - 8.92
- e - 10.92
- f - 12.26
- g - 12.32

% Absorption

Wavelength (mμ)
Fig. 12

Absorption spectograms

0.18 M Arsenious acid

% Absorption

Wavelength (μm)

240

260

280

10 20 30 40 50 60 70 80 90

pH of solution:

- a - 5.0
- b - 3.42
- c - 8.86
- d - 11.96
- e - 12.10
Fig. 13

0.1 M Arsenious acid —
Change of spectrograms with increase in pH of solution

Wavelength (nm) corresponding to 50% absorption

pH

0.1 M soln. at its natural pH
Fig. 14

0.18M Arsenious acid
Change of spectrogram with increase in pH of solution

![Graph showing change in wavelength (nm) corresponding to 50% absorption with pH of solution for 0.18M Arsenious acid solution at its natural pH.](image-url)
DISCUSSION

0.18 M solutions of arsenious acid.

The natural pH of the solution is ca. 5.0, and the sorption of arsenic from 75 ml. of solution on 1 g. of the resin appears to begin at pH ca. 5.1. This is in direct contrast to the data obtained by study of almost saturated solutions of boric acid (see page 43) which required a relatively large pH increase before boron was sorbed on the resin under similar conditions. In view of the similar dissociation constants of monomeric boric and arsenious acids, this suggests that the polyarsenite ions present in almost saturated arsenious acid solutions either exist in far greater quantity or have a greater affinity for the resin than polyborate ions under corresponding circumstances.

The maximum sorption of arsenic was found at pH 9.2, whereas a maximum in the desorption of chloride occurred at pH 10. As in the anion-exchange investigation of boric acid, this "chloride shift" indicates that as the pH of the arsenious acid solution is increased by addition of alkali, a transition occurs from the sorption of a univalent condensed ion by the resin to the sorption of a multivalent ion of lower R value.

The sorption of a mixture of $\text{As}_3\text{O}_5^{\--}$ (R: 3) and $\text{As}_2\text{O}_4^{2--}$ (R: 1) in the pH region 5-9 would explain these results,
the ionic equilibrium in solution changing in favour of As₂O₄⁻ as the pH increases. In this way the decrease in R value from ca. 2.8-2.5 down to 1 will be accounted for. As the maximum R value obtained closely approaches 3 but does not actually attain this value, it is reasonable to suppose that the most highly condensed ionic form (As₃O₅⁻) is always sorbed with an appreciable quantity of the species of lower condensation (As₂O₄⁻).

From the theoretical considerations described previously (p. 19) the bivalent diarsenite ion (R: 1) should reach maximum concentration in solution at a pH intermediate between that corresponding to the peak arsenic sorption (pH 9.2) and that of the maximum in chloride desorption (pH 10). It is significant that the R value obtained in this region does in fact closely approach unity.

But whereas the value of R remains steadily at unity in the pH region 10-11, the desorption of chloride decreases. This implies a further change from As₂O₄⁻ to H₂AsO₃⁻ (both of R: 1). Above pH 11 the chloride desorption curve rises steadily, whereas the arsenic sorption curve falls and flattens out. The R value in this region tends towards 0.5. This suggests that at higher pH values the species HAsO₃⁻ is being sorbed, and is in agreement with the observations of Goldfinger and von Schweinitz (58).

We may summarise the above conclusions as follows.
The ionic system present in concentrated arsenious acid solutions at a given pH is a direct consequence of a decondensation reaction involving several ionic forms. The predominant species are given below:

\[
\text{As}_2\text{O}_5^- \rightleftharpoons \text{As}_2\text{O}_4^- \rightleftharpoons \text{H}_2\text{AsO}_3^- 
\]

In 0.18M solutions, it is probable that \(\text{As}_3\text{O}_5^-\) is always present in conjunction with appreciable quantities of \(\text{As}_2\text{O}_4^-\). As the pH increases, a decondensation proceeds through \(\text{As}_2\text{O}_4^-\) (which should be at maximum concentration in solution at a pH between 9.2 and 10) and eventually the acid completely decondenses into \(\text{H}_2\text{AsO}_3^-\) at pH ca. 10. Between pH 10 and 11, the univalent monoarsenite exists predominantly.

It would be reasonable to expect that the ion \(\text{HAs}_2\text{O}_4^-\) (R: 2) will also exist as an intermediate, since the divalent ion of the same degree of condensation is indicated. But this form cannot be resolved by an ion-exchange technique, and it is probable that its concentration at any time is relatively small.

If the above interpretation is correct, and if the quantities of the various ionic species sorbed on the resin are related to the ionic state of the solution when the resin is absent, then there should be a resemblance between the pH values corresponding to changes observed in the ultraviolet spectrum, and the pH values at which an ionic change
is inferred from ion-exchange data. This is indeed obtained, and we find (Figs. 13-14) that in the pH range ca. 6-10 there is a large displacement in the spectrograms. This may be attributed to the decondensation from the univalent triarsenite to the monoarsenite (with the diarsenite as an intermediate) which occurs in solution as the pH is increased. In the pH region 10-11, the displacement of absorption edges is negligible, and coincides with a steady R value of unity obtained by ion-exchange methods. Spectrophotometric results indicate therefore that in this region of pH the $\text{H}_2\text{AsO}_3^-$ ion is the sole form present in solution, although the ion-exchange data seems to suggest that a significant quantity of $\text{As}_2\text{O}_4^{2-}$ ions is also present, especially at pH ca. 10.

Above pH 11, the displacement of absorption edges increases and is probably due to formation of polyvalent non-condensed arsenite ions in solution, as shown by a steady decrease in R to give fractional values.

0.1 M solutions of arsenious acid.

As shown in fig.9, a maximum R value of unity is maintained in the pH region 7-9.5. This would at once suggest the sorption of the non-condensed arsenite $\text{H}_2\text{AsO}_3^-$ since the concentration of solution is sufficiently low for condensed ions to be absent or exist only in negligible quantity as shown by the results of other workers (26, 56, 59, 61).
Nevertheless, solely on the basis of ion-exchange experiments, an R value of unity would also suggest the ion $\text{As}_2\text{O}_4^{2-}$ which has already been cited as occurring in solutions of higher concentration.

Ion-exchange data alone is insufficient to differentiate between these two ions, but spectrophotometric results (fig.13) show that a marked shift of absorption edges occurs over the same pH range as that at which the R value remains at unity. If therefore the ionic state of an arsenious acid solution is unaltered by the presence of the resin (and results already quoted show this to be so for 0.18M solutions), then we may correlate the ion-exchange results with those obtained by spectrophotometry. Thus we may interpret the shift in absorption edges observed as indicating that an ionic change is taking place in the pH region 7-9.5. As this coincides with a steady R value of one, the change must be:

$$\text{As}_2\text{O}_4^{2-} \rightarrow \text{H}_2\text{AsO}_3^-$$

Above pH 9.5, the arsenic sorption decreases and concurrently the value of R becomes progressively less than unity, suggesting a gradual formation of $\text{HAsO}_3^{2-}$ ions ($R: 0.5$) in solution. This tendency is slight at first, as shown by the flatness of the chloride desorption curve in the pH range 9.5-11.5, and also by the fact that little change in the ultraviolet spectrum is found over this range. But as pH 12.5 is approached, at which R becomes 0.5, the desorption of chloride
increases appreciably with a corresponding decrease in the sorption of arsenic, which could only be explained by the sorption of a multivalent ion (i.e. HAsO$_3$$.^+$$. ). A marked increase in displacement of the absorption edges is also found at this point.

Above pH 12.5, there is a yet more rapid decrease in the sorption of arsenic, coupled with a steady increase in the desorption of chloride. This suggests the sorption of hydroxyl ions by the resin, the concentration of which is now becoming appreciable in solution. But it is not precluded that a species such as AsO$_3$$.^{-}$$. (R: 0.33) may be taken up by the resin in this pH region. The existence of this ion in solutions above pH 12 has been suggested by the work of Brintzinger and Ratanarat (57) and Goldfinger and von Schweinitz (58).

That the sorption of hydroxyl ions is not as great as might be expected at such high pH is shown by the fact that although at high alkalinity the pH values of the equilibrium solutions were found to be consistently lower than those of the initial solutions, nevertheless this discrepancy was never greater than ca. 0.2 pH unit over the whole pH range studied.

We may therefore interpret the ionic changes occurring in 0.1M solutions of arsenious acid, as being due to a gradual transition taking place as the pH is increased, as follows:

$$\text{As}_2\text{O}_4^{-} \rightarrow \text{H}_2\text{AsO}_3^{-} \rightarrow \text{HAsO}_3^{-} \rightarrow \text{AsO}_3^{-}$$
Decondensation is complete at pH ca. 9.5, and the univalent monoarsenite is probably the predominant species in the pH region 9.5-10.5 although it is always present here with a significant quantity of $\text{As}_2\text{O}_4^{--}$ or $\text{HAsO}_3^{--}$. This latter is at a maximum concentration at pH ca. 12.5.

