STUDIES OF COMPLEX FORMATION IN THE SYSTEM CHROMIUM (111) - PHOSPHORIC ACID

by

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SUMMARY

The aim of the work described in this thesis has been to further the existing knowledge of the chromium (111) - phosphoric acid system in aqueous media.

Because of the length of time required for the system to attain equilibrium at room temperature, the majority of the solutions investigated were aged at 70°C. Methods for deciding whether equilibrium had in fact been reached were determined.

At 70°C. a phase diagram study of the system Cr_2O_3-P_2O_5-H_2O gave a series of parallel tie-lines and no compound could be isolated as such. A preliminary investigation into the nature of the solid material indicated that it behaved as an ion exchanger. Possible structures have been put forward.

The results of ion-exchange studies carried out on both saturated and unsaturated solutions of the system indicated the existence of polynuclear species. The batch studies using cation exchange resins of varying degrees of cross-linking show that there is a marked 'sieving out' effect where the cross-linking is heavy. From the chromatographic separations employing the technique of gradient elution the PO_4 : Cr ratio of a number of these complexes have been evaluated. Probable structures have been allocated to these 7 complexes. Modes of formation have also been discussed.

The structure of the cationic complexes existing in solution and the nature of the solid phase in contact with a saturated solution are discussed in terms of a concept of "-olation" which is held to be capable of extension.

CONTENTS

PART ONE. GENERAL INTRODUCTION

PART TWO. BASIC EXPERIMENTAL PROCEDURES

PART THREE. EXPERIMENTAL WORK AND RESULTS

CONTENTS (Contd.)

The work described in this Thesis was carried out in the Chemistry Research Laboratories of the Battersea College of Technology under the supervision of Dr. J. E. Salmon to whom thanks are due for continued advice and encouragement during the course of the work.

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PART I

GENERAL INTRODUCTION

SECTION A.

HISTORICAL BACKGROUND.

1. Chromium (111) Compounds and Solutions.

The existence of two well-defined series of chromium (111) compounds has been known for a long time. The chronological bibliography by Graham (1) who surveyed the literature from 1841 - 1912 provide examples in relation to the chromium (111) sulphate system. In many instances the division into these two series is perpetuated when the compounds are dissolved in aqueous media.

SERIES A. - Violet Chromium (111) Compounds and Solutions.
Two examples may be quoted, namely the violet chromium (111) fluoride hexahydrate perpared by Werner and Costachescu (2) and the violet chromium (111) chloride hexahydrate prepared by Recoura (3).

SERIES B. - Green Chromium (111) Compounds and Solutions.
Two examples may be quoted as illustrating this, namely the pale green chromium (111) chloride hexahydrate prepared by Bjerrum (4) and chromium (111) chloride trihydrate prepared by Recoura (5).
For a fuller review the list compiled by Pfeiffer (6) in 1908 may be consulted.

From a study of physical and chemical properties of SERIES A compounds and solutions it has been established that the structure of the violet forms is $[Cr(H_2O)_6]A_3\ xH_2O$ with the six water molecules octahedrally disposed around the central Cr ion. This view is supported by the evidence of crystal studies and polarographic studies on violet chromium (111) trichloride hexahydrate by Andress and Carpenter (7) and by Willis (8), and polarographic studies on violet chromium (111) sulphate by Datar and Kulkurni (9).

In general, in the SERIES B Compounds, it has been shown that an anionic ligand group or atom has entered the co-ordination sphere of the hydrated chromium (111) ion to give a complex ion of the type $\left[Cr\ (H_2O)_xA_y\right]^{(3-y)-}$

For example Bjerrum (4) has shown that the pale green chromium (111) chloride hexahydrate when treated with silver nitrate precipitates 2/3 of the total chlorine indicating a formula for the compound of $\left[Cr(H_2O)_5Cl\right]Cl_2H_2O$ He supported thisevidence by showing that the two chlorides could be replaced by other anions - preparing inter alia $\left[Cr(H_2O)_5Cl\right]\ PtCl_65H_2O$. Colson (10) has shown that there are three classes of chromium (111) sulphates in which 1/3, 2/3, or 3/3 of the total sulphate is not precipitated by the addition of a cold barium chloride solution. He concluded that the sulphate was linked to the chromium.

The literature on SERIES B compounds and solutions seems to distinguish between two principal types of compound or complex ion.

Type B_1 - The Mononuclear Series.

This may be typified by quoting the example of the three green modifications of the chromium (111) trichloride hydrates as described by Bjerrum (4), Werner and Gubser (11) and Recoura (5) which have been shown to be the following compounds:

1). $[Cr(H_2O)_5Cl]\ Cl_2\ H_2O$.

2). $[Cr(H_2O)_4Cl_2]\ Cl\ \ 2H_2O$.

3). $[Cr(H_2O)_3Cl_3]$

The complex part of the compound is mononuclear and of general formula

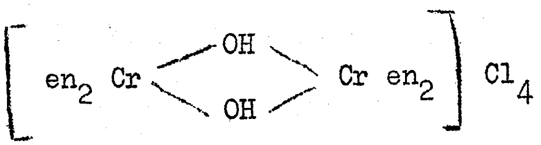
$$\left[Cr\ (H_2O)_{6-x}\ X_x\right]^{(3-nx)+}$$

Where n is the valency of x and assuming x to be a monodentate ligand group or atom.

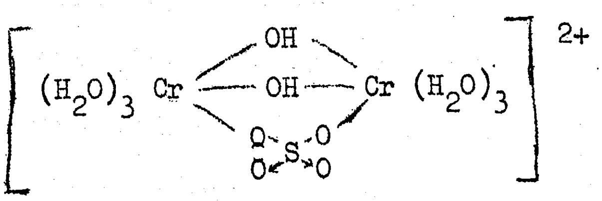
Type B2 - The binuclear and polynuclear series.

Such compounds have been prepared and discussed by many workers notably Dubsky (12), Jensen (13), Stiasny (14), Balanyi (15), Erdmann (16), Hall and Eyring (17), Gustavson (18).

These structures have been examined by various methods - principally conductimetric methods and the suggested structures involve bridging through hydroxyl, -oxo- or oxyanion - between two or more chromium (111) ions. e.g. the ethylenediamene complex described by Dubsky (12) is formulated as :



and Erdmann (16) explains the behaviour in chromium (111) sulphate solutions under the conditions of his examination in terms of ions such as



and the well known -ol series as described by Bjerrum (19) and the -oxo series described by Stiasny (14) in which the bridges are -OH- and -O- respectively.

11. Chromium (111) - Phosphoric Acid System.

Few systematic reports were available of work on the phosphates of the tervalent metals - particularly the nature of the complexes existing in solution except in the case of the iron (111) - phosphoric acid system - until the work of Salmon and his school see e.g. Salmon (20).

In the chromium (111) - phosphoric acid system few compounds have been described although the existence of both green and purple compounds indicates the presence of complexing as well as simple ions and salts. The previous work which is relevent to the present study of this system may be divided into 2 parts.

PART 1. Solid materials formed.

PART 2. Solution chemistry investigations.

PART 1. A brief summary of the solid materials that have been characterised. These may be divided into Series A violet compounds and Series B green compounds as follows.

Series A. Purple-Violet Modifications. The following chromium (111) phosphates have been described.

A.	Cr_2O_3 P_2O_5 $12H_2O$	Dull purple hexagonal plates.
B.	$2Cr_2O_3$ $3P_2O_5$ H_2O	Black irregular shaped crystals.
C.	Cr_2O_3 $2P_2O_5$ $19H_2O$	Purple hexagonal sectioned crystals.
D.	Cr_2O_3 $3P_2O_5$ $18H_2O$	Bright - purple crystals.

A has been described by Gluhmann(21), Rammelsberg (22), Joseph and Rae (23), Ness, Smith and Edwards (24), Jameson and Salmon (25). C has been described by Haushofer (26) and Jameson and Salmon (25), and B and D by Jameson and Salmon (25). These last workers described these solids and suggested possible structures as a result of a Phase Diagram study carried out at 0°C.

Series B. Green Modifications. The following chromium (111) phosphates have been described.

A. $Cr_2O_3 \cdot P_2O_5 \cdot 12H_2O$	Pale green microcrystalline solid.
B. $Cr_2O_3 \cdot 2P_2O_5 \cdot 8H_2O$	Dark green semicrystalline solid.
C. $Cr_2O_3 \cdot 3P_2O_5 \cdot 10H_2O$	Bright green crystals.

A has been described by Glühmann (21), Rammelsberg (22) and Jameson and Salmon (25), whilst B and C have been isolated by Jameson and Salmon (25). These last workers described these solids as a result of a Phase Diagram study carried out at 40°C.

PART 2.

Investigations on solutions of the chromium (111) phosphates in phosphoric acid have been carried out by Jameson and Salmon(25) and by Holroyd and Salmon (27). Their work indicates that in freshly prepared solutions of the purple, tertiary chromium (111) phosphate (i.e. $[Cr(H_2O)_6]PO_4$) dissolved in phosphoric acid over a range of concentration of 1% -25% P_2O_5 there is no evidence at all for the complex formation involving the phosphate ion in the dichroic purple-red solution - that is that such solutions consist of $[Cr(H_2O)_6]^{3+}$ together with H_3O^+, $H_2PO_4^-$, and HPO_4^{2-}, together with undissociated H_3PO_4.

However if such solutions were aged at 25°C or 40°C for some considerable time they turned green slowly and a number of complexes were reported. 40°C was apparently selected for the bulk of the investigation since at this temperature conversion of the purple-red solution to a stable green solution took place at a reasonable rate (i.e. a matter of weeks rather than a matter of months as it was for many solutions maintained at 25°C or lower); also, because these workers reported that a radical change seemed to take place in solutions maintained above this temperature. This was in accord with an observation noted by Vauguelin (28). Holroyd and Salmon (29) have reported that there is little evidence, by ion-exchange experiments, for the existence of cationic or anionic complexes in solutions heated considerably above 40°C. The pH and ion-exchange studies by Holroyd and Salmon (27) on solutions aged at 25° and 40°C indicate the formation of complexes. Whilst the ion-exchange studies of Jameson and Salmon (25) on saturated solutions aged at 40°C suggest that the following complexes do exist $\left[Cr(PO_4)_2\right]^{3-}$, $\left[Cr(HPO_4)\right]^{+}$ and less likely $\left[CrH_2PO_4\right]^{2+}$ and $\left[Cr(H_2PO_4)_2\right]^{+}$. It is however clear from their work that there were other complexes in equilibrium as well.

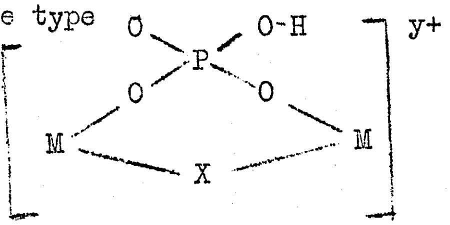
Note. In the formulation of complex ions the co-ordinated water molecules which are also present are omitted both for sake of clarity and for conciseness.

SECTION B.

Reasons for undertaking the present work.

From the discussion in the previous section there emerge a number of reasons which made it desirable to further the work in the field of the chromium (111) - phosphoric acid system.

a). Work on the phosphate complexes with various tervalent metals suggests that the phosphate ligand has the possibility of behaving as a mono-,di-,or tri-dentate ligand: whilst the last is theoretically, possible and, in fact, postulated by Weinland (30) it seems unlikely from geometrical considerations. The first two possibilities seem however to be the most likely. There is one further possibility - namely that of phosphate serving as a bridging ligand in a polynuclear complex to give an ion of the type



It seemed desirable then to extend the work already done in order to throw some light upon the role of phosphate as a ligand in the green aged chromium (111) phosphate solutions.

b). The passing observation that at a temperature somewhere above 40°C the solution of chromium (111) phosphate in phosphoric acid undergoes a radical change is one which challenges investigation.

c). Particular interest stems upon the behaviour of chromium (111) in forming two green series of compounds and complexes - especially with regard to the formation of polynuclear complexes.

d). The chemistry of iron and aluminium is often compared to that of chromium and work on the parallel systems to chromium (111) - phosphoric acid i.e. iron (111) and aluminium (111) phosphoric acid has been carried much further and a more complete picture is available - hence it seemed desirable to bring the state of knowledge in the chromium (111) field up to the level of the other two.