**CONCLUSIONS AND GENERAL COMMENTS.**

The results of ion-exchange and spectrophotometric investigations of solutions of arsénious acid suggest the following information:

**a** The most condensed species present in concentrated aqueous solutions of arsénious oxide appears to be the univalent triarsenite ion $\text{As}_3\text{O}_5^{--}$ or $\text{H}_2\text{As}_3\text{O}_6^{--}$, this being in agreement with the majority of previous workers. The concentration of this species at low pH is sufficiently high for it to be sorbed in appreciable quantity on a strongly basic anion-exchanger under the conditions of the equilibrium experiments described. Nevertheless the ion is always sorbed with significant quantities of a species of lower condensation.

**b** A divalent species of intermediate condensation undoubtedly exists. From $R$ value considerations, this ion is thought to be $\text{As}_2\text{O}_4^{--}$, although the sorption of a species such as $\text{HAs}_3\text{O}_6^{--}$ ($R$: 1.5) instead of or along with $\text{As}_2\text{O}_4^{--}$ might also be considered possible on the above evidence.
As the pH of solution is increased, a gradual decondensation to the univalent monoarsenite takes place. On further increase in alkalinity R values of less than one are obtained, which cannot be explained solely on the basis of sorption of hydroxyl ions on the resin. Evidence therefore points to the existence of a bivalent (and possibly also trivalent) monoarsenite ion. Thus the formula of monomeric arsenious acid is thought to be H₃AsO₃ and not HAsO₂ (cf. 68) and among the ionic forms which may be present in solution under various conditions, we may expect As₃O₅, As₂O₄, H₂AsO₃, HAsO₃⁻ and AsO₃⁻. It is not precluded that other intermediate species may also exist.

As shown by a comparison of spectrophotometric and ion-exchange results, the ionic state of the solution is similar whether the resin is present or not, and depends only on the pH and the concentration.

Comparison with solid arsenites.

A phase diagram of the system Na₂O-As₂O₅-H₂O at 30°C was obtained some years ago by Schreinemaker and de Baat (72). But this did not stand up to a later examination by Nelson (73), who found that his observations on the sodium arsenites were inconsistent with some of the data reported. Accordingly Nelson repeated the phase diagram at 35°C and found that only four arsenites were formed:
(a) $\text{Na}_2\text{O} \cdot 3\text{As}_2\text{O}_3$ (NaAs$_3$O$_5$)
(b) $\text{Na}_2\text{O} \cdot \text{As}_2\text{O}_3$ (Na$_2$As$_2$O$_4$ or NaAsO$_2$)
(c) $2\text{Na}_2\text{O} \cdot \text{As}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ (Na$_4$As$_2$O$_5$ \cdot 7\text{H}_2\text{O})
(d) $2\text{Na}_2\text{O} \cdot \text{As}_2\text{O}_3$ (Na$_4$As$_2$O$_5$)

The compound $5\text{Na}_2\text{O} \cdot 2\text{As}_2\text{O}_3 \cdot 26\text{H}_2\text{O}$ (Na$_{10}$As$_4$O$_{11}$ \cdot 26 \text{H}_2\text{O}) claimed by Schreinemaker and de Baat was not obtained.

The existence of compounds (a) and (b) is consistent with the presence of the condensed arsenite ions As$_3$O$_5$$^-$ and As$_2$O$_4$$^{2-}$ already cited. In compounds (c) and (d) the comparison breaks down, unless they are considered to be derived from the ion H$_2$As$_2$O$_5$$^{2-}$ (the hydrated form of As$_2$O$_4$$^{2-}$) by the replacement of the two hydrogen atoms.

It is noteworthy that in the K$_2$O-As$_2$O$_3$-H$_2$O system at 25°C Schreinemaker found the compounds K$_2$As$_4$O$_7$ and K$_6$As$_4$O$_9$ \cdot 12\text{H}_2\text{O} which do not fit the above classification at all.
TABLE 8
(Data for fig. 9)

1.0g. Amberlite IRA 400-Cl, 75ml. of solution (0.1M arsenious acid)

<table>
<thead>
<tr>
<th>pH</th>
<th>As absorbed</th>
<th>Cl desorbed</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.37</td>
<td>0.051</td>
<td>0.055</td>
<td>0.96</td>
</tr>
<tr>
<td>7.59</td>
<td>0.090</td>
<td>0.082</td>
<td>1.09</td>
</tr>
<tr>
<td>8.00</td>
<td>0.146</td>
<td>0.138</td>
<td>1.05</td>
</tr>
<tr>
<td>8.08</td>
<td>0.168</td>
<td>0.157</td>
<td>1.07</td>
</tr>
<tr>
<td>8.27</td>
<td>0.180</td>
<td>0.178</td>
<td>1.02</td>
</tr>
<tr>
<td>8.52</td>
<td>0.224</td>
<td>0.217</td>
<td>1.03</td>
</tr>
<tr>
<td>8.77</td>
<td>0.260</td>
<td>0.250</td>
<td>1.00</td>
</tr>
<tr>
<td>9.10</td>
<td>0.323</td>
<td>0.317</td>
<td>1.02</td>
</tr>
<tr>
<td>9.24</td>
<td>0.324</td>
<td>0.319</td>
<td>1.01</td>
</tr>
<tr>
<td>9.40</td>
<td>0.333</td>
<td>0.340</td>
<td>0.98</td>
</tr>
<tr>
<td>9.44</td>
<td>0.326</td>
<td>0.338</td>
<td>0.96</td>
</tr>
<tr>
<td>9.50</td>
<td>0.330</td>
<td>0.337</td>
<td>0.98</td>
</tr>
<tr>
<td>9.65</td>
<td>0.328</td>
<td>0.333</td>
<td>0.93</td>
</tr>
<tr>
<td>9.74</td>
<td>0.334</td>
<td>0.350</td>
<td>0.95</td>
</tr>
<tr>
<td>9.98</td>
<td>0.319</td>
<td>0.362</td>
<td>0.88</td>
</tr>
<tr>
<td>10.28</td>
<td>0.297</td>
<td>0.366</td>
<td>0.81</td>
</tr>
<tr>
<td>10.70</td>
<td>0.280</td>
<td>0.363</td>
<td>0.79</td>
</tr>
<tr>
<td>11.02</td>
<td>0.268</td>
<td>0.367</td>
<td>0.73</td>
</tr>
<tr>
<td>11.31</td>
<td>0.256</td>
<td>0.367</td>
<td>0.70</td>
</tr>
<tr>
<td>11.50</td>
<td>0.246</td>
<td>0.377</td>
<td>0.65</td>
</tr>
<tr>
<td>11.82</td>
<td>0.236</td>
<td>0.399</td>
<td>0.60</td>
</tr>
<tr>
<td>11.83</td>
<td>0.242</td>
<td>0.377</td>
<td>0.64</td>
</tr>
<tr>
<td>12.11</td>
<td>0.224</td>
<td>0.406</td>
<td>0.55</td>
</tr>
<tr>
<td>12.27</td>
<td>0.221</td>
<td>0.420</td>
<td>0.53</td>
</tr>
<tr>
<td>12.53</td>
<td>0.204</td>
<td>0.443</td>
<td>0.46</td>
</tr>
<tr>
<td>12.73</td>
<td>0.180</td>
<td>0.462</td>
<td>0.39</td>
</tr>
<tr>
<td>12.85</td>
<td>0.165</td>
<td>0.484</td>
<td>0.34</td>
</tr>
</tbody>
</table>
### TABLE 9
(Data for fig. 10)

1.0 g. Amberlite IRA 400-Cl, 75 ml. of solution (0.18 M arsenious acid)

<table>
<thead>
<tr>
<th>pH</th>
<th>moles/equiv. of arsenious acid</th>
<th>moles/equiv. of Cl</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As sorbed</td>
<td>Cl desorbed</td>
<td>R</td>
</tr>
<tr>
<td>5.30</td>
<td>0.007</td>
<td>(0.022)</td>
<td>-</td>
</tr>
<tr>
<td>5.57</td>
<td>0.007</td>
<td>(0.025)</td>
<td>-</td>
</tr>
<tr>
<td>5.78</td>
<td>0.057</td>
<td>0.023</td>
<td>2.54</td>
</tr>
<tr>
<td>5.97</td>
<td>0.026</td>
<td>(0.032)</td>
<td>-</td>
</tr>
<tr>
<td>6.03</td>
<td>0.058</td>
<td>0.024</td>
<td>2.43</td>
</tr>
<tr>
<td>6.04</td>
<td>0.066</td>
<td>0.025</td>
<td>2.62</td>
</tr>
<tr>
<td>6.07</td>
<td>0.066</td>
<td>0.028</td>
<td>2.41</td>
</tr>
<tr>
<td>6.18</td>
<td>0.066</td>
<td>0.027</td>
<td>2.50</td>
</tr>
<tr>
<td>6.46</td>
<td>0.092</td>
<td>0.033</td>
<td>2.76</td>
</tr>
<tr>
<td>6.69</td>
<td>0.103</td>
<td>0.037</td>
<td>2.76</td>
</tr>
<tr>
<td>6.86</td>
<td>0.136</td>
<td>(0.022)</td>
<td>-</td>
</tr>
<tr>
<td>7.38</td>
<td>0.183</td>
<td>0.087</td>
<td>2.12</td>
</tr>
<tr>
<td>7.74</td>
<td>0.290</td>
<td>0.126</td>
<td>2.32</td>
</tr>
<tr>
<td>8.32</td>
<td>0.456</td>
<td>0.244</td>
<td>1.86</td>
</tr>
<tr>
<td>8.62</td>
<td>0.523</td>
<td>0.275</td>
<td>1.90</td>
</tr>
<tr>
<td>9.00</td>
<td>0.590</td>
<td>0.371</td>
<td>1.59</td>
</tr>
<tr>
<td>9.22</td>
<td>0.596</td>
<td>0.394</td>
<td>1.51</td>
</tr>
<tr>
<td>9.47</td>
<td>0.589</td>
<td>0.414</td>
<td>1.42</td>
</tr>
<tr>
<td>9.99</td>
<td>0.496</td>
<td>0.430</td>
<td>1.15</td>
</tr>
<tr>
<td>10.12</td>
<td>0.444</td>
<td>(0.473)</td>
<td>0.94</td>
</tr>
<tr>
<td>10.42</td>
<td>0.414</td>
<td>0.410</td>
<td>1.00</td>
</tr>
<tr>
<td>10.67</td>
<td>0.383</td>
<td>0.397</td>
<td>0.96</td>
</tr>
<tr>
<td>10.70</td>
<td>0.418</td>
<td>0.399</td>
<td>1.04</td>
</tr>
<tr>
<td>11.18</td>
<td>0.361</td>
<td>0.399</td>
<td>0.90</td>
</tr>
<tr>
<td>11.35</td>
<td>0.350</td>
<td>0.405</td>
<td>0.85</td>
</tr>
<tr>
<td>11.69</td>
<td>0.341</td>
<td>0.432</td>
<td>0.79</td>
</tr>
<tr>
<td>11.75</td>
<td>0.359</td>
<td>0.435</td>
<td>1.04</td>
</tr>
<tr>
<td>11.98</td>
<td>0.350</td>
<td>0.446</td>
<td>0.78</td>
</tr>
<tr>
<td>12.20</td>
<td>0.319</td>
<td>0.466</td>
<td>0.68</td>
</tr>
<tr>
<td>12.47</td>
<td>0.323</td>
<td>0.499</td>
<td>0.65</td>
</tr>
<tr>
<td>12.70</td>
<td>0.292</td>
<td>0.505</td>
<td>0.58</td>
</tr>
<tr>
<td>12.75</td>
<td>0.324</td>
<td>0.517</td>
<td>0.63</td>
</tr>
<tr>
<td>12.89</td>
<td>0.291</td>
<td>0.526</td>
<td>0.55</td>
</tr>
<tr>
<td>13.02</td>
<td>0.301</td>
<td>0.559</td>
<td>0.54</td>
</tr>
</tbody>
</table>
PART IV

STUDIES OF SOLUTIONS OF TELLURATES
HISTORICAL

Introductory.

That telluric acid is quite different from sele-nic and sulphuric, is shown by its strong tendency to polyme-rise and to form colloidal solutions (74). The simple form H₂TeO₄, analogous to H₂SO₄, does not exist although its salts are known. But apart from a few exceptions, the tellurates are not isomorphous with the sulphates and selenates (75).

Of the numerous forms of telluric acid reported, only two are now generally recognised as definite compounds and can be isolated (76). These are the ortho acid H₆TeO₆ and the poly-meta or "allo" acid (H₂TeO₄)ₙ, which is formed when the ortho acid is heated to 140°C in a sealed tube. Nevertheless all preparations of allotellutic acid contain some ortho acid, from which they cannot be separated. (77)

The constitution of allotelluric acid has been determined by Patry, whose conductivity and neutralisation experiments give n a value of 10, whereas ebullioscopic data on methyl and ethyl esters suggest that n is 11 + 1 (78). The allo acid is far stronger than orthotelluric acid and its conductivity is three or four times that of the latter. But on standing, the conductivity of an aqueous solution of the allo acid gradually falls to a value characteristic of the ortho acid, thus showing a depolymerisation which takes about three days for completion (79, 80).
Telluric acids of intermediate condensation.

So far, the two extreme states of telluric acid have been described: the non-condensed ortho acid $H_6TeO_6$ and the condensed "allo" form $(H_2TeO_4)_10$. Nevertheless salts of the hypothetical acids $H_2Te_2O_7$, $H_2Te_3O_{11}$, and $H_2Te_4O_{13}$ have been reported although the acids themselves have not been isolated. (80, 81)

The fact that orthotelluric acid and its alkali salts have a tendency to polymerise seems to have been first reported by Rosenheim and Jander (82) as a result of conductivity measurements. They state that on heating the acid gradually polymerises, with subsequent formation of colloidal solutions and finally of allotelluric acid. But on cooling, the solution partially or wholly reverts to its original state. Polymerisation is also favoured by an increase in concentration of the solution, and conductivity experiments show that the polymer is more strongly ionised. However it was shown cryoscopically that the polyacids exist only in very low concentration at low temperatures.

Rosenheim and Jander also showed that the lithium, sodium and potassium tellurates behave in many ways like the free acid. Thus on heating an alkali tellurate, an optically inhomogeneous solution is obtained ("half colloid").

An investigation of the coagulation of telluric acid sols by chlorides of the alkali metals has been performed.
by Ghosh and Dhar, in presence of various quantities of the hydroxyl ion (83). They found that the hydroxyl ion sensitizes the coagulation, and the mechanism was attributed to a transition:

\[
\text{colloidal telluric} \leftrightarrow \text{polymerised single molecules in solution} \rightarrow \text{in solution}
\]

the displacement to the right being caused by the hydroxyl ion.

Little appears to have been done subsequently to elucidate the process of condensation from the ortho to the allo acid, until the work of Souchay and Teyssedre. In a brief report in 1953 (84) these workers stated that on the basis of cryoscopy and titration experiments it appears that that condensation of telluric acid is dependent on two factors: the concentration of the acid, and the pH of solution. It was thought further that in solution the monosodium tellurate \( \text{NaH}_2\text{TeO}_6 \) gives rise to tetracondensed ions, and also that the ion \( \text{HTe}_2\text{O}_7^- \) is obtained as an intermediate, this being analogous to the formation of the dichromate from the chromate.

The noncondensed tellurate ion is thought by Souchay and Teyssedre to exist only in solutions of weak concentration.

Recently the above work has been reported more fully by Lourijsen-Teyssedre (85). She states that both cryoscopic studies involving measurement of the depression of transition point between sodium sulphate decahydrate and the anhydrous salt, and potentiometric studies on 0.125-1.5M solu-
tions of telluric acid show that in that concentration range the free acid is practically uncondensed. However the tellu­rates formed on gradual neutralisation of telluric acid are reported to show definite signs of condensation, as is veri­fied by pH measurements and partition work using butyl alcohol and water.

Assuming the following equilibrium to exist in solutions of tellurates:

\[ n\text{H}_2\text{TeO}_6^- \rightleftharpoons (\text{HTeO}_4^-)_n \]

Lourijsen-Teyssedre derived a straight-line relationship between the number of ions present in solution (N), the concentration, and the degree of condensation (n) of the tellu­rate ions. A value for N was obtained by cryoscopy, and it was found that the desired straight line was only obtained if the value for n was taken as four. Hence Lourijsen­Teyssedre inferred that during the process of neutralisation a polytellurate ion is formed whose formula is \((\text{HTeO}_4)_4\cdot\). Results of partition studies show further that a species of intermediate condensation also exists, such that the ratio Te/Na is 2, the anion being thought to be \(\text{HTe}_2\text{O}_7^-\).

On the basis of the existence of \(\text{H}_2\text{TeO}_6^-\), \(\text{HTe}_2\text{O}_7^-\) and \((\text{HTeO}_4)_4\cdot\) Lourijsen-Teyssedre has calculated the proportion of various ions present in telluric acid solutions at various stages of neutralisation with sodium hydroxide.
Thus if \( x \) is the degree of neutralisation (i.e. the ratio \( \text{Na}/\text{Te} \)), then for 0.5M solutions the following results are found:

(a) at \( x = 0 \), no condensed ions are found and the free acid is presumed to exist as a monomer.

(b) As \( x \) increases, the concentration of \( \text{HTe}_2\text{O}_7^- \) increases also, becoming a maximum at ca. \( x = 0.4 \), and decreasing to zero at \( x = 1 \).