SECTION C.

Scope of the present work and discussion of the methods used.

The Scope of the present work.

The main objective of the present study has been the elucidation of the nature of the cationic complex ions present in solution above 40°C. For this purpose work has been carried out on solutions of $[Cr(H_2O)_6]PO_4$ dissolved in phosphoric acid which were aged at 70°C. Other objectives have been the elucidation of the nature of any solid phases present at this temperature and estimations on the amount of anionic, cationic and neutral complexes present in certain solutions. In addition a certain amount of work has been carried out at 25°C, 40°C and 100°C in an attempt to clarify and amplify the knowledge provided by the earlier work in the field.

The methods employed in the investigation were as follows.

a). 'Dynamic' studies.

b). Phase diagram studies.

C). Spectrophotometric studies.

d). Ion-exchange studies.

The objectives it was hoped to achieve with each of these methods.

a). 'Dynamic' Studies. Mere visual observation of a solution of chromium (111) - phosphate in phosphoric acid is obviously insufficient to decide when a given solution could be regarded as completely aged. An ion-exchange and a spectrophotometric method have been devised which were shown to be perfectly adequate for this.

b). Phase diagram studies.

A phase diagram study of the system chromium (111) oxide - phosphoric oxide water was carried out at 70° in order to determine (i) The nature of the solid phases at this temperature. (ii) The composition of the solutions in contact with the solid phases at this temperature i.e. the solubility isotherm.

c). Spectrophotometric methods.

Since all solutions of the chromium (111) phosphoric acid system are highly coloured it seemed logical to investigate the system spectrophotometrically. However, apart from providing a method for deciding whether a solution was fully aged or not little information could be gained from this method.

d). Ion-exchange studies.

Ion-exchange resins have been used in the elucidation of a number of systems of complex ions in solution, in consequence studies using this technique constituted the main method of approach in the present study. Four different ways were employed to this end.

1). Batch Experiments;displacement of the sorbed Cr (111) species from the resin phase.

A number of batches of resin were treated with various chromium (111) phosphate - phosphoric acid solutions and after washing and air-drying treated with various acids and salt solutions in order to investigate the behaviour of the complexes in the process of removal from the resin phase. The information gained from these experiments was of value in deciding the conditions under which column separations of the various complexes should be carried out.

(11) Batch experiments; Sorption of Cr (111) species by the resin phase.

A large number of batch experiments were carried out with strongly acidic cation exchangers in the H form in order to determine the nature and charge of the various cationic complexes present in saturated and unsaturated chromium (111) phosphate - phosphoric acid solutions. Primarily these solutions were aged at 70° but work was also done on solutions aged at 25°, 40° and 100°C.

(111) & (1V) Column experiments.

A number of column experiments were carried out in attempts to separate and identify the cationic and anionic complexes present in the solutions under investigation. Whilst separations were achieved a number of difficulties have been encountered which made the results of this work rather difficult to interpret.

The theoretical discussion of the methods employed.

A) 'Dynamic' studies. see under Basic Experimental Procedures. (Part 2 Section A).

B) Phase diagram studies.

The system under investigation is essentially a solid-liquid one and hence it is possible to disregard the pressure variable and to assume that atmospheric conditions represents a constant pressure. Thus this system of three components, namely Cr_2O_3 - P_2O_5 - H_2O which has four degrees of freedom, has one degree of freedom fixed. The other variables which may be varied independantly are temperature and the concentrations two of the components. The object of the present work was to secure information at 70° consequently it is possible to work under isothermal conditions, and this means that only the two concentration terms may be varied independently.

In representing results of such a system the most usual method used is the triangular diagram. The use of an equilateral triangle is standard practice and has a number of advantages. Each side is taken as representing 100% of one component. 100% of component A is represented by the apex at which A is located. Then the side opposite apex A namely BC (see Fig. 1) represents 0% of component A then :-

1) For any point (P) in the equilateral triangle (see Fig 1) the sum of the distances of this point to the sides of the triangle (represented by Pa, Pb, Pc in the figure) are equal to the length of the side of the equilateral triangle which means that Pa + Pb + Pc = 100% and thus P represents in a unique manner the compound or mixture comprising Pa % A, Pb% B and Pc % C. Generally however the composition of P is measured along the sides of the triangle namely BB', AA', CC', where

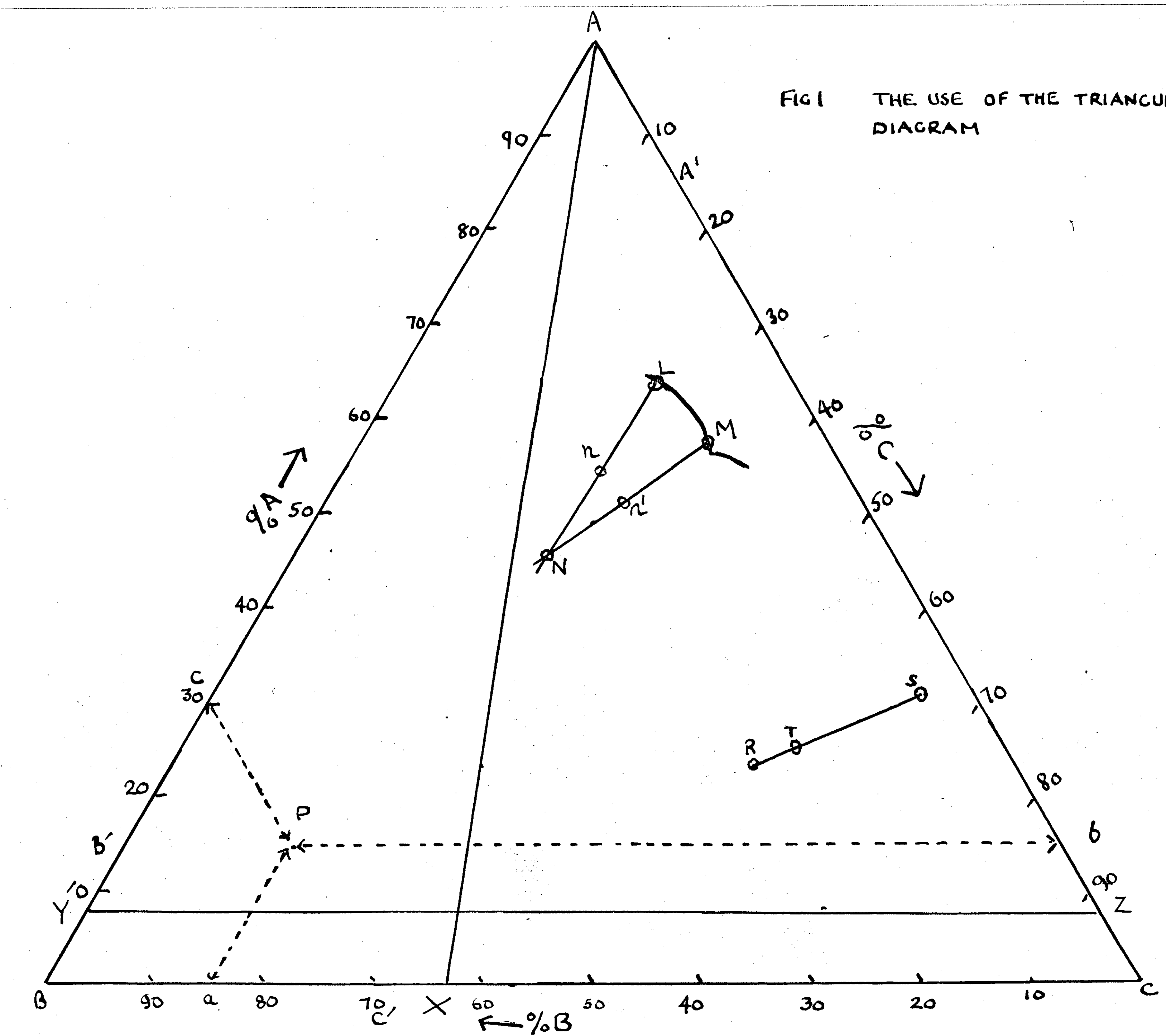
Pa = BB' , Pb = CC' , Pc = AA'

2) If a line is drawn through any corner (say A) to a point on the opposite side (say X) then the line represents differing amounts of A while the other 2 components B and C will bear a constant ratio to each other.

3) A line parallel to any side represents a constant amount of the component represented by the corner opposite to that side whilst the amounts of the other two components vary. (Thus YZ in the figure represents a constant amount of component A).

4) If R and S represent the composition of two mixtures of the three components, then any point on the line joining R and S, such as T (see Fig 1.) will represent a mixture of R and S in the proportions TS and TR respectively.

FIG I THE USE OF THE TRIANGULAR DIAGRAM



From (4) a number of important principles arise.

a) When one mixture is added to another, then the point representing the product will move in a straight line towards that mixture which is being added. If the mixture (in terms of the components) is water then one may deduce what the effect of dilution on a particular mixture will be.

b) If the composition of one phase is known and also the composition of a mixture partially of this known phase and partially of another unknown phase then the composition of the latter may be determined by extrapolation.

Use of this is made in the so-called "wet-residue" method due to Schreinemakers (31) on which one can find the composition of the solid phase in equilibrium with a given saturated liquid. Thus if the line LM represents a series of saturated solutions and N the solid that is in equilibrium with them. By direct analysis it is possible to ascertain the composition of two such solutions say L and M, but to obtain the composition of N directly may be extremely difficult especially if the solid phase corresponding to N is hygroscopic or cannot be washed free of mother liquor without decomposition. However if the samples of solid are taken still moist with mother liquor analyses will give say the points n and n'. Then the intersection of Ln and Mn' produced will give the composition of N. In normal practice it is usually necessary to have four or more such 'tie-lines' in order to fix accurately the composition of the solid phase corresponding to N.

It is thus possible to construct a complete three component phase diagram by analyses of a series of saturated solutions in contact with solid materials.

Occasionally the tie-lines obtained do not meet at a point but may be parallel or even diverge. If the tie-lines are parallel this may be indicative of the fact that the system is metastable (see Jameson and Salmon. 32) or alternatively that the system forms a series of solid solutions effectively behaving as an ion-exchange material.

C) Ion-exchange Resins.

The main requirements of solid ion-exchange materials are that they should

1) posses an open structure with pores or channels of such a size so as to permit entry and exit of both solvent and the solvated ions.
2) be chemically inert to the solvents to be used and to oxidizing and reducing agents.
3) be thermally stable - preferably so that if necessary they may be oven dried at 110°C.
4) comprise a semi-rigid network with attached or incorporated ionic groups of one charge type (i.e. either positive or negative) and preferably of one chemical type $-SO_3^-$, $-COO^-$, NR_3^+ to quote three examples. All the ions of opposite charge are bound by electrostatic forces only and constitute the counter-ions which are capable of exchange in a reversible manner.
5) be physically stable - that is, that under conditions of swelling or contraction normally met with in a changing ionic media the beads do not undergo physical disintegration.
6) be effective as an exchanger over a wide range of pH.

Such requirements are closely approached by the modern ion-exchange resins based on a cross linked polystyrene matrix. To the resin beads are attached by chemical methods the various types of active groups as quoted above in requirements (4).

A typical synthesis of a strongly acidic cation ion-exchange resin is shown in Fig. 2A and of a strongly basic anion-exchange resin is shown in Fig. 2B .

FIG 2 A+B TYPICAL SYNTHESES OF ION-EXCHANGE RESINS BASED ON POLYSTYRENE.