(c) The proportion of \( (\text{HTeO}_4)_4^- \) ions increases from zero at \( x = 0 \) to a maximum at \( x = 1 \), and the proportion of \( \text{H}_5\text{TeO}_6^- \) increases in a similar manner. At \( x = 1 \), about 10% of the tellurium is in the form of the \( \text{H}_5\text{TeO}_6^- \) ion whereas the rest is in the form of \( (\text{HTeO}_4)_4^- \).

In 0.1M solutions of telluric acid the ion \( (\text{HTeO}_4)_4^- \) becomes negligible, and at \( x = 1 \) all the tellurium is in the form of \( \text{H}_5\text{TeO}_6^- \).

Earley and Edwards (86) have studied solutions of orthotelluric acid conductimetrically, and conclude that a dimer and a trimer are formed in solutions of up to 1.0M, but suspect that higher polymers may also be present in yet more concentrated solutions. This is in agreement with later conductivity studies of Antikainen (87), who further calculated the complex formation constants of the dimer and the trimer.
Absorptiometric studies.

The ultra-violet absorption spectrum of telluric acid solutions has been studied by Stuber, Braida and Jander (71) who found that a considerable displacement of the absorption curves was brought about by a change in the pH of the solution. This they thought to be analogous to the visible colour change in solutions of dichromates, observed as the pH is increased. Stuber and coworkers therefore considered telluric acid to behave like an inorganic indicator acid whose colour change takes place in the ultra-violet range of light. But whereas the colour change observed in dichromates is now well known to be due to a decondensation to the chromate, Stuber and coworkers could not detect any condensation in telluric acid by cryoscopy and diffusion studies (cf. Lourijsen-Teyssedre 85). They therefore concluded that the ultra-violet displacement brought about by change in pH is not due to a condensation-decondensation reaction, but is due rather to some intermolecular rearrangement such as:

\[
\text{Te(OH)}_6 \rightleftharpoons \text{H}_2\text{TeO}_4^{aq.} \rightleftharpoons \text{H}^+ + \text{HTeO}_4^{-aq.}
\]

This work was repeated by Ley and König (88) using very dilute tellurate solutions at high alkalinity, but no useful conclusions could be reached.

More recently the ultra-violet absorption of aqueous solutions of telluric acid at various concentrations has again been measured (89), and the shift in absorption
The strength and basicity of telluric acid.

The formula of telluric acid is now generally accepted to be not $\text{H}_2\text{TeO}_4 \cdot \text{H}_2\text{O}$ but $\text{H}_6\text{TeO}_6$ giving an acid which is, theoretically at least, six-basic. The evidence for this includes freezing point measurements and dehydration experiments, absorption spectra, Raman spectra, osmotic studies and X-ray analysis (90).

The strength of telluric acid is approximately similar to boric and hydrocyanic acids (82, 91). A recent determination by Pouasson (92) from conductivity and pH studies gives the following values:

$$K_1 = 1.55 \times 10^{-8} \text{ at } 22^\circ\text{C}$$
$$K_2 = 4.7 \times 10^{-11} \text{ at } 18^\circ\text{C}$$

but Pouasson was unable to determine the other constants by ordinary methods. The latter is in agreement with the work of Souchay and Hessaby (64), who failed to evaluate $K_3-K_6$ by a cryoscopic method and concluded these constants to be smaller than $10^{-15}$.

Orthotelluric acid by itself does not react with indicators and does not catalyse the inversion of cane sugar (93). Pouasson (92) performed conductimetric titrations of molar solutions of telluric acid with molar sodium hydroxide,
and claims to have obtained breaks in the curve at NaOH/H₆TeO₆ mole ratios of 1, 2, 4 and 6. This would be consistent with the formation of NaH₅TeO₆, Na₂H₄TeO₆, Na₄H₂TeO₆ and Na₆TeO₆, but Fouasson's results are questioned by Souchay and Hessaby (64), whose conductivity studies of telluric acid solutions showed no evidence of a basicity greater than two as regards the sodium salts. They nevertheless claim to have prepared lithium tellurates containing 2, 3, and 4 atoms of lithium, thus showing that telluric acid is more than one-basic. Salts such as Cu₃TeO₆, Ag₆TeO₆, Zn₅TeO₆ and Hg₃TeO₆ are known to exist (81).
SCOPE OF THE PRESENT WORK.

On the basis of interpretations quoted in the preceding sections, it seems clear that an increase in temperature or in concentration of telluric acid solutions favours the formation of polytelluric acids. According to cryoscopic (82) and diffusion (71) measurements these polyacids seem to be present only in very low concentration at low temperature. But both Antikainen (87) and Earley and Edwards (86) agree that a dimer and a trimer are formed during the course of condensation, although the latter workers further suggest that this is not the ultimate degree of condensation of telluric acid. Lourijsen-Teyssedre gives ample evidence of a tetramer but states that in free telluric acid, irrespective of concentration, condensation is negligible and condensed ions only come into evidence on addition of alkali. Thus although Souchay and Teyssedre do agree that condensation of telluric acid is pH dependent, nevertheless according to their interpretation the ion $\text{HTe}_2\text{O}_7^-$ (derived from the dimeric acid) appears at low pH values, whereas the tetracondensed ($\text{HTeO}_4^4$) is formed as the pH is increased. This would appear to contradict the rule, obeyed by boric and arsenious acids, that in general an oxyacid liable to condensation will tend to decondense on increasing the pH.

In the work to be described:

(1) an attempt will be made to comment critically on Souchay
and Teyssedre's interpretation.

2. In view of the fact that little evidence was found by other workers for the condensation of telluric acid both at low temperature and in solutions of low concentration, an investigation will be made using comparatively weak solutions of orthotelluric acid at room temperature in order to find if condensation can be detected by ion-exchange methods.

3. The course of the condensation-decondensation reaction will be traced, both as the concentration and as the pH of telluric acid solution is increased.

4. A correlation between ion-exchange and spectrophotometric results will be sought.
(a) ION-EXCHANGE STUDIES

I. Preliminary.

Anion Exchanger. Preliminary investigations showed that telluric acid is sorbed by the strong base anion-exchanger Amberlite IRA 400 in the chloride form, as in the case of boric and arsenious acids. The exchanger was prepared as described previously (p.36).

Preparation of solutions. The solubility of telluric acid is reported to be 2.16 gram formulae per 1000 g. of water at 20°C (94), but it was found that solutions whose strength is as low as 0.2M show a slight opalescence due to presence of colloidal matter. This opalescence gradually disappears on prolonged standing, but after several weeks the solutions show signs of ageing.

It was decided to investigate solutions of 0.5M concentration, and below. For this purpose stock solutions (0.75, 0.62, 0.42, 0.30 and 0.21M) were prepared. In a preliminary experiment samples (50 ml.) of stock solutions were diluted to 75 ml. by addition of various quantities of sodium hydroxide and water. The pH values of these solutions were determined, and graphs of pH against the quantity of sodium hydroxide added were plotted. From these graphs 75 ml. samples of telluric acid (0.5, 0.41, 0.28, 0.20 and 0.14M) could later be formulated at any desired pH value.
II. Equilibrium Experiments

These were carried out in a similar way to those for boric and arsenious acid (pages 38 and 39). One gram quantities of resin were used throughout the experiments. Each sample of resin was added to 75 ml. of the telluric acid solution suitably adjusted in pH. Each mixture was then left for a maximum of seven days to attain equilibrium, unless the pH was such that the solution had a tendency to crystallise—in which case only two days were allowed for the attainment of equilibrium. Every flask was subjected to mechanical shaking for ca. 2 hours daily, and after equilibrium had been attained each solution was filtered off from the resin using a small dry column containing a glass wool plug. The filtrate was retained for analysis, and the subsequent treatment of the resin was exactly as described for boric acid (p.39).

III. Analytical Methods.

Tellurium in the filtrate was determined as telluric acid, by titration with standard sodium hydroxide. The tellurium sorbed on the resin was then calculated by difference.

Telluric acid is not sufficiently strong to be titrated by itself, but it gives strongly acid complexes with glycerol and mannitol and can be titrated to phenolphthalein (95). Antikainen (96) has investigated the telluric acid complexes by potentiometric, cryoscopic and other methods.
He found that the complexes formed are made up of one molecule of glycerol or mannitol to one molecule of telluric acid, and that their ionisation constants are of the order of $10^{-5}$. Formation of the complex is a slow reaction in each case, but Antikainen finds that formation of the mannitol complex is nearly complete when the concentration of mannitol is three times that of telluric acid. This is in agreement with the work of Fouasson (92), who finds that telluric acid can be titrated with good precision if a great excess of mannitol is used.

In the present work it was found that consistent results were obtained as follows: 10 ml. portions of the filtrate were made neutral to methyl-orange by addition of dilute nitric acid. (Hydrochloric acid tends to reduce telluric to tellurous acid, with the liberation of chlorine). A large excess was then added (appx. 4-8 g.) and each mixture was heated on the steam bath to ca. 60°C before titrating hot with standard sodium hydroxide to a phenolphthalein end-point. Chloride determinations and pH measurements were performed as described on p.40.

**IV. Results of Ion-Exchange studies**

For the five concentrations of telluric acid studied (0.14, 0.20, 0.28, 0.41 and 0.5M), the sorption of tellurium, desorption of chloride, and the R values at various
0.14 M Telluric acid
(1.0 g. of resin)

Moles per equiv. of resin

pH

Tellurium sorbed
Chloride desorbed
"R" value
Fig. 16

0.2 M Telluric acid

Tellurium sorbed
Chloride desorbed
"R" value

Moles per equiv. of resin

pH

1.0 g of resin
Fig. 17

0.28 M Telluric acid

Moles per equiv. of resin

(1.0 g. of resin)

pH

Tellurium sorbed
Chloride desorbed
"R" value
Fig. 18

0.41 M Telluric acid
(1.0 g. of resin)

Moles per equiv. of resin

pH

Tellurium sorbed

Chloride desorbed.

"R" value
Fig. 19

0.5 M Telluric acid
(1.0 g of resin)
alkalinites are shown in figures 15-19, and in tables 10-14. The pH values quoted are those of the equilibrated solutions.

The sorption of tellurium exhibits a maximum for each concentration studied, the position of the peak moving to a lower pH value as the concentration of solution is increased. This is shown in fig. 20 below, where the pH corresponding to the maximum sorption of tellurium is plotted against the molarity of solution. The graph obtained approximates to a straight line.

![Fig. 20](image)

Fig. 21 shows the maximum R value found for each of the concentrations studied. It will be noticed that at concentrations between 0.28 and 0.41M the maximum R value obtained remains steadily at 2 whereas for both 0.14 and 0.20M solutions the
maximum R value is 1.5.

In 0.5M solutions (see fig.19) although the maximum R value obtained is greater than two, nevertheless a point of inflexion exists in the R value curve, which remains constantly at 2 in the region of pH 5.5-6.5.

For the 0.14M solutions, which were studied most extensively, no chloride shift was found. The chloride desorption curve did not exhibit a peak but reached a constant value which was maintained in the pH range 8-10.5. For the other concentrations the pH range studied is incomplete, but the general trend of values suggests that sorption and desorption graphs are of similar shape to those obtained for 0.14M solutions.
The maximum quantity of tellurium sorbed from solution by the resin was ca. 27, 20, 16, 13 and 12% of the total, for the 0.14, 0.20, 0.28, 0.41 and 0.5M solutions respectively.

Crystallisation of sodium tellurates.

As has been stated in the experimental section (p.97), at certain pH values telluric acid-sodium hydroxide solutions tended to yield crystals on standing. Consequently the batch experiments were allowed only two days to attain equilibrium in order to avoid crystallisation on the resin.

The conditions for crystallisation were investigated in a series of blank experiments - i.e. in the absence of the resin. It was found that 0.14M telluric acid solutions were stable up to pH ca. 7.0, but an even crystallisation on the walls of the vessel resulted after appx. 2 days if the solution had a pH in the range ca. 7-9.5. Crystallisation was most ready at pH 8-9. The Na/Te ratio in solution then approached unity and the salt that crystallised out was found on analysis to have a Na/Te ratio corresponding to NaH$_5$TeO$_6$. In the pH region 9.5-11.5 no crystallisation took place, and the solutions appeared to be stable indefinitely, but at higher pH values after ca. two days standing the solutions deposited clumps of crystals which were visibly different from those obtained at pH 8-9. On analysis these proved to have a Na/Te ratio corresponding to Na$_2$H$_4$TeO$_6$.

These observations lend support to the work of
Fouasson (92) who has extensively investigated the conditions for formation of mono- and di-sodium tellurates.

It was found in the present study, that the presence of the resin and agitation of the solution tended to decelerate crystallisation of sodium tellurates. In 0.28-0.5M solutions of telluric acid crystallisation appears to begin above pH ca. 7. These crystals are similar in appearance to those obtained in 0.14M solutions at pH 8-9.
(b) SPECTROPHOTOMETRIC STUDIES.

Experimental. A "Unicam" S.P. 500 spectrophotometer was used throughout, and the experimental procedure was exactly as described for arsenious acid (p.75). Only one concentration of telluric acid was studied fully, this being the 0.14M solution for which ion-exchange results are the most complete.

Results. The ultra-violet spectrograms obtained show sharp absorption edges which move to longer wavelengths as the pH of the solution is increased (see fig.22). This is in agreement with the results of other workers (71, 88, 89), but it was noticed that the change in the spectrum above ca. pH 8 was only very slight compared to the change observed at lower pH values. An approximate indication of the extent of change in the spectrograms as the pH is increased, was obtained by plotting the wavelength corresponding to 50% absorption against the pH of solution giving the spectrogram. The results are shown in fig.23.

It was found that a shift of absorption edges to longer wavelengths also occurs on raising the telluric acid concentration of solution (fig.24)
Fig. 22

0.14 M Telluric acid
Absorption Spectrograms.

pH
a... 4.67
b... 6.86
c... 6.14
d... 6.10
e... 6.16
f... 6.93
g... 7.45
h... 8.00
i... 9.96-

% Absorption

Wavelength (mμ)
0.14 M telluric acid
Change of spectrogram with increase in pH
(see page 103 of text)
Fig. 24
Spectrograms of Telluric acid solutions

% Absorption

Wavelength (mμ)

Molarity of solution:
A - 0.05 M
D - 0.1
C - 0.2
D - 0.3
E - 0.4
F - 0.6
G - 0.8
DISCUSSION.

For each concentration of telluric acid studied the value of R decreases on raising the pH or on decreasing the tellurium concentration of solution. Thus the results of ion-exchange studies clearly indicate that a decondensation takes place both as the pH of solution is increased and as the telluric acid concentration is decreased.

The above trend would be expected by analogy with the behaviour of other condensed oxyacids, and has been shown in this work to hold for boric and arsenious acids. This direct dependence of the degree of condensation of telluric acid on the concentration of solution is in agreement with the work of Jander and coworkers (82). However, the depolymerisation of telluric acid observed on increasing the pH is contrary to the conclusions of Lourijsen-Teyssedre (85, see also p.89-90).

It remains now to explain the ion-exchange results in terms of definite anionic species. Any interpretation put forward must satisfy the following conditions:

(1) That a decondensation takes place on raising the pH or lowering the tellurium concentration of solution.

(2) That an ionic species of R value greater than 2 exists, as shown by study of 0.5M solutions.

(3) That intermediate ionic species exist the R values of which are 2 and 1.5, as shown by the constancy of these
R values on the graph of molarity of solution versus maximum R (fig. 21), and by the constancy of R: 2 between pH 5.5 and 6.5 in 0.5M solutions (fig. 19).

The fact that a definite but fractional R value of 1.5 is obtained at telluric acid concentrations of 0.2M and below, suggests that a multivalent ion exists at some stage of the decondensation process. A reasonable explanation of an R value of 1.5 would be the existence of the ion Te$_{3}O_{10}^{--}$, and indeed the ion-exchange results could be explained on the basis of the following decondensation:

\[(HTe_{4}O_{13}^{-}) \rightarrow Te_{4}O_{13}^{-} \rightarrow (HTe_{3}O_{10}^{-}) \rightarrow Te_{3}O_{10}^{-} \rightarrow H_{5}TeO_{6}^{-} \rightarrow H_{4}TeO_{6}^{-}\]

R:4  R:2  R:3  R:1.5  R:1  R:0.5

bearing in mind that the salts of the hypothetical acids H$_{2}Te_{4}O_{13}$ and H$_{2}Te_{3}O_{10}$ have been reported. (80, 81)

As already seen, evidence for the tetramer and dimer has been given by Lourijsen-Teyssedre (85) whereas a dimer and trimer have been suggested by Earley and Edwards and by Antikainen (86, 87).

The existence of the ion HTe$_{4}O_{13}^{-}$ would explain why R values greater than two were obtained in 0.5M solutions at low pH. The formation of Te$_{4}O_{13}^{-}$ on increasing the pH would be a logical one, and would explain the inflexion observed at R:2 in the R value curve for 0.5M telluric acid solutions. An R value of 1.5 observed in solutions of lower Te concentration would then be explained by the formation of Te$_{3}O_{10}^{--}$.
although one would expect this ion to be formed via $\text{HTe}_3\text{O}_{10}^-$ (R: 3). But there is no evidence in the R value graphs for the sorption of a univalent tritellurate, and one must assume that if $\text{HTe}_3\text{O}_{10}^-$ exists at all it must be present only in negligible quantity. The $\text{Te}_3\text{O}_{10}^-$ ion eventually decondenses into $\text{H}_5\text{TeO}_6^-$ (R: 1) as shown by the data obtained from 0.14M solutions (fig.15) where the R value is found to decrease steadily from 1.5 at pH 7 to unity in the pH region 9.0-9.5. It is noteworthy that in this pH region the Na/Te ratio in solution is also unity as shown in figure 25 below.