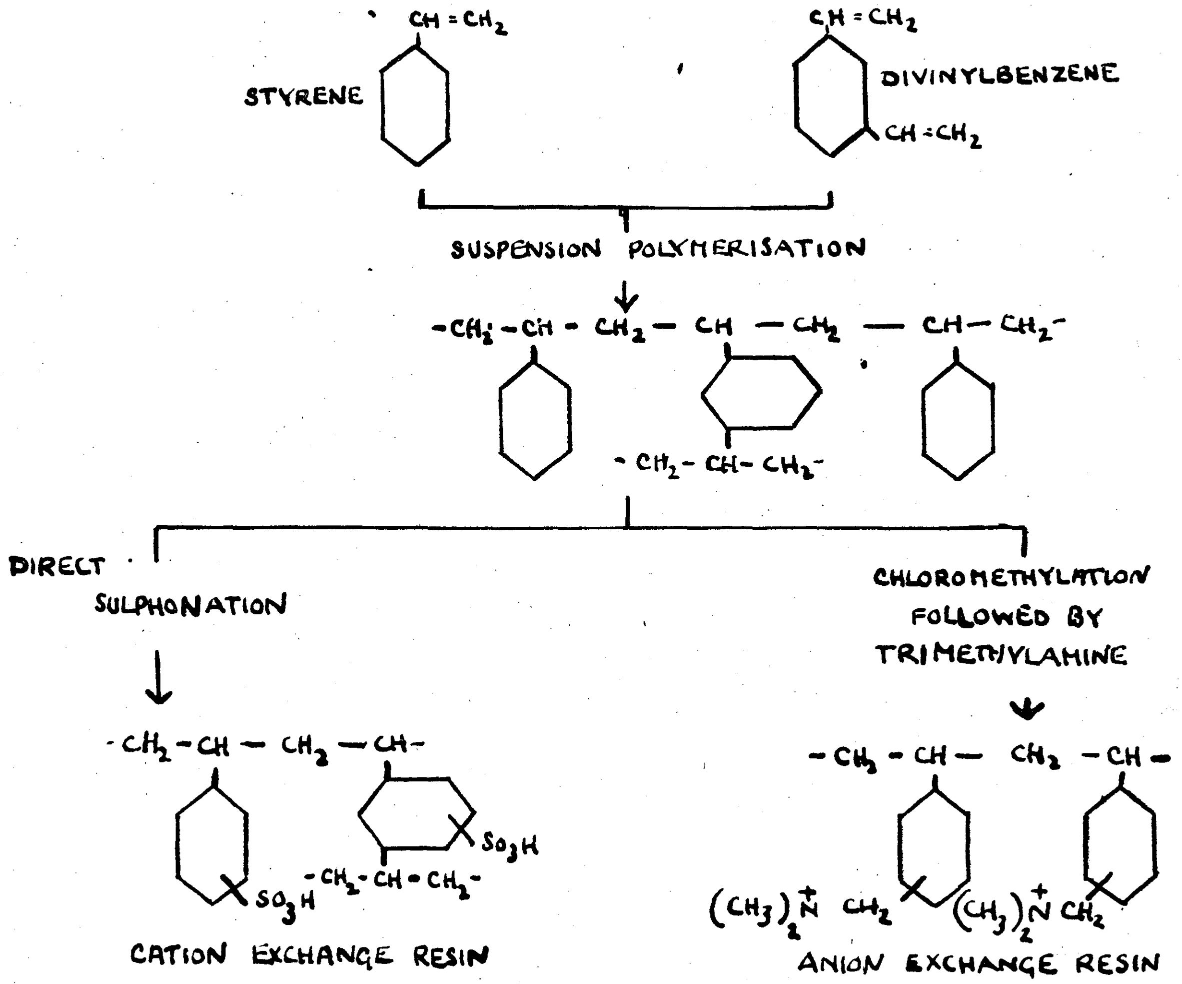
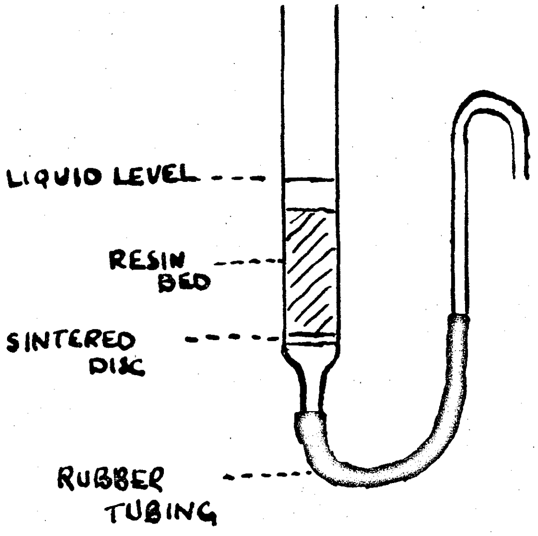


FIG 2c DIAGRAM OF AN ION EXCHANGE COLUMN



Behaviour of the Resin.

Before discussing the application of ion-exchange resins to the study of complex systems in solution it is of importance to recognize the type of behaviour that is to be expected of resins when they are placed in solution.

The presence of polar groups in the resin will tend to make the resin swell in water. Whereas the presence of the cross linkages in the resin matrix will tend to oppose this effect. Hence an increase in the number of effective cross linkages will tend to decrease the amount of swelling. At the same time a high degree of cross linking will tend to reduce the rate of diffusion of small ions through the resin beads and will entirely or partially prevent the passage of larger ions. A further effect on the rate of diffusion in the resin bead will be brought about by changing the particle size and small particle size will increase the rate of diffusion.

As has been said there is generally little or no interaction between the sorbed species and the fixes polar groupings or the resin matrix.

From these remarks it will be clear that in a system which may involve large inorganic ions it is necessary to choose the resin, degree of cross linking and particle size with care.

The degree of cross-linking may be expressed in two ways.

1) as a % of the cross linking agent added to the reaction mixture. - In the case of a cross linked polystyrene resin the normal cross-linking agent used in divinylbenzene and the degree of cross linking would be expressed as % DVB (divinylebenzene). Thus a resin having 20% DVB would be very heavily cross linked whilst one with 1% DVB would be very lightly cross linked. This way of stating the degree of cross linking is reasonably

accurate but it does not take account of the fact that there may be an uneven distribution of cross linkages nor the fact that additional links may be formed on subsequent treatment - in particular on the introduction of the quartenary ammonium groups for the preparation of a strongly basic anion exchanger.

2) Consequently a quantity entitled Water Regain or Weight swelling has been defined to give more accurately a comparison between different resins.

It is defined as follows:

$$\text{Weight Swelling} = \frac{\text{Weight wet resin} - \text{Weight dry resin}}{\text{Weight dry resin}}$$

determined under carefully defined conditions. It is purely an empirical expression depending to a certain extent on the conditions laid down. Nevertheless a set of values of weight swelling of a number of resins determined under the same conditions affords an accurate and helpful comparison of the degree of the mean cross linking in these resins.

In the course of the present studies the following resins have been used.

Cation Exchanger. Permutit Zeokarb 225 which is a cross linked sulphonated polystyrene. A whole range of resins of different degree of cross linking was used viz. %DVB ranging from 1/2- 20 and the weight swelling values ranging between 22 and 0.43.

Anion Exchanger. Permutit Deacidite FF was used. This is a cross linked polystyrene with incorporated quartenary ammonium groups.

Equilibrium of Exchange.

One of the earliest observations concerning ion-exchange was that it was a reversible process and one that takes place by equivalents. If the reaction between a cation exchange resin in the Hydrogen (H+) form and a metal M^{m+} (ignoring co-ordinated water molecules) is considered

An equilibrium is established which may be written

$$M^{m+} + \overline{mH^{+}} \rightleftharpoons \overline{M^{m+}} + mH^{+} \quad \text{——}(1)$$

where barred formulae represent ions in the resin phase)

The following features have been established.

a) The reaction proceeds stoichiometrically and hence, for every gramme equivalent of ion M^{m+} taken up by the resin a gramme equivalent of H^{+} will pass into the solution.

b) The reaction is reversible and whichever way the equilibrium is approached this equilibrium with a given solution and a given quantity of resin will always be the same. It is possible if the resin is held in a glass column to 'force' the reaction represented in equation (1) to go to completion by the passage down the column of a large excess of the metal ion.

c) Provided the cross linking of the resin beads is sufficiently open to permit the entry of the ions under investigation all the exchange sites are accessible to these ions. Thus the total exchange capacity (usually expressed as milliequivalents of metal ions or H+ ions per gm of dry resin) is the same for all cations. The capacity of an anion exchanger may be described in a similar manner.

d) One of the most important properties of ion-exchange resins is that they show different affinities for different ions see eg. Kitchener (33)

The equilibrium represented by equ^{n} (1) is independent of the anions present in solution. However if one or more of the anions present in the same solution normally forms complexes with the metal M^{m+} the situation is somewhat modified and merits separate discussion.

The use of ion-exchangers in the investigation of complex ions.

In any study of complex formation in an inorganic system it is necessary to establish:

1) That complex formation does occur.
2) The nature of the complexes i.e. whether they are netural, cationic, or anionic.
3) The composition of the complexes.
4) The number of complexes.
5) The change on each complex.

Ion Exchange techniques have been used successfully for all these and a large amount of work has been carried out in this field. In the system under discussion present work has utilised results of ion-exchange studies towards elucidation of points 2 - 5.

The following different approaches have been used.

a) Batch experiments - Desorption of Cr (III) species
b) Batch experiments - Sorption of Cr (III) species
c) Column separations.
d) Ion exchange chromatography.

The essentials of the batch method.

The essential steps in the batch method are as follows:-

A known volume of solution of known composition is shaken or stood in contact with a known weight of air dried resin until equilibrium is attained. The resin and solution are then separated usually by filtration through a small dry column with a sintered disc sealed in position (see Fig.2c).

The filtrate may be retained by collecting in a dried container for subsequent measurements and analysis to be made on it.

The transference of resin to the column is best completed using a jet of water and the resin is washed very rapidly with water under suction. In this way any solution adhering to the resin is quickly displaced and

a) interaction between partly diluted solution and the resin is avoided,

b) the washing off of any lightly held complex is kept to a minimum.

The column is filled with water (with an upward flow to displace air from below the sintered disc and from between the resin beads), and then washed thoroughly with a downward dropwise flow of water to remove any last traces of the adhering solution. Finally the species sorbed on the resin may be removed by eluting the column with a suitable eluting agent. An analysis of the eluate may be carried out if required.

The following advantages may be noted.

1) Smaller quantities of exchanger and smaller volumes of solution may be employed. The ratio of volume of solution to mass of resin has to be arranged so that the changes occurring in the composition of the solution on exchange are small.
2) Attainment of equilibrium may be hastened by shaking the exchanger with the solution.
3) The results of quantitative experiments are often more easily interpreted.
4) The extent of exchange after a given time may be determined if necessary.

There are two main types of batch experiments called, respectively a) batch removal experiments, and b) batch uptake experiments. - Where the terms removal or uptake are applied to the ion or ions being studied.

<u>Batch Experiments</u> - Desorption of metal ions.

The removal of a polyvalent metal M^{m+} by an acid from the resin may be expressed by the following equilibrium.

$$\overline{M^{m+}} + mH^{+} \rightleftharpoons M^{m+} + \overline{mH^{+}} \quad -(2)$$

Normally anions present in solution have little or no effect on this equilibrium unless they are capable of forming complex ions with the metal cations. Such complex formation would be indicated by a disturbance of the equilibrium.

Complex formation between a metal cation and an anion A may be represented as follows

$$M^{m+} + nA^{z-} \rightleftharpoons MA_n^{\;y-} \quad - (3)$$

Thus, if complexing is occurring there is an effective decrease in the concentration of M^{m+} in solution and equilibrium (2) would be displaced and a greater amount of M^{m+} would be removed from the resin.

Batch experiments involving the metal form of the resin and various acids over a pH range can furnish one with a semiquantitative measure of the complexing power of that acid anion (see Genge and Salmon 34).

The limits of pH usually chosen lie between 0.05 - 1.5 for tervalent metals and within these limits it is possible to make the following assumptions.

1) At a given pH, the hydrogen ion concentration is the same for all acids.
2) That a dibasic or tribasic acid is ionized principally to yield only the first hydrogen i.e. phosphoric acid yields primarily H_3O^+ and $H_2PO_4^-$.
3) Therefore the anion concentration must also be the same.

The applications of this method are:-

A) Any differences in the amount of M^{m+} removed from a resin in the metal form by different acids at the same pH will be a rough measure of the complexing power of those acids.

B) If one uses different metal forms of the resin with one acid it is possible to get either

1) an idea of the relative affinity of the metal ions for the resin

or

11) an idea of the order of complexing power of the given acid anion with the metal ions.