![Graph](image)

A further examination of the above graph shows that above pH 9.8 the R values become progressively less than one, and tend towards 0.5 at pH ca.11.5. At this pH the Na/Te ratio in
solution becomes 2, thus experimental evidence points to the sorption of \( H_4TeO_6^- \) (R: 0.5). It seems therefore that the effect of sorption of hydroxyl ions on the resin is negligible in this pH region.

Other interpretations.

It would be reasonable to expect that a ditellurate ion exists as an intermediate between the tritellurate and the monotellurate, but this ion cannot be deduced from the R value graphs. (Cf. the conclusions of Earley and Edwards, and of Antikainen). Furthermore, the results quoted cannot be interpreted on the basis of the transition:

\[
\text{Uncondensed} \quad \rightarrow \quad \text{HTe}_2O_7^- \quad \rightarrow \quad (\text{HTeO}_4)_4^- \quad \rightarrow \quad H_5TeO_6^- \quad \text{R:2} \quad \text{R:1} \quad \text{R:1}
\]

brought about by an increase in pH or decrease in concentration as suggested by Lourijsen-Teyssedre. The reasons for this are as follows:

1. Although Lourijsen-Teyssedre states that free telluric acid is largely uncondensed, ion-exchange studies show that even in the most diluted solutions investigated there is evidence of sorption of condensed ions at low pH.

2. Lourijsen-Teyssedre has calculated that in 0.5M solutions the ion \( \text{HTe}_2O_7^- \) (R: 2) exists at maximum concentration when the Na/Te ratio is appx. 0.4, but ion-exchange data on 0.5M solutions indicate that R:2 occurs only at
a Na/Te ratio of ca. 0.05-0.35, and at higher Na/Te ratios the R value decreases (see fig. 26 below).

Furthermore if a steady R value of two (obtained in this study) is attributed to the ion \( \text{HTe}_2\text{O}_7^- \) and not to \( \text{Te}_4\text{O}_{13}^- \) then difficulty will be experienced in the interpretation of the steady R value of 1.5 obtained at lower concentrations, since by analogy with other oxyacid systems a decondensation and not a condensation would be expected here.

(3) If we assume that Lourijsen-Teyssedre's interpretation is correct, and admit that the concentration of a tetrameric ion \( (\text{HTeO}_4)_4^- \) rises as the pH of solution is increased, then we would expect ion-exchange results to
show a marked increase in the desorption of chloride at high pH, since a univalent ion HTo$_2$O$_7^-$ is being replaced by a quadrivalent one. But in fact the observed gradient of the chloride desorption curve tends to decrease rather than increase at the higher pH values, this being found for all the concentrations studied.

One is forced to conclude therefore that the most adequate interpretation of the present work appears to depend on the existence of a tetra-, tri- and possibly also a di-condensed telluric acid. The possibility of yet more condensed acids in solutions of higher concentration is not within the scope of the present limited study.

The tellurate system and the "chloride shift".

So far it has been stated that only two condensed tellurate ions are definitely indicated by ion-exchange results, these being the bivalent tetratellurate Te$_4$O$_{13}^- \equiv$ and the bivalent tritellurate Te$_3$O$_{10}^- \equiv$. The presence of the ion HTo$_4$O$_{13}^- \equiv$ has been inferred in 0.5M solutions at low pH values, but this soon gives rise to Te$_4$O$_{13}^- \equiv$. In solutions of lower concentration the univalent tetratellurate appears to exist in such small quantity that it is undetectable. We have therefore a system where a condensed ion (Te$_4$O$_{13}^- \equiv$) decondenses to an intermediate ion (Te$_3$O$_{10}^- \equiv$) without any alteration in ionic charge. A "chloride shift" of the type exhibited by
boric and arsенич acids would not therefore be expected.
The results obtained with the two extreme concentrations stu-
died will now be considered in greater detail.

0.5M solutions of telluric acid.

At low pH a mixture of HTe₄O₁₃⁻ (R: 4) and Te₄O₁₃⁻ (R: 2) is thought to be sorbed on the resin, as shown by the
R value being greater than 2. In the pH region 5.5-6.5 the
ion Te₄O₁₃⁻ appears to be sorbed exclusively (as shown by the
R value), but on increasing the pH this gradually decondenses
to Te₃O₁₀⁻ (R: 1.5) as shown by a marked decrease in the over-
all sorption of tellurium. Since a bivalent ion is being
replaced on the resin by another bivalent one, the chloride
desorption graph does not acquire a negative gradient (cf.
borate and arsеничite systems). Nevertheless tritelluric acid
is less condensed and therefore undoubtedly less dissociated
than tetratelluric acid (79, 80), therefore it would be expec-
ted that a smaller quantity of Te₃O₁₀⁻ ions would be sorbed
on the resin than was the case with Te₄O₁₃⁻ ions. This expla-
ins not only the sudden decrease in tellurium sorption above
pH 6.5, but also the gradual decrease in slope of the chloride
desorption graph as observed in this pH range.

0.14M solutions of telluric acid.

Here we have evidence only of Te₃O₁₀⁻, the sorp-
tion of which is predominant in the pH region 4.5-7. At pH
7.3 the tellurium sorption comes to a maximum, and at higher
alkalinity it begins to decrease. Concurrently the gradient of the chloride desorption curve decreases and becomes zero in the pH range ca. 8.5-10. This is consistent with a replacement of the ion $\text{Te}_3\text{O}^{10-}$ by $\text{H}_5\text{TeO}_6^-$ on the resin in the pH region 7-8.5, and is supported by the crystallisation of $\text{NaH}_5\text{TeO}_6$ from solution in this region. That the ion $\text{H}_5\text{TeO}_6^-$ is sorbed predominantly at pH 8.5-10 is shown by the inflexion of the tellurium sorption curve in this region. Above pH 10 there is sorption of an increasing proportion of $\text{H}_4\text{TeO}_6^{12-}$ ions, but since $K_2$ for telluric acid is very small (cf. p.92) the concentration of this ion in solution would be expected to be slight. This will explain the sudden decrease observed in the tellurium sorption at and above pH 10. But since a univalent ion is being replaced on the resin by a bivalent one, the influence of the decrease in Te sorption on the desorption of chloride is only slight. The value of $R$ becomes 0.5 at pH ca. 11.5, and it is significant that this is near the pH region in which $\text{Na}_2\text{H}_4\text{TeO}_6$ crystallises from solution on standing.

An examination of the results of spectrophotometry (fig.22-23) will show that the greatest change in the spectrograms occurs in the pH region ca. 5-7, whereas no change is in evidence in the pH region ca. 8.5-11. It would appear therefore that an ionic change takes place in solution at pH values below 8.5, and this could be explained by the transition:

$$\text{Tritelluric} \rightarrow (\text{Ditelluric} \rightarrow \text{Monotelluric})$$

acid

acid

acid
At pH values above 8.5, ion-exchange results give evidence of non-condensed ions, and the fact that no change in the spectrograms is observed in this pH region suggests that the absorption spectra of $\text{H}_5\text{TeO}_6^-$ and $\text{H}_4\text{TeO}_6^{--}$ are similar.

**Comparison with solid tellurates**

An extensive study of solid tellurates has been made by Berzelius and later by Hutchins (97). Of the alkali tellurates, compounds such as $\text{LiHTe}_2\text{O}_7$ aq. and $\text{NaHTe}_2\text{O}_7$ are stated to have been prepared by spontaneous evaporation of a solution containing the stoichiometric proportions of telluric acid and the alkali carbonate. On heating, these compounds yield the insoluble $\text{Li}_2\text{Te}_4\text{O}_{13}$ and $\text{Na}_2\text{Te}_4\text{O}_{13}$. In a similar manner the tritellurate $\text{K}_2\text{Te}_3\text{O}_{16}.5\text{H}_2\text{O}$ has been obtained. No solid tellurates of higher Te content appear to have been reported.
CONCLUSIONS AND GENERAL COMMENTS

From this limited study of telluric acid solutions it appears:

(1) That condensed tellurate ions are sorbed on the resin even from solutions of concentration as low as 0.14M.

(2) That an adequate interpretation of the present work can be given on the basis of the existence in solution of ions derived from a tetra-, tri-, and possibly di-telluric acid. This interpretation is consistent with the results obtained if it is accepted that a decondensation takes place both on raising the pH of the tellurate solution and on dilution.

(3) A correlation appears to exist between the ions sorbed on the resin and the ionic state of solution when the resin is absent.
TABLE 10
(Data for fig.15)

1.0g. Amberlite IRA 400-Cl
75ml. solution (0.14M Telluric Acid)

<table>
<thead>
<tr>
<th>pH</th>
<th>Te sorbed</th>
<th>Cl desorbed</th>
<th>R</th>
<th>Na/Te ratio in solution phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.70</td>
<td>0.050</td>
<td>0.040</td>
<td>(1.26)</td>
<td></td>
</tr>
<tr>
<td>4.88</td>
<td>0.133</td>
<td>0.069</td>
<td>(1.92)</td>
<td></td>
</tr>
<tr>
<td>5.28</td>
<td>0.205</td>
<td>0.130</td>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td>5.45</td>
<td>0.291</td>
<td>0.186</td>
<td>1.57</td>
<td></td>
</tr>
<tr>
<td>5.64</td>
<td>0.414</td>
<td>0.227</td>
<td>(1.83)</td>
<td></td>
</tr>
<tr>
<td>5.94</td>
<td>0.477</td>
<td>0.325</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>6.32</td>
<td>0.699</td>
<td>0.472</td>
<td>1.48</td>
<td></td>
</tr>
<tr>
<td>6.36</td>
<td>0.709</td>
<td>0.459</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>6.59</td>
<td>0.836</td>
<td>0.555</td>
<td>1.51</td>
<td></td>
</tr>
<tr>
<td>6.94</td>
<td>0.947</td>
<td>0.635</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td>7.36</td>
<td>0.957</td>
<td>0.708</td>
<td>1.36</td>
<td></td>
</tr>
<tr>
<td>7.38</td>
<td>0.974</td>
<td>0.699</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
<td>7.83</td>
<td>0.927</td>
<td>0.731</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>8.48</td>
<td>0.833</td>
<td>0.746</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>8.70</td>
<td>0.812</td>
<td>0.744</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td>9.03</td>
<td>0.774</td>
<td>0.746</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>9.42</td>
<td>0.751</td>
<td>0.743</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>9.69</td>
<td>0.726</td>
<td>0.746</td>
<td>0.97</td>
<td>1.05</td>
</tr>
<tr>
<td>10.37</td>
<td>0.602</td>
<td>0.750</td>
<td>0.80</td>
<td>1.21</td>
</tr>
<tr>
<td>10.54</td>
<td>0.507</td>
<td>0.742</td>
<td>0.68</td>
<td>1.41</td>
</tr>
<tr>
<td>10.92</td>
<td>0.433</td>
<td>0.728</td>
<td>0.59</td>
<td>1.64</td>
</tr>
</tbody>
</table>
TABLE 11
(Data for fig. 16)
1.0 g. Amberlite IRA 400-Cl
75 ml. solution (0.20M Telluric acid)

<table>
<thead>
<tr>
<th>pH</th>
<th>Te sorbed</th>
<th>Cl desorbed</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.79</td>
<td>0.105</td>
<td>0.080</td>
<td>1.30</td>
</tr>
<tr>
<td>5.36</td>
<td>0.290</td>
<td>0.192</td>
<td>1.51</td>
</tr>
<tr>
<td>5.92</td>
<td>0.571</td>
<td>0.368</td>
<td>1.55</td>
</tr>
<tr>
<td>6.30</td>
<td>0.806</td>
<td>0.520</td>
<td>1.55</td>
</tr>
<tr>
<td>6.59</td>
<td>0.967</td>
<td>0.620</td>
<td>1.56</td>
</tr>
<tr>
<td>6.84</td>
<td>1.016</td>
<td>0.678</td>
<td>1.50</td>
</tr>
<tr>
<td>7.16</td>
<td>1.020</td>
<td>0.702</td>
<td>1.45</td>
</tr>
</tbody>
</table>

TABLE 12
(Data for fig. 17)
1.0 g. Amberlite IRA 400-Cl
75 ml. solution (0.28M Telluric Acid)

<table>
<thead>
<tr>
<th>pH</th>
<th>Te sorbed</th>
<th>Cl desorbed</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.88</td>
<td>0.279</td>
<td>0.142</td>
<td>1.96</td>
</tr>
<tr>
<td>5.55</td>
<td>0.682</td>
<td>0.348</td>
<td>1.96</td>
</tr>
<tr>
<td>6.25</td>
<td>1.027</td>
<td>0.611</td>
<td>1.69</td>
</tr>
<tr>
<td>6.57</td>
<td>1.164</td>
<td>0.690</td>
<td>1.69</td>
</tr>
<tr>
<td>6.80</td>
<td>1.212</td>
<td>0.735</td>
<td>1.65</td>
</tr>
<tr>
<td>7.00</td>
<td>1.209</td>
<td>0.771</td>
<td>1.57</td>
</tr>
</tbody>
</table>
**TABLE 13**
(Data for fig. 13)

1.0g. Amberlite IRA 400-Cl
75ml. solution (0.4M Telluric Acid)

<table>
<thead>
<tr>
<th>pH</th>
<th>moles per equiv. of resin</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Te sorbed</td>
<td>Cl Desorbed</td>
<td>R</td>
</tr>
<tr>
<td>4.55</td>
<td>0.296</td>
<td>0.145</td>
<td>2.05</td>
</tr>
<tr>
<td>4.96</td>
<td>0.494</td>
<td>0.255</td>
<td>1.94</td>
</tr>
<tr>
<td>5.68</td>
<td>0.970</td>
<td>0.530</td>
<td>1.83</td>
</tr>
<tr>
<td>6.16</td>
<td>1.29</td>
<td>0.682</td>
<td>1.89</td>
</tr>
<tr>
<td>6.61</td>
<td>1.42</td>
<td>0.771</td>
<td>1.84</td>
</tr>
<tr>
<td>6.90</td>
<td>1.39</td>
<td>0.809</td>
<td>1.72</td>
</tr>
</tbody>
</table>

**TABLE 14**
(Data for fig. 19)

1.0g. Amberlite IRA 400-Cl
75ml. solution (0.5M Telluric Acid)

<table>
<thead>
<tr>
<th>pH</th>
<th>moles per equiv. of resin</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Te sorbed</td>
<td>Cl Desorbed</td>
<td>R</td>
</tr>
<tr>
<td>4.66</td>
<td>0.587</td>
<td>0.220</td>
<td>2.66</td>
</tr>
<tr>
<td>5.35</td>
<td>1.10</td>
<td>0.477</td>
<td>2.30</td>
</tr>
<tr>
<td>5.68</td>
<td>1.25</td>
<td>0.603</td>
<td>2.07</td>
</tr>
<tr>
<td>6.11</td>
<td>1.51</td>
<td>0.728</td>
<td>2.07</td>
</tr>
<tr>
<td>6.55</td>
<td>1.60</td>
<td>0.791</td>
<td>2.03</td>
</tr>
<tr>
<td>6.85</td>
<td>1.35</td>
<td>0.827</td>
<td>1.63</td>
</tr>
<tr>
<td>7.41</td>
<td>1.26</td>
<td>0.852</td>
<td>1.48</td>
</tr>
</tbody>
</table>
ANNEX
ANNEX I

Washing the resin.

As has been mentioned previously, the capacity of each resin sample was determined (in terms of moles of chloride per gram of resin) by first converting it to the chloride form by passage of hydrochloric acid, and then removing excess acid by washing with water. The chloride on the resin could then be displaced by elution with nitric acid and determination in the eluate as silver chloride. Nevertheless it was found that even when deionised water was used for washing, the capacity of the resin varied slightly with the amount of washing water used. It appears therefore that excessive washing tends to remove some of the chloride actually sorbed on the resin. In order to determine the optimum quantity of water to be used, several capacity determinations were performed on a 1.0g. sample of Amberlite IRA 400-Cl, the volume of washing water being progressively increased. For comparison, both distilled water which had been deionised by passage through Bio-Deminrolit, and distilled water in equilibrium with the atmosphere, were used in the experiment. The results for the capacities (in terms of grams of silver chloride precipitated) are given overleaf.

From the data accumulated it appears that reasonably constant results are obtained when the resin is washed with 300-600 ml. of deionised water, but inconsistencies appear
when the volume of washing water is increased further. Washing with equilibrium-distilled water appears to give unreliable results.

<table>
<thead>
<tr>
<th>300 ml. quantities of water used</th>
<th>capacity found (grams of AgCl) after washing with de-ionised water</th>
<th>capacity found (grams of AgCl) after washing with equil. dist. water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4236 0.4212 0.4243 washing 0.4256 insufficient</td>
<td>0.4194 0.4187 0.4209 0.4220</td>
</tr>
<tr>
<td>2</td>
<td>0.4206 0.4206 average: 0.4199 0.4202</td>
<td>0.4183 0.4195 0.4179 0.4167</td>
</tr>
<tr>
<td>3</td>
<td>0.4196 0.4201 average: 0.4204 0.4203</td>
<td>0.4175 0.4163 0.4151 0.4168</td>
</tr>
<tr>
<td>4</td>
<td>0.4178 0.4163 average: 0.4173 0.4179</td>
<td>0.4148 0.4134 0.4143</td>
</tr>
<tr>
<td>6</td>
<td>0.4160 0.4152 0.4178</td>
<td>0.4125 0.4127 0.4138</td>
</tr>
</tbody>
</table>
ANNEX II

Calculation of data for fig. 8

\[ R = \frac{\text{Moles of boron sorbed}}{\text{Moles of chloride desorbed}} = \frac{S}{E} \]

(a) Assuming only \( \text{B}_5\text{O}_8^- \) and \( \text{B}_4\text{O}_7^- \) to be sorbed:

Let \( x \) be the number of active sites occupied by \( \text{B}_4\text{O}_7^- \), then the total number of atoms of boron sorbed as this ion will be \( 2x \). Therefore the total number of active sites occupied by \( \text{B}_5\text{O}_8^- \) will be \( (E-x) \).