C) It is also possible to compare the relative affinity of a number of complex ions for the resin in a similar way.

Present work has been carried out and information gained on points A and C above.

Batch Experiments. - Sorption of metal ions.

The equilibrium between a cation exchanger in the hydrogen form and a solution containing hydrated M^{m+} ions will be represented by equ^{n} (1) and is independent of the ions present unless complexes are formed.

The formation of complexes with a ligand group L will lead to complexes of the type ML, ML_2 ML_3 ..... ML_n. If L is neutral then the complexes formed will all be cationic. But if L is anionic the complexes in addition to being cationic may be neutral or anionic as well. Any cationic complexes present in solution coming into contact with a cation exchanger in the H^+ form may be sorbed by the exchanger and the equilibrium will be of the type represented by the equation:

$$(ML)^{x+} + \overline{xH^+} \rightleftharpoons \overline{(ML)^{x+}} + xH^+ \quad \text{----(4)}$$

Information from batch experiments of this type will establish.

1) That complex formation is occuring in the solution if L is detected in the eluate from a resin sample originally in the H^+ form after that sample has been separated from the solution, and thoroughly washed and eluted with acid.

2) It is possible, if uptake may be regarded as complete, (and the ions in question - provided that the pH is not too low - will have a relatively high affinity for the resin) to make certain calculations on the assumption that the capacity of the resin may be wholy accounted for in terms of free metal ions (if any) and the complex species involved. These calculations may be applied and the most likely complexes existing may be elucidated.

Discussion of the calculations that may be made is deferred to the relevant section but a review of this method of approach is given by Salmon (35).

The Essentials of the Column Method.

In column experiments the essentials are:-

A glass column (usual size 10in x $\frac{1}{2}$in) with a sintered disc sealed in position (see Fig 2) or alternatively plugged with glass wool is loaded with a slurry of resin. Satisfactory packing of the column is achieved by allowing the resin to settle under gravity after back-washing with a stream of water of sufficient velocity to lift the resin bodily to the top of the column. If this process of back-washing is carried out twice the column will be ready for usage. The column is then loaded by passage of the appropriate solution. In general only a very small amount of the total resin capacity of the column is utilised (5 - 15%).

Column Separations.

One of the ways in which column work has been applied to the present study has been the separation of complex ions into the three different classes namely cationic, anionic and if any, neutral complexes present in a particular solution.

Two colums were set up in series - the first contained a cation exchanger in the H^+ form and the second an anion exchanger. The solution of dhromium (111) - phosphoric acid was added dropwise to the top of the first column and subsequently washed through the two columns with water. The cationic complexes were sorbed at the top of the first column and the anionic and neutral were unaffected and passed through to the second column where the anionic complexes were sorbed as a band. The neutral complexes, if any, passing through into the final effluent. After thorough washing each column was eluted separately and analysis gave % cationic % anionic and % neutral complexes present in the particular solution being investigated.

The second way in which column experiments were used was in the separation of the various cationic complexes present in solution. The actual design of the column is discussed in the experimental section later.

In the course of the present work two methods of trying to achieve a clear separation of the complexes was tried.

a) Step-wise Elution.

After loading the column (to about 1/10 capacity) and washing free of anionic and neutral species a very dilute eluant is passed down the column. The most lightly held complex is then eluted.

FIG 3A BASIC GRADIENT ELUTION APPARATUS

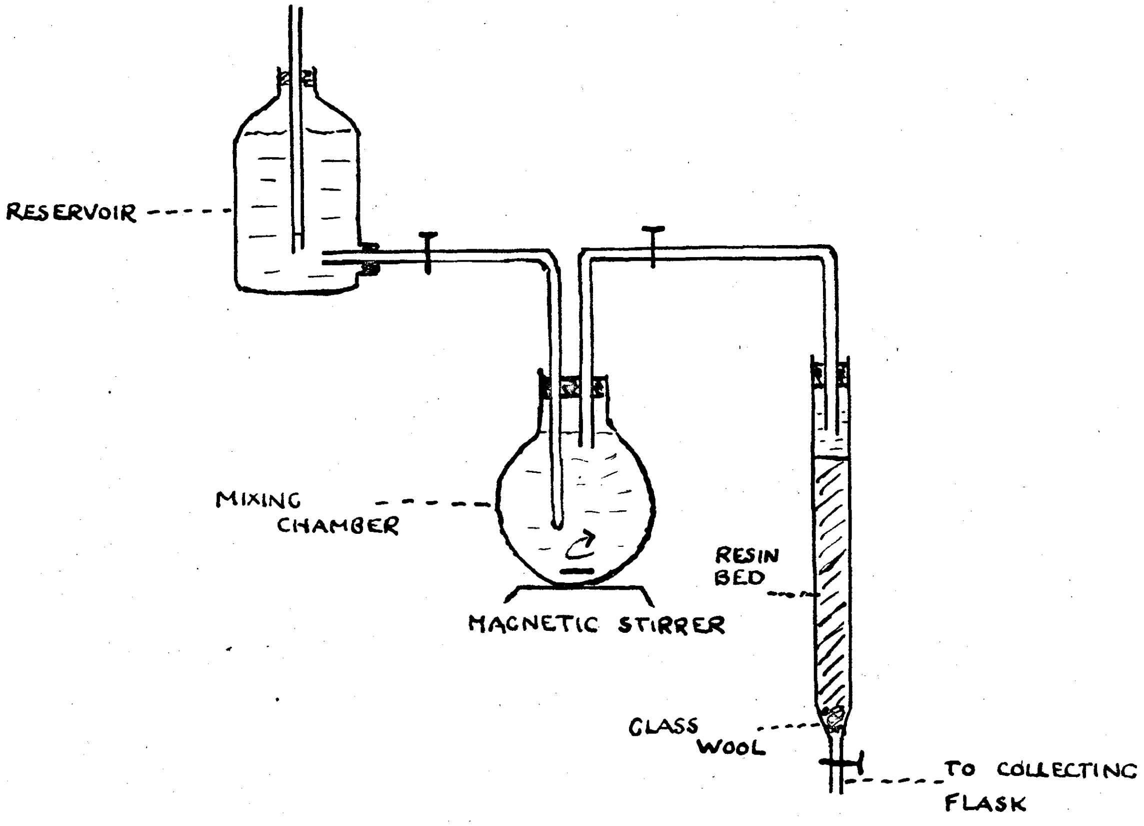
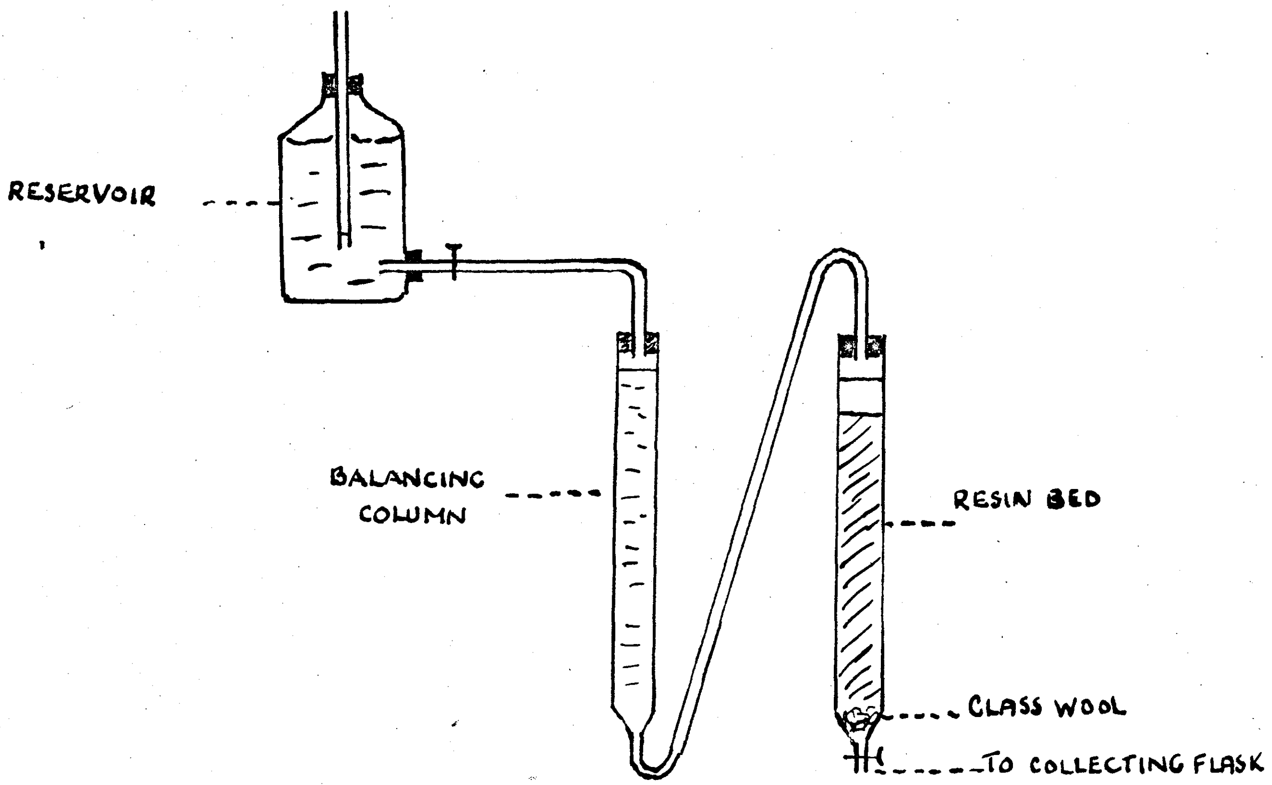


FIG 3B ARRANGMENT FOR STEPWISE ELUTION



Subsequent complexes are held more firmly and with a change to a more concentrated eluant these are eluted.

There is one main disadvantage to this method, namely, that if a change in eluting agent concentration is made before the lightest held complex on the column at any one time is incompletely desorbed it is possible to get the appearance of a spurious band which one assumes to be a further complex; on this basis it is hard to ascertain the actual number of complexes actually present in solution. This disadvantage was overcome to a certain extent by the second method that was applied.

b) Gradient Elution.

The essential of the method is to continuously increase the concentration of the eluant. This is achieved by an apparatus shown in Fig.3A.

It is possible to calculate the exact concentration of the eluant entering the column at any one time and by suitably varying the size of the mixing chamber and the concentration of the solution in the mixing chamber initially and in the resevoir suppose

r = rate of flow of eluant through column.

t = time of flow.

V_o = volume of the mixing chamber.

The volume of eluant V delivered after time t may be expressed as follows

$$V = rt$$

If c = normality (or concentration) of eluant at time t

c_1 = normality (or concentration) of solution in the reservoir

c_o = initial concentration of the mixing chamber.

Rate of change of concentration of solution leaving mixing chamber $\frac{dc}{dt} = \frac{-r(c-c_1)}{V_o}$ ----(1)

$$\therefore \frac{dc}{c-c_1} = \frac{-r}{V_o} dt \qquad \text{----(2)}$$

Integrating $\ln(c-c_1) = \frac{-rt}{V_o} + K$ ----(3)

at $t = 0$ $c = c_o$ $\therefore$ $K = \ln(c_o-c_1)$

$\therefore$ substituting in equation 3 we get

$$\ln \frac{c_o-c_1}{c-c_1} = \frac{rt}{V_o} \qquad \text{----(4)}$$

Expressed in terms of the volume passed through the columns equation (4) becomes

$$V_o \ln \frac{c_o-c_1}{c-c_1} = V \qquad \text{----(5)}$$

or

$$e^{V/V_o} = \frac{c_o - c_1}{c - c_1} \qquad \text{----(5a)}$$

This may be rewritten in terms of c

$$c = \frac{c_1(e^{V/Vo} - 1) + c_o}{e^{V/Vo}} \qquad \text{----(6)}$$

Under the experimental conditions used in the present study the mixing chamber always contained water initially i.e. $c_o = 0$

Thus equation (6) becomes

$$c = \frac{c_1(e^{V/V_o} - 1)}{e^{V/V_o}} \qquad \text{----(7)}$$

The derivation of this equation was based on ideas developed in conjunction with Dr. Z. Ernst (36). Employing this technique a clearer separation of the complexes may be achieved.

D Spectrophotometric Studies.

The principle of spectrophotometry is to allow a beam of light to pass through the liquid or solution under investigation (this is contained in a silicacell with parallel faces) the emergent beam enters a quartz prism or grating spectrograph; then, by a suitable device, usually a photo sensitive cell the extent of the light transmission at each wavelength or frequency may be determined.

A plot of the light transmitted against the wavelength gives a curve characteristic of the solution or substance. In the visible region the absorption spectrum is related to the colour of the substance or solution and this arises directly from the energy changes associated with electronic transitions. Also the interaction between the solute and solvent will exert a modifying effect on the spectrum.

The interaction between hexa aquo chromium (111) and phosphate to form phosphate complexes exerts a considerable modifying effect on the spectrum both in the visible and the U.V. region of the spectrum. Thus it proved possible to follow the changes which occur on aging a solution. of chromium (111) phosphate in phorphoric acid. There is both a shift and an increase in the height of the characteristic absorption peaks. From this it has proved possible to determine when a solution is fully aged.

It was hoped to apply the method of Job (37) as outlined by Vosburgh and Cooper (38) in the elucidation of the complexes present but as is well known, this method of continuous variations is not easily applicable to the study of a system where a number of complexes occur, and as it was shown by the ion-exchange column experiments that there were a number of complexes it did not prove possible to carry this out.

SECTION D.

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PART 2.

BASIC EXPERIMENTAL PROCEDURES

SECTION A

PREPARATION OF THE STARTING MATERIALS

In the phase diagram studies and in all the studies on the solutions of the system chromium (111) - phosphoric acid, the purple tertiary salt was used as a starting point. This was due to the fact that it could be produced as a nicely crystalline solid in a high state of purity.

The method of preparation was similar to that of Smith, Ness, and Edwards (1) and to that of Jameson and Salmon (2), namely :

120 gm.(0.24 mole) of AnalaR chromium (111) potassium sulphate was dissolved with stirring in 1500 ml. of distilled water. The solution was then filtered to remove any undissolved residue. A solution of 30 gm. (0.21 mole) of AnalaR disodium hydrogen phosphate (anhydrous) in 1000 ml. of distilled water was then added dropwise (with continual and thorough mechanical stirring). Immediately following this addition the mixture was buffered by the dropwise addition of a solution of 30 gm. AnalaR ammonium acetate in 500 ml. of distilled water. The stirring was continued for a further period of two hours to ensure the formation of a nicely crystalline precipitate. The precipitate was washed several times by decantation and subsequently transferred to a Buchner funnel and washed with further batches of distilled water until the damp precipitate gave no sodium flame. A damp yield of about 50 gms. was obtained (which implies almost a 100% yield). It was found preferable to carry out the reaction at a temperature below 15°C. Some typical analyses of the compound

prepared by this method are given in Table 1 on page 42 .

Preparation of solutions and mixtures

(i) Mixtures for Phase Diagram Studies

The method used for preparing the initial mixtures for the phase diagram studies was to add the solid $[Cr(H_2O)_6] PO_4$ to solutions containing H_3PO_4 and H_2O in various proportions.

(ii) Solutions for Ion-Exchange studies and spectrophotometric studies.

For solutions that were going to be used either for ion-exchange or for spectrophotometric work the starting constitution of the solutions was known in terms of Cr_2O_3, P_2O_5, H_2O; either, since points on the solubility isotherm had been selected as giving the concentration or, by choosing the appropriate quantities for the unsaturated solutions which were to be studied. By a simple calculation the constitution of these solutions in terms of $[Cr(H_2O)_6] PO_4$, H_3PO_4, H_2O could be determined and the appropriate solutions made up by taking the right weights of these compounds.

Aging of Solutions

In the case of solutions aged at 25°, 40° and 70° the solutions were placed in clean stoppered bottles or flasks and closed with cleaned polythene stoppers or rubber bungs. The bottles or flasks were cleaned with chromic acid - sulphuric acid mixture and thoroughly washed with distilled water and dried before use. The rubber bungs were boiled in a sodium carbonate mixture, washed with distilled water, boiled in distilled water and allowed to dry before use.

(i) Aging at 25°C.

The bottles were sunk by means of an attached heavy weight in a conventional water bath controlled at 25.0 ± 0.01°C. by means of a toluene-mercury regulator and a 'Sunvic' relay. The whole being efficiently stirred and heated by means of a 40 watt electric light bulb.

(ii) Aging at 40° and 70°C.

The bottles or flasks containing the solution were placed in an oven, the temperature of which was controlled by means of a bimetallic strip contact and a 'Sunvic' relay. The variation in air temperature was around 40° ± 1°C. and 70° ± 1.5°C. Tests on the variation of the temperature of the solutions showed that they maintained the temperature of the oven to within ± 0.02°C.

(iii) Aging at around 100°C.

The solutions were placed in a bolthead flask fitted with a 'quickfit' double surface condenser and the temperature was that of the refluxing solution. The actual boiling points of the solutions were within the range 101° ± 0.5°C.

Tests whether aging could be considered complete

(i) Ion-Exchange.

Solutions aged at 25°, 40° and 70°C. were checked in this way.

At suitable periods an aliquot of the aging solution was removed and transferred to a 150 ml. clean and dry conical flask into which had been introduced ½ gm. cation exchanger or 1 gm. anion exchanger. The solution was allowed to stand in contact with the resin for a fixed time; occasional swirling of the flask was carried out to ensure a thorough mixing of the contents. The resin was then transferred to a small column as described in Part I, Section C, page 20. The absorbed species was eluted with 2 or 4 N nitric acid using the 'spurts' technique. (That is to say that the resin in the column is allowed to stand in contact with successive small portions of the eluting agent. Each portion is allowed to remain in contact with the resin for some considerable time (it was found best if at least one portion remained in contact with the resin overnight)). The advantages of this method of eluting the resin are :

(a) That a number of the complexes encountered and $[Cr(H_2O)_6]^{3+}$ have a very high affinity for the resin and consequently if the conventional method of continuous elution is employed, the volume of eluting agent needed to ensure complete removal of the sorbed species would be large.

(b) Further, that it avoids the presence of a large excess of nitric acid which would otherwise interfere with the subsequent determination of chromium, 25 ml. or 50 ml. being sufficient in every case to ensure complete removal.

An analysis of the eluted solution for chromium or phosphate was carried out and a table of results drawn up. A plot of the uptake of chromium (or phosphate) on exactly similar portions of resin against time of aging shows a smooth curve relationship reaching a constant value (maximum or minimum) after a certain time. The reaching of this constant value was taken as the criteria for considering when a solution could be considered fully aged. Tables of the results obtained are on page 43.

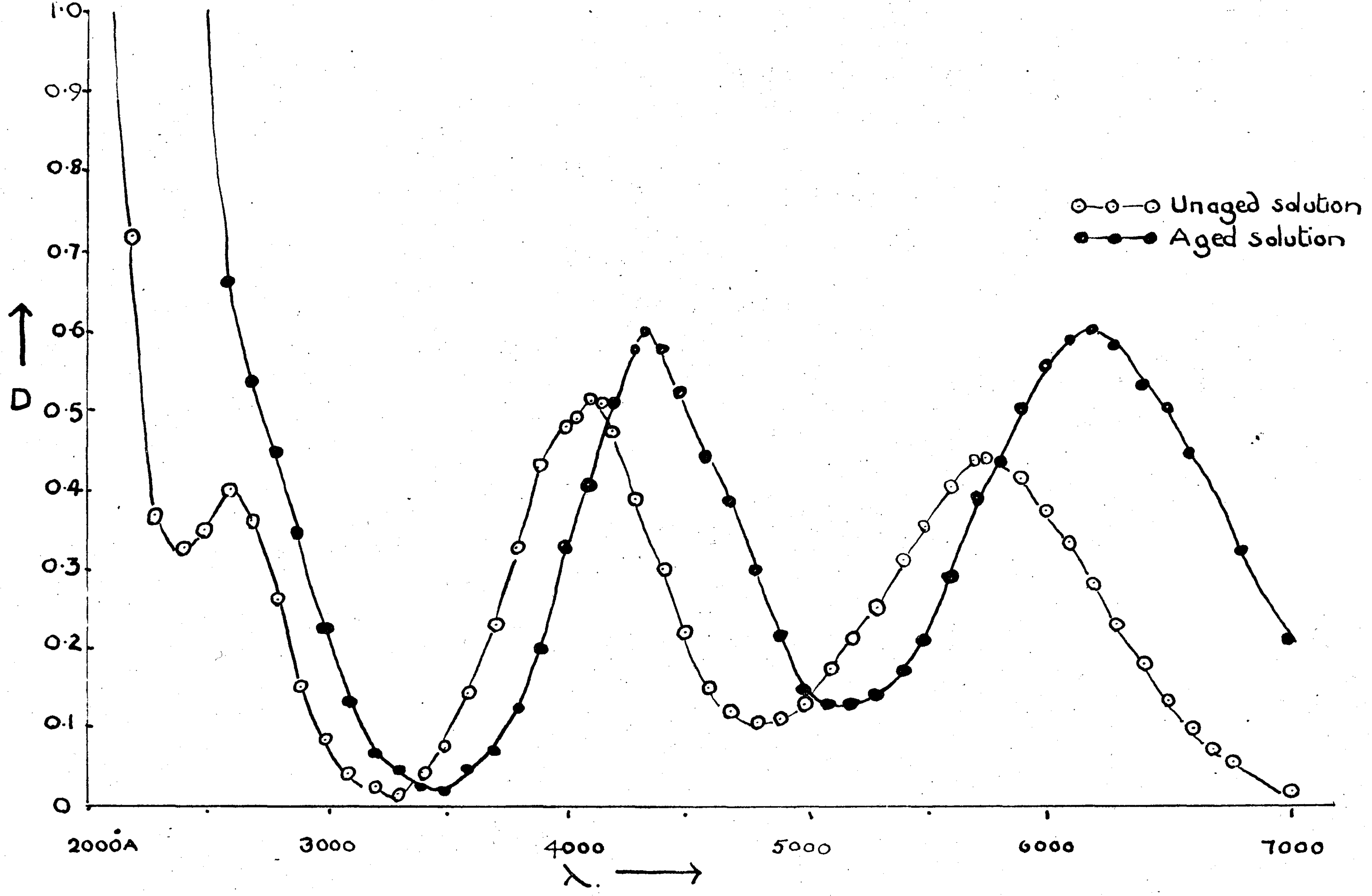
The $7\frac{1}{2}\%$ P_2O_5 solution was chosen since from Jameson and Salmon's (2) work at 25°C it appeared that at this temperature it took the longest to age of any of the saturated solutions selected from along the solubility isotherm.

(ii) Spectrophotometric.

Solutions aged at 70° were checked in this way. In the first instance measurements were carried out on two solutions - one that was freshly prepared and one that although of exactly similar composition was fully aged (as determined the ion-exchange method outlined above). The method used was to take a suitable aliquot of the unaged solution, transfer to a graduated flask and dilute with water. A sample from this flask was introduced into a 1 cm. silica cell, which was placed in a Unicam SP 500. A reference cell containing water was also placed in the instrument. (See Part 1, Section C for a fuller description of the use of the spectrophotometer). The optical density for the solution was then measured for a series of different wavelengths in the range 2,000 - 10,000Å. A similar aliquot of the same solution fully aged was treated in the same manner. For results see Table 3 on page 44 and Fig.4.

Secondly a series of measurements was made on an aging solution, suitable aliquots being withdrawn at 45 minute intervals and after the appropriate dilution a similar set of measurements was made on each diluted, partly aged solution as soon as possible. For results see Table 4 on page 46.

FIG 4 SPECTROPHOTOMETRIC COMPARISONS OF AGED AND UNAGED SOLUTIONS (SEE TABLE 3)



Finally, to check whether the inferences which could be drawn from the two experiments carried out were valid, three more experiments were carried out.

(a) Measurements made on an undiluted solution of the same original composition - Table 5.

(b) Measurements made on a solution of the same original solution but diluted more before the measurements were made - Table 6.

(c) Measurements made on a solution of different composition - Table 7.