If sorption is expressed in moles per equivalent of resin then at a particular pH value:

\[ S = 2x + 5(E-x) = 5E-3x \]

therefore \[ x = \frac{5E-3S}{3} \]

Hence for a total sorption of \( S \) moles of boron:

quantity of boron sorbed as \( \text{B}_5\text{O}_8^- \)  \( = \frac{5(E-x)}{3} = \frac{5S-10E}{3} \) moles

quantity of boron sorbed as \( \text{B}_4\text{O}_7^- \)  \( = \frac{2x}{3} = \frac{10E-2S}{3} \) moles

NB. The values of \( S \) and \( E \) may then be obtained from fig. 7
(b) Assuming only $B_4O_7^{-}$ and $HgBO_3^-$ to be sorbed.

If $S$ atoms of boron are sorbed for $E$ atoms of Cl desorbed, let $x$ be the number of sites occupied by $B_4O_7^-$, then the total number of atoms sorbed as this ion is $2x$. Therefore the total number of exchange sites occupied by $HgBO_3^-$ is $(E-x)$, and this also equals the number of atoms of boron sorbed as $HgBO_3^-$. 

Therefore at a particular pH value:

$$S = 2x + (E-x) = E + x$$

therefore $x = S-E$

Hence for a total sorption of $B$ moles of boron:

quantity of boron
sorbed as $B_4O_7^-$ $= 2x = \frac{S}{2}$

quantity of boron
sorbed as $HgBO_3^-$ $= (E-x) = 2E - \frac{S}{2}$

(2) Jander and coworkers, Kolloid Beihefte. 1934.41.1,297 ibid. 1942.72.1

(3) Brintzinger, Z.anorg.Chem. 1935.224.97
Jander and Exner, Z.phys.Chem. 1942.190.195

See also "Properties of Heteropolymolybdates", Climax Molybdenum Co. 500, Fifth Av. New York 36.


(7) Samuelson - "Ion-exchangers in Analytical Chemistry"
Nachod (editor) "Ion-exchange", Academic Press, N.Y.,1949

Thompson - ibid. 1850.11.68

(9) Gans - Jahrb.preuss.geol.Landesanstalt (Berlin)
1905.29.179, 1906.27.63

(10) Folin and Bell - J.Biol.Chem. 1917.29.329


(12) Adams and Holmes - J.Soc.Chem.Ind. 1935.54.1-6T

(13) Wheaton and Bauman - Ind.Eng.Chem 1951.43.1088
Gregor, Belle and Marcus - J.A.C.S. 1955.77.2713

(14) Kunin and Myers - J.A.C.S. 1947.69.2874
Kunin and McGarvey - Ind.Eng.Chem. 1949.41.1265


18) Warren, Vosburgh and Cooper - J.A.C.S. 1941.63.437-42
19) Jander and Spandau - Z.anorg.Chem. 1942.249.65-75
21) Auerbach - Z.anorg.Chem. 1903.37.353
22) Kolthoff - Rec.Trav.Chim. 1926.45.501
Kolthoff and Bosch - ibid. 1927.46.180
23) Menzel - Z.anorg.Chem. 1927.164.22
26) Carpeni and Souchay - J.Chim.Phys. 1945.42.149
27) Carpeni - Compt.Rend. 1948.226.807
Bull.Soc.chim.France. 1948.505
Compt.Rend. 1945.221.99
30) Carpeni - Compt.Rend. 1949.228.89
1952.1010.
33) Souchay - Bull.Soc.chim.France. 1951.932
Souchay and Teyssedre - ibid. 1951.938;
Compt.Rend. 1953.236.1965
Byé - Bull.Soc.chim.France. 1953.390
Souchay - ibid. 1953.395.
34) Stetten - Analyt.Chem. 1951.23.1177
35) Edwards - J.A.C.S. 1953.75.6151
(39) D'Aus and Lax - "Taschenbuch für Chemiker und Physiker"
Springer-Verlag, Berlin.

Hodgman (editor) - "Handbook of Chemistry and Physics"

Suomen Kemistilehti 1956.10.179

(41) Lundberg - Z.phys.Chem. 1909.69.442
Menzel - ibid. 1922.100.276
Owen - J.A.C.S. 1934.56.1695

(42) Hahn and Klockmann - Z.phys.Chem. 1930.151.80

(43) Britton - "Hydrogen Ions" vol I, Chapman and Hall, p.203

(44) Thomson - J.Soc.Chem.Ind. 1893.12.432
Bösekan - Rec.Trav.Chim. 1930.49.711


(46) Edwards, Morrison, Ross and Schultz - J.A.C.S. 1955.77.226


(48) Dukelski - Z.anorg.Chem. 1906.50.38; 1907.54.45

(49) Sborgi and Mecacci - Atti accad.Lincei. 1916.25II.327, 455.

(50) Menzel, Schultz and Dekert - Z.anorg.Chem. 1934.220.49
Kracek, Mosey and Mervin - Amer.J.Sci. 1938.(5).35A.43

(51) Gilbert and Levi - J.C.S. 1929.527


(53) Zachariason - Z.Krist. 1934.88.150

(54) Kahovec - Z.phys.Chem. 1938.340.135

(55) Garret, Holmes and Laube - J.A.C.S. 1940.62.2024

(56) Roth and Schwartz - Ber. 1926.59.338

(57) Brintzinger and Ratanarat - Z.anorg.Chem. 1935.222.317
(60) Souchay and Teyssedre - Compt. Rend. 1953. 236. 1965
(63) Hampson and Stosick - J.A.C.S. 1938. 60. 1814
(64) Souchay and Hessaby - Bull. Soc. chim. France. 1953. 614-21
Cernatescu and Meyer - Z. phys. Chem. 1932. 160. 309
(66) Wood - J.C.S. 1908. 93. 411
(67) Hughes - J.C.S. 1928. 941.
Britton and Jackson - J.C.S. 1934. 1048
1940. 19. 136
British Abstracts. 1940. A.I. 321
(69) Bridgleb - Z. Electrochem. 1944. 50. 35
(71) Stuber, Braida and Jander - Z. phys. Chem. 1934. A171. 320
(72) Schreinemaker and de Baat - Chem. Weekbl. 1917. 14. 262, 288
(73) Nelson - J.A.C.S. 1941. 63. 1870
(76) Patry - Bull. Soc. chim. France. 1936. 3. 845-60
(78) Patry - Compt. Rend. 1935. 201. 71-3
Pascal and Patry - Compt. Rend. 1935. 200. 701-11


(82) Rosenheim and Jander - Kolloid.Z. 1918.22.23-44 J.C.S. 1918.114 11.194-5

(83) Ghosh and Dhar - Z.anorg.Chem. 1930.190.421-7

(84) Souchay and Teyssedre - Compt.Rend. 1953.236.1965-6


(86) Earley and Edwards - United States Technical Reports published in 1955:
Dept. of the Army, project no. 5B99-01-004
Ordnance Res. and Development project no. TB2-0001
Office of Ordnance Res. Project no. 1349

(87) Antikainen - Soumen Kemistilehti 1955.28.135 ibid 1957.530.22-3 (English)

(88) Ley and König - Z.phys.Chem. 1938.41.365


(90) Gutbier - Ber. 1901.34.2724; Z.anorg.Chem. 1904.40.260 and 42.174
Karve - Journ.Ind.Chem.Soc. 1925.1.247 and 2.128
Venkateswaran - Proc.Ind.Acad.Sci. 1938.7A.13-20, 144-55
Stehlik - Chem.Zvesti 1948.2.229-31
Emeleus and Anderson - "Mod.Asp. of Inorg.Chem", p.333

(91) Blanc - J.Chim.Phys. 1920.18.28

(92) Fouasson - Compt.Rend. 1946.222.958-9
Ann.Chim. 1948.5.594-643

(93) Karve - Quat.Journ.Ind.Chem.Soc. 1924.2.128

(94) Mylius - Ber. 1901.34.2209
International Critical Tables vol.IV, p.217

(95) Heberlein - Diss.Basel. 1898
(96) Antikainen - Suomen Kemistilehti 1956.B29.135
    ibid 1956.B29 no.2.14-20

(97) Berzelius - Poggendorff Annalen. 1832.28.392; 1834.32.577

Hutchins - J.A.C.S. 1905.27.1157