See pages 47 - 49 for Tables 5, 6, and 7 respectively.

From a consideration of the results of the above experiments, it will be seen that the non-aged solution has absorption peaks at 2600Å, 4100Å, and 5700Å, whilst in a fully aged solution the peak at 2600Å has disappeared and the two latter peaks have shifted towards the l.R. to give peaks at 4350Å and 6200Å respectively.

Thus a suitable criteria for judging whether a solution had completely aged would be to measure the optical density at, say, 4350Å and 6200Å and when D was a maximum, then it could be considered that the solution was fully aged.

A similar treatment would be possible for solutions aged at other temperatures.

SECTION B

ANALYSIS OF SOLUTIONS AND SOLIDS

The methods outlined by Jameson and Salmon (2) for the analysis of chromium and phosphate were adopted - with a few modifications.

Since most of the work was concerned with solutions in which some or most of the phosphate was attached as a ligand group to Cr (111), it was necessary to ensure the breakdown of the complex ions prior to analysis. Hence the method of titration of phosphate by means of a solution of $BiOClO_4$ employing thiourea as indicator, see Salmon and Terrey, and Genge and Salmon (3(i) and (ii)), after the passage of the solution through a cation exchanger to remove $[Cr(H_2O)_6]^{3+}$ ions was not used even in those cases where the phosphate was not complexed. A similar standard approach was adopted for all determinations of phosphate.

The following procedures were used :

Chromium

The determination of chromium was achieved by the oxidation of the Cr (111) to chromate in alkaline solution, followed by acidification and the addition of a known amount of standard ferrous ammonium sulphate sufficient to be present in excess: followed by the back titration of the excess with standard potassium dichromate solution.

Detailed method.

A suitable sample of the Cr (111) solution was treated with 1 ml.

or, preferably, less of AnalaR '100 volume' H_2O_2 and made alkaline by the addition of 40% caustic soda solution. The excess H_2O_2 to that required to oxidise Cr (111) - Cr (VI) was destroyed by boiling the solution for some time on an electric hot plate or by heating on a water bath for several hours. (As it is imperative to remove every trace of excess H_2O_2 it was found desirable :

(a) To use as little H_2O_2 as possible over that required to bring about the oxidation.

(b) To keep the volume of the solution about 100 ml.

(c) To cover the flask with a watch glass as in this way the breakdown of the H_2O_2 was seen to be facilitated).

After removing the solution from the source of heat, the hot solution was acidified with a sulphuric-phosphoric acid mixture (25 mls. of a solution made up by mixing phosphoric acid, sulphuric acid, and water in the proportions of 1 : 1 : 8.) The solution was allowed to cool. A known volume of a standard ferrous ammonium sulphate solution (approx. N/20 made up in 2 N H_2SO_4) was added. The amount added being in excess of that required to effect the reduction of the dichromate. The excess was then titrated against a standard $K_2Cr_2O_7$ solution (approx. N/20), using a few drops of a solution of barium diphenylamine indicator in water to a sharp change from green - purple.

The presence of reasonable amounts of nitric acid or of ammonium nitrate in the original solution could be tolerated in this determination provided :

(a) The solution was adequately cooled before the standard ferrous solution was added.

(b) The titration was carried out immediately after the addition of the ferrous solution.

Phosphate

The determination of phosphate was achieved by the precipitation of the phosphate as ammonium phosphomolybdate and drying at 110°. The amount of phosphate present was determined using a conversion factor after carrying out a series of experiments with known amounts of phosphate.

Since, in many of the determinations, the phosphate was complexed to the Cr (111) it was essential to ensure that the complex ions were broken down and that before precipitation the phosphate ions were present as such in the solution to be analysed. It was shown in early work that consistent results could only be achieved if this was the case. The following methods are available to ensure this :

(a) In the presence of a large excess of H^+ ions the tendency is for Cr (111) complexed $\longrightarrow$ Cr (111) hexaäquo ions. This conversion is facilitated by boiling the solution.

(b) By conversion of Cr (111) $\longrightarrow$ Cr (VI) the electronegativity of the chromium is increased and the bonding of Cr to phosphate is certain to be broken in the formation of chromate.

The method which was finally adopted for all determinations in which the phosphate was complexed in fact utilises both these facts.

Detailed method

A suitable sample of the phosphate solution was treated with a few drops of AnalaR '100 volume' H_2O_2 and made alkaline by the addition of excess 880 ammonia. After a few minutes standing the conversion of Cr (111) $\longrightarrow$ Cr (VI) was observed to be complete and 5 ml. of concentrated nitric acid was added carefully. The solution was then diluted to 150 mls. and boiled for a period of some hours, keeping the volume between 100 - 150 mls. Finally, 2 g. NH_4NO_3 (AnalaR) and 100 mls. H_2O was added and the temperature of the solution was adjusted to 40°C. To this solution was added 35 mls. of a stock solution of AnalaR ammonium molybdate in nitric acid also at 40°C. (Stock solution contained 75 g. of ammonium molybdate in 3 N nitric acid). The addition was carried out rapidly and after 1 minute the solution stirred vigorously for a short time. The solution and precipitate were allowed to stand overnight. The precipitate was transferred to a sintered glass crucible and washed first with a solution of ammonium nitrate in nitric acid and finally with two 10 ml. portions of a 1% nitric acid solution. The precipitate was dried at 110°C. for 1 hour and then, after cooling, weighed.

The above procedure ensures :

(a) Complete breakdown of any complexes present in the initial solution.

(b) The non-interference of Cr (VI) and of H_2O_2 with the determination, the essential sequence of the reaction being :

Cr (lll) - phosphate complex ions $\xrightarrow[\text{alkaline}]{H_2O_2}$ Cr (VI) and phosphate ions

$\xrightarrow[H_2O_2]{\text{acid}}$ Cr (Vl) (as unstable peroxychromate) and phosphate ions

$\xrightarrow{\text{rapidly}}$ Cr (lll) as $[Cr(H_2O)_6]^{3+}$ and phosphate ions.

$\xrightarrow{\text{boil}}$ slow breakdown of H_2O_2 in acid conditions

and also conversion of Cr (lll) complexed to Cr (lll) uncomplexed if any Cr (lll) initially remained unconverted to Cr (Vl). This procedure ensured that the controlled conditions needed for the 'clean' precipitation of phosphate could be accurately reproduced and that the precipitate of ammonium phosphomolybdate was of a constant composition - thus justifying the use of an empirical factor for determining the amount of phosphate present in the initial sample.

SECTION C

TABULAR RESULTS

TABLE 1

Typical Analyses of the prepared chromium (111) phosphate

	Cr_2O_3 %	P_2O_5 %	H_2O %
Theoretical for $[Cr(H_2O)_6]PO_4$	29.80	27.83	42.37
Sample 1	29.68	27.83	42.36*
Sample 2	29.84	27.64	42.56
Sample 3	29.74	27.74	42.50

* By difference

TABLE 2

Ion-Exchange methods to determine when Chromium (111) - phosphoric acid solutions aged at different temperatures had reached equilibrium.

Aging Temp.	Resin Used	Wt. Resin	Time of Aging	m.moles Cr/gm. resin	m.moles/PO_4 gm. resin
25°C	1R112H	0 .5000 g.	42 days	1.225	-
	1R112H	0 .5000 g.	218 days	1.527	not measured
	1RA400 PO_4	1.0000 g.	42 days	2.1095	"
	1RA400 PO_4	1.0000 g.	218 days	0.2260	"
40°C	1RA400 PO_4	1.0000 g.	10 days	0.0955	"
		1,0000 g.	30 days	0.1798	"
		1.0000 g.	50 days	0.1955	"
		1.0000 g.	70 days	0.2256	"
		1.0000 g.	90 days	0.2244	"
70°C	De-acidite FF PO_4	1.0000 g.	-	-	1.8615
		1.0000 g.	1 day	0.1168	1.6829
		1.000 g.	2 days	0.1110	1.6510
		1.0000 g.	3 days	0.1136	1.6750
		1.0000 g.	4 days	0.1124	1.6656
	Z.K.225 H	.5000 g.	-	1.142	-
		.5000 g.	1 day	1.050	0.3606
		.5000 g.	2 days	1.005	0.3606
		.5000 g.	3 days	1.012	0.3622
		.5000 g.	4 days	0.998	0.3465

Solution used contained 7½% P_2O_5, 1¼% Cr_2O_3, 91¼% H_2O.

In every case 50 mls. of solution in contact with resin for 2 hours (flask agitated on mechanical shaker).

TABLE 3

Spectrophotometric method to demonstrate the effect of aging a chromium (111) - phosphoric acid solution

Wavelength	D Unaged Soln.	D Aged Soln.	Wavelength	D Unaged Soln.	D Aged Soln.
2000 Å	-	-	4300	0.385	0.573
2100	1.10	-	4350	0.353	0.600
2200	0.723	-	4400	0.300	0.575
2300	0.372	2.20	4500	0.220	0.520
2400	0.325	2.10	4600	0.155	0.437
2500	0.350	1.07	4700	0.120	0.382
2600	0.400	0.657	4800	0.106	0.295
2700	0.360	0.538	4900	0.110	0.210
2800	0.265	0.446	5000	0.128	0.146
2900	0.156	0.340	5100	0.177	0.132
3000	0.086	0.222	5200	0.212	0.135
3100	0.045	0.131	5300	0.250	0.141
3200	0.027	0.065	5400	0.310	0.171
3300	0.018	0.042	5500	0.350	0.210
3400	0.043	0.038	5550	0.370	0.256
3500	0.076	0.020	5600	0.400	0.286
3600	0.143	0.048	5650	0.425	0.325
3700	0.228	0.066	5700	0.435	0.387
3800	0.325	0.125	5750	0.438	0.404
3900	0.432	0.198	5800	0.432	0.435
4000	0.478	0.323	5850	0.423	0.476
4050	0.485	0.355	5900	0.412	0.500
4100	0.512	0.401	5950	0.392	0.520
4150	0.510	0.458	6000	0.372	0.550
4200	0.470	0.510	6050	0.365	0.575
4250	0.447	0.540	6100	0.330	0.585

Solution containing 5.0% P_2O_5 0.5% Cr_2O_3 94.5% H_2O.

Diluted 1:1 Ref.solution H_2O. Temperature: Room temperature.
1 cm.cell (silica)

continued overleaf.

TABLE 3 (Contd.)

Wavelength	Unaged solution	Aged solution
6150Å	0.303	0.592
6200	0.278	0.602
6250	0.258	0.590
6300	0.223	0.580
6350	0.212	0.565
6400	0.180	0.525
6450	0.152	0.510
6500	0.132	0.500
6600	0.098	0.442
6700	0.068	0.332
6800	0.064	0.320
7000	0.016	0.208
7200	0.000	0.110
7400	0.000	0.046
7600	0.000	0.000

TABLE 4

Optical density at different wavelengths of a Chromium (111) - Phosphoric acid solution after various periods of aging at 70°C.

Wave-length	45 mins	90 mins	135 mins	180 mins	225 mins.	260 mins	305 mins.	365 mins.	48 hrs.
2300Å	0.442	0.795	1.18	1.90	-	-	-	-	-
2400	0.335	0.436	0.545	0.820	1.05	-	-	-	-
2500	0.398	0.405	0.410	0.516	0.612	0.75	0.86	1.045	1.040
2600	0.389	0.415	0.400	0.452	0.468	0.524	0.650	0.695	0.705
2700	0.367	0.410	0.382	0.441	-	0.444	0.495	0.530	0.555
2800	0.270	0.312	0.308	0.348	0.352	0.408	0.405	0.446	0.460
4000	0.480	0.474	0.453	0.415	0.374	0.362	0.331	0.320	0.324
4100	0.505	0.510	0.504	0.495	0.465	0.460	0.450	0.440	0.438
4150	0.472	0.505	0.515	0.510	0.495	0.496	0.489	0.482	0.492
4200	0.467	0.495	0.515	0.535	0.515	0.520	0.538	0.535	0.530
4250	0.432	0.475	0.510	0.525	0.496	0.535	0.552	0.555	0.555
4300	0.399	0.420	0.485	0.512	0.515	0.533	0.525	0.570	0.568
4350	0.356	0.415	0.445	0.477	0.490	0.539	0.528	0.580	0.575
4400	0.311	0.368	0.410	0.452	0.470	0.535	0.540	0.578	0.565
4500	0.220	0.290	0.338	0.383	0.407	0.458	0.475	0.530	0.500
5500	0.362	0.362	0.337	0.313	0.280	0.258	0.248	-	0.247
5600	0.399	0.385	0.385	0.375	0.352	0.323	0.308	-	0.317
5700	0.422	0.435	0.433	0.430	0.407	0.392	0.395	-	0.399
5800	0.427	0.454	0.458	0.453	0.441	0.446	0.450	-	0.455
6000	0.385	0.422	0.460	0.482	0.493	0.522	0.535	-	0.560
6100	0.347	0.390	0.432	0.470	0.490	0.527	0.550	-	0.568
6150	0.322	0.373	0.415	0.455	0.478	0.523	0.562	-	0.572
6200	0.290	0.330	0.385	0.438	0.480	0.546	0.542	-	0.575
6250	0.264	0.312	0.375	0.413	0.434	0.496	0.535	-	0.550
6300	0.230	0.286	0.338	0.381	0.400	0.480	0.493	-	0.520
6400	0.162	0.221	0.295	0.335	0.390	0.442	0.465	-	0.484

Solution containing 5.0% P_2O_5 0.5% Cr_2O_3 94.5% H_2O

Diluted 1:1 Reference solution H_2O. Temperature: Room Temperature

1 cm. cell (silica). Aged at 70°C.

TABLE 5

Measurement of optical density at different wavelengths
of a Chromium (111) - Phosphoric Acid solution

Wavelength	Unaged	Aged	Wavelength	Unaged	Aged
2400 Å	0.750	-	5100 Å	0.400	0.242
2500	0.875	2.050	5300	0.585	0.267
2600	0.890	1.330	5600	0.880	0.570
2700	0.840	1.047	5700	0.925	0.726
2800	0.638	0.905	5800	0.910	0.950
2900	0.405	0.658	5900	0.910	1.025
3100	0.186	0.248	6000	0.828	1.121
3300	0.121	0.090	6100	0.727	1.178
3700	0.515	0.128	6150	-	1.220
3900	0.898	0.365	6200	0.604	1.235
4000	1.048	0.595	6250	-	1.195
4100	0.070	0.838	6300	0.495	1.153
4200	1.014	1.028	6400	0.396	0.965
4300	0.870	1.132	6500	0.256	0.915
4350	-	1.235	6600	0.220	0.820
4400	0.665	1.177	6800	0.136	0.662
4500	0.508	1.062	7000	0.065	0.420
4600	0.388	0.942	7500	0.026	0.065
4700	0.298	0.771	8000	0.012	0.000
4900	0.282	0.403			

Solution containing 5.0% P_2O_5 0.5% Cr_2O_3 94.5% H_2O

Undiluted Reference solution H_2O. Temperature: Room temperature.

1 cm. cell (silica) Solution aged at 70°C.

TABLE 6

Measurement of optical density at different wavelengths of a Chromium (111) - Phosphoric Acid solution

Wavelength	Unaged	$1\frac{1}{2}$ hours	$3\frac{1}{2}$ hours	$5\frac{1}{2}$ hours	30 hours
2300 Å	0.166	0.290	0.980	-	-
2400	0.146	0.189	0.425	0.760	1.058
2500	0.155	0.178	0.248	0.385	0.505
2600	0.173	0.183	0.205	0.265	0.332
2700	0.157	0.172	0.180	0.221	0.256
2800	0.119	0.135	0.157	0.192	0.218
4000	0.215	0.193	0.168	0.149	0.137
4100	0.223	0.199	0.196	0.188	0.185
4200	0.206	0.188	0.214	0.219	0.224
4250	0.193	-	0.212	0.228	0.240
4300	0.172	0.161	0.207	0.232	0.243
4350	-	-	-	0.227	0.248
4400	0.135	0.131	0.188	0.223	0.246
4500	0.094	0.098	0.157	0.200	0.222
4600	0.073	0.072	0.128	0.170	0.189
5500	0.167	0.143	0.123	0.112	0.103
5700	0.191	0.168	0.167	0.170	0.167
5900	0.183	0.167	0.195	0.210	0.222
6000	0.162	0.160	0.198	0.222	0.238
6100	0.145	0.140	0.193	0.225	0.250
6200	0.118	0.122	0.182	0.220	0.245
6300	0.094	0.100	0.166	0.206	0.227
6400	0.075	0.080	0.145	0.186	0.212
6600	0.042	0.046	0.104	0.145	0.153
7000	0.011	0.011	-	-	0.080

Solution containing 5.0% P_2O_5 0.5% Cr_2O_3 94.5% H_2O.

Diluted 1:5 Reference solution H_2O Temperature: Room Temperature
1 cm. cell (silica) Solution aged at 70°.

TABLE 7

Measurement of optical density at different wavelengths of a Chromium (111) - Phosphoric Acid solution

Wavelength	Optical Density	Wavelength	Optical Density
3600 Å	0.046	5700 Å	0.385
3700	0.060	5900	0.518
3900	0.187	6000	0.553
4100	0.410	6100	0.560
4200	0.515	6200	0.570
4300	0.570	6300	0.533
4350	0.578	6400	0.492
4400	0.568	6500	0.450
4500	0.508	6700	0.301
4700	0.342	6900	0.224
4900	0.172	7100	0.114
5100	0.105	7300	0.053
5300	0.134	7500	0.022
5500	0.236	8000	0.000

Solution containing 7.5% P_2O_5 1.26% Cr_2O_3 91.24% H_2O

Diluted 1:5 Reference solution H_2O Temperature : Room temperature

1 cm. cell (silica) Solution aged at 70° for a few days.

SECTION D

BIBLIOGRAPHY

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(2) Jameson and Salmon, J.C.S. 1955, 360.

(3) (i) Salmon and Terrey, J.C.S. 1950, 2813 - 2824.

(ii) Genge and Salmon, Lab. Practice 1957, 6, 325.

PART 3

EXPERIMENTAL WORK AND RESULTS

SECTION A.

PHASE DIAGRAM AT 70°.

1. Apparatus

In the phase diagram experiments the samples were contained in Pyrex glass boiling tubes with B24 standard ground glass sockets fitted with B24 ground glass stoppers. The tubes were held in a metal box, the sides of which were insulated with glass wool and the whole placed in an oven which was thermostatically controlled at 70+1°C. The variation in the lagged box was less than 0.1°C. and variation of the temperature of the samples in the tubes was not significant.

2. Technique

Each sample was made up by the addition of the solid hexaäquo chromium (111) phosphate to a phosphoric acid solution. The range of concentrations of phosphoric oxide which was used namely, 0.25% - 60% P_2O_5, was obtained by the appropriate dilution of AnalaR syrupy phosphoric acid with distilled water.

The samples were stirred daily and more solid was added where necessary until a suitable amount of a permanent precipitate had formed. After this the samples were stirred regularly for a week or so and then allowed to stand undisturbed for a few weeks before analysis.

3. Determination of solubility curve and composition of the solid phase

The moist solids were separated from the mother liquors as completely as possible by filtration through sintered glass crucibles and transferred into tared dry weighing bottles. Known volumes of the liquids were pipetted into tared weighing bottles (this giving an approximate value of the density of the saturated solution.)

The solids were dissolved in a minimum of concentrated nitric acid and the solutions obtained made up to suitable volumes. The liquids were stabilised by the addition of approximately 1 ml. of concentrated nitric acid and made up to suitable volumes. An analysis for chromium and for phosphate was then carried out on each of the solutions prepared in the manner described.

From these results the percentages of Cr_2O_3 and P_2O_5 were calculated and the results were plotted on triangular graph paper. The appropriate tie lines were drawn. The results of the phase diagram study at 70° are recorded in Table 8, on page 77 and a plot of those results in Fig.5

The procedure was adopted of analysing alternate tubes in the first instance and then analysing the remainder at a later date. The results so obtained led to a smooth solubility isotherm and consequently it was considered that equilibrium conditions had in fact been reached.

The results are discussed in Part 4, Section A on page 116.

As a system of parallel tie lines was found certain portions of the study were repeated maintaining the samples at 70° for a considerably longer period but again in this second instance parallel tie lines were observed. Identification of the solid and liquid phases at a P_2O_5

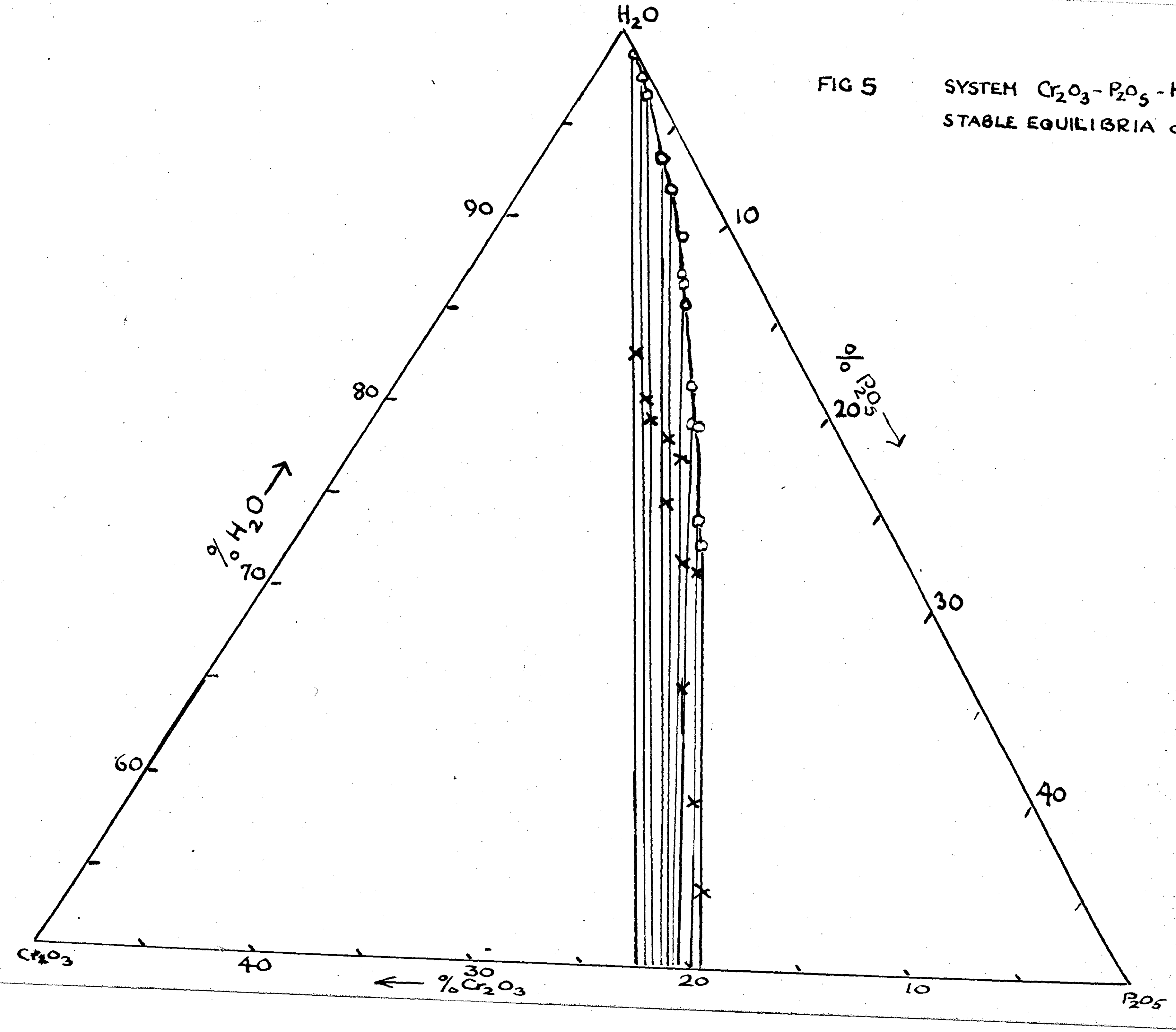


FIG 5 SYSTEM $Cr_2O_3 - P_2O_5 - H_2O$
STABLE EQUILIBRIA at 70°C

percentage greater than about 20 proved to be impossible since even with the exercise of great care the contents of the tube turned into a jelly-like substance which passed through a sintered glass crucible leaving no solid material at all.

SECTION B.

BATCH EXPERIMENTS - (i) DESORPTION OF Cr(111) SPECIES

1. Desorption of Cr(111) species from Zeo Karb 225

A number of different series of experiments were carried out. In every case ½ gm. of the air dried resin sample in the form with the appropriate metal or complex metal ion sorbed was allowed to stand in contact with 50 mls. of a solution for seven days. Subsequently the solution was analysed for chromium and/or for phosphate as indicated in the tables.

SERIES A (1)

This first series was a study of the effect of various acids over a fixed pH range on the desorption of the hexaäquo chromium (111) form of the resin. The resin (Zeo Karb 225) was prepared by treating it with an approx. 1 M solution of chrome alum until no more chromium was sorbed on the resin - since the affinity of chromium (111) hexaäquo ions for the resin is very high the amount of K ions sorbed is correspondingly small. The resin was subsequently washed and air dried. ½ gm. samples were taken and allowed to remain in contact with the solution for seven days at room temperature, with occasional swirling to ensure thorough contact of the bulk of the solution with the resin beads. A series of acids was used - namely phosphoric, sulphuric, hydrochloric, nitric, and perchloric acids and in each case the pH range was from 0.05 - 1.5. Solutions of each of these acids were made up having the following pH values 0.05, 0.25, 0.50, 0.75, 1.00, 1.25 and 1.5. At the end of the period an aliquot of the solution was removed and the amount of chromium estimated and expressed as a percentage of the original metal content of the resin sample. The results are given in Table 9 on page 78 and in graphical form in Fig. 6.

SERIES A (2)

The second series was to study the effect of the same acids over the same pH range on the desorption of cationic chromium (111) phosphate complexes from the resin. ½ gm. samples of [chromium (111) phosphate]$^{x+}$ resin - which was prepared by treating it with a fully aged solution of chromium (111) phosphate in phosphoric acid, the resin was subsequently washed and air dried - were allowed to stand in contact with solutions of the same acids at the same pH values. After seven days the percentage chromium removed from the resin samples was calculated from the results of the estimations. The results are given in Table 10 on page 79 and in graphical form in Fig. 7.

SERIES B.

One of the problems which arose in the early attempts at achieving a chromatographic separation of the various cationic chromium (111) phosphate complexes existing in solution was the phenomenon referred to as'phosphate-drift' (q.v. page 130). This drift is interpreted as being due to the splitting off of one or more of the acid phosphate groups bonded to the chromium (111) ion, by the medium used for eluting the species from the

FIG 6 THE REMOVAL OF $[Cr(H_2O)_6]^{3+}$ FROM ZEOKARB 225
AFTER SEVEN DAYS

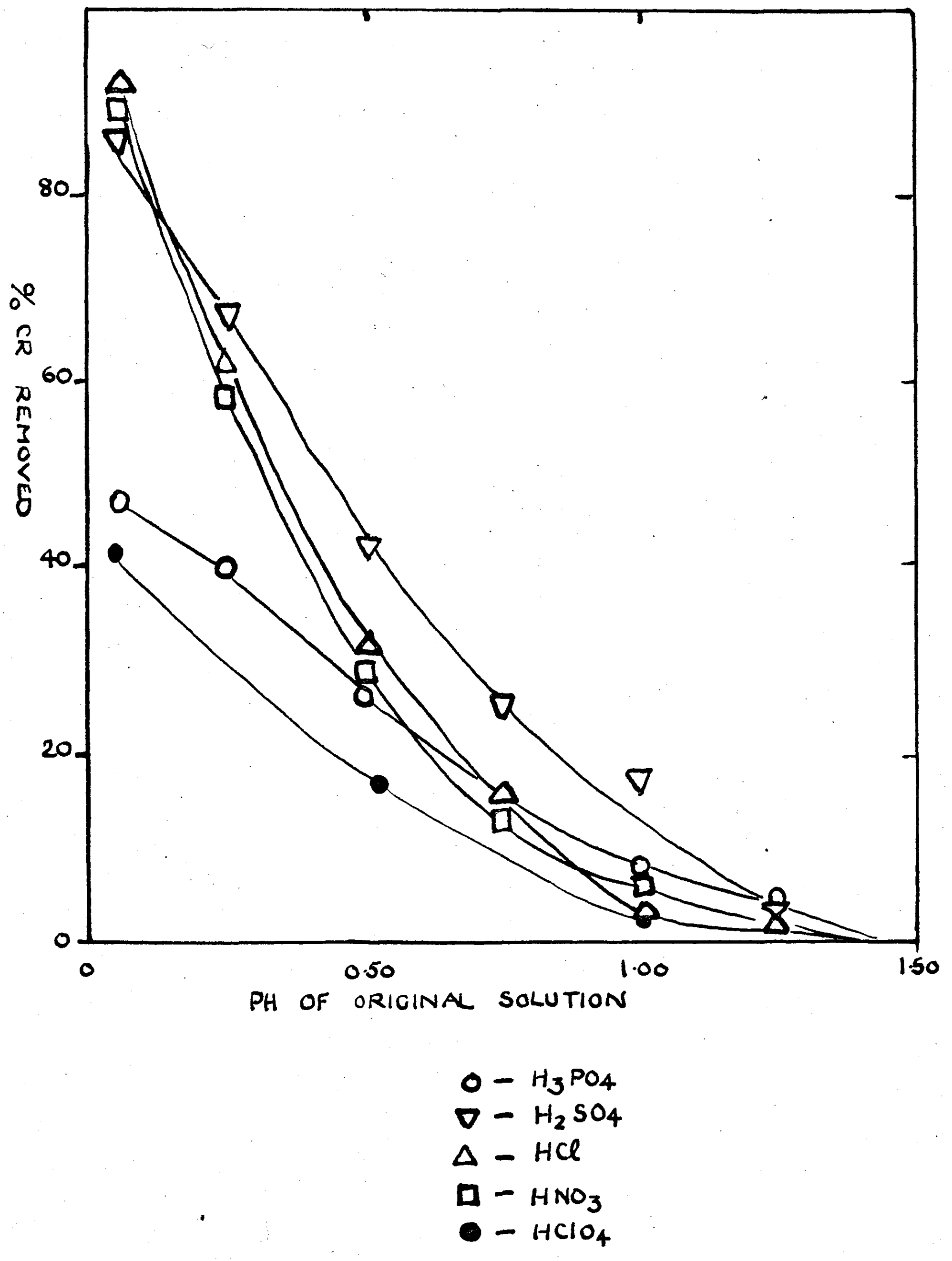
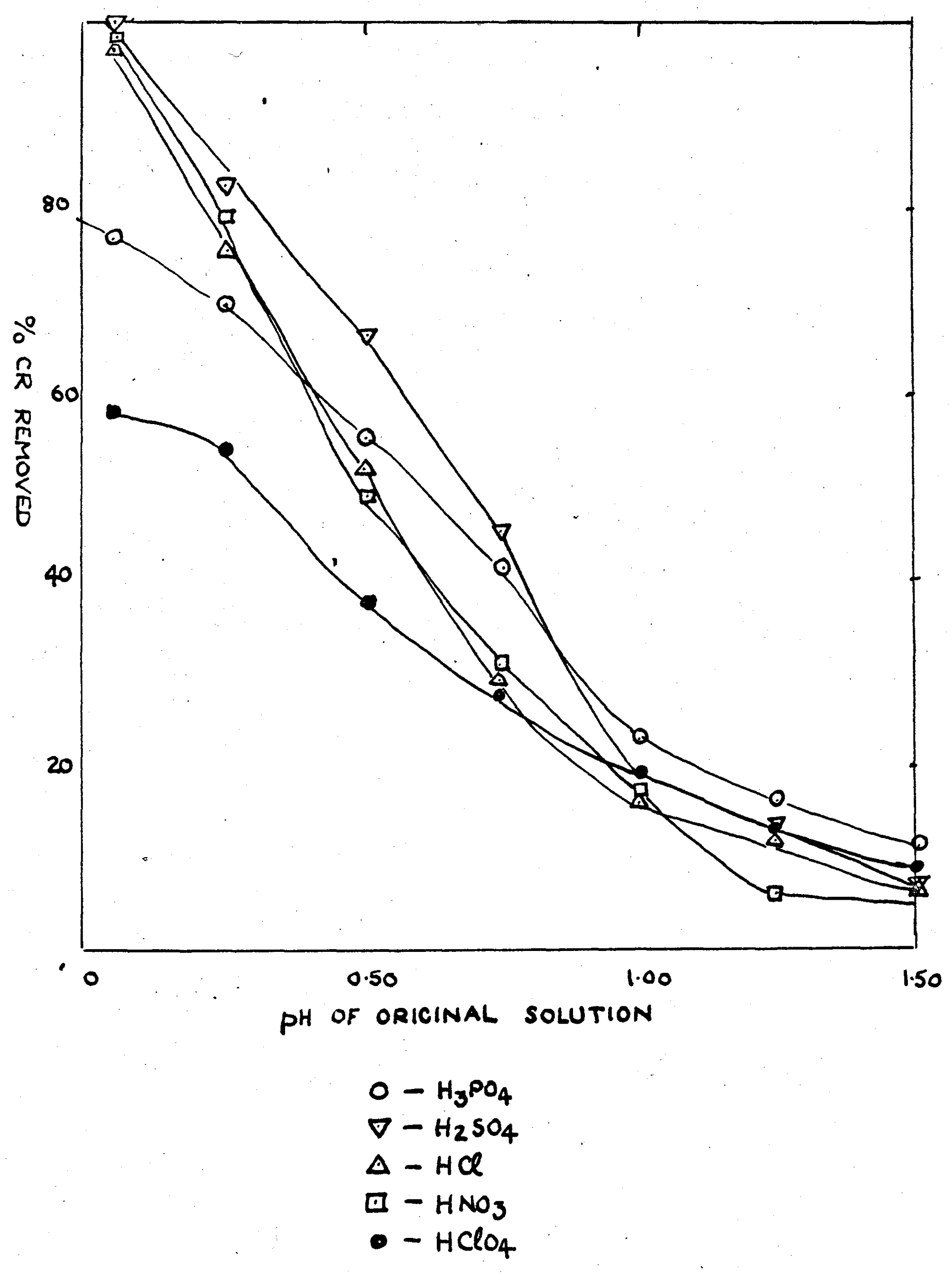


FIG 7 THE REMOVAL OF [Cr(III) Phosphate]$^{x+}$ FROM ZEOKARB 225

AFTER SEVEN DAYS



column. Accordingly a series of batch experiments was devised in order to (a) illustrate this effect more accurately, and (b) to see if the problem could be overcome by the choice of a different eluting agent.

The original choice of eluting agent for the separation was nitric acid due to the fact that it could be tolerated, at least to a reasonable extent, in the subsequent determination of chromium and was necessary in the determination of phosphate. The logical choice of a more suitable eluting agent is ammonium nitrate since, as is discussed on page 131, the probable cause of breakdown of the complex ions is the presence of excess H^+ ions and as this compound does not interfere in the determination of chromium and phosphate.

½ gm. resin samples (Zeo Karb 225) were prepared in a similar manner to those used in Series A(2) and were treated with 50 mls. of Anala R ammonium nitrate solutions of the following molarities, 0.25, 0.50, 1.00, 2.00, which were adjusted to be of constant pH. Further resin samples were prepared by standing Zeo Karb H form resin in contact with a fully aged solution for 1½ hours and also for 7 days and subsequent washing and air-drying, and these were treated with nitric acid solutions in the pH range investigated before, namely 0.05 - 1.5.

In every case both the chromium and the phosphate removed was estimated. The results are given in Tables 11 - 13 on pages 80 - 82, and a graph of the % removed in Fig. 8. By difference the % retained was also estimated and these results are recorded as well and given in graphical form in Fig. 9.

FIG 8 REMOVAL OF CR AND PO4 FROM ZEOKARB 225 BY NITRIC ACID AND AMMONIUM NITRATE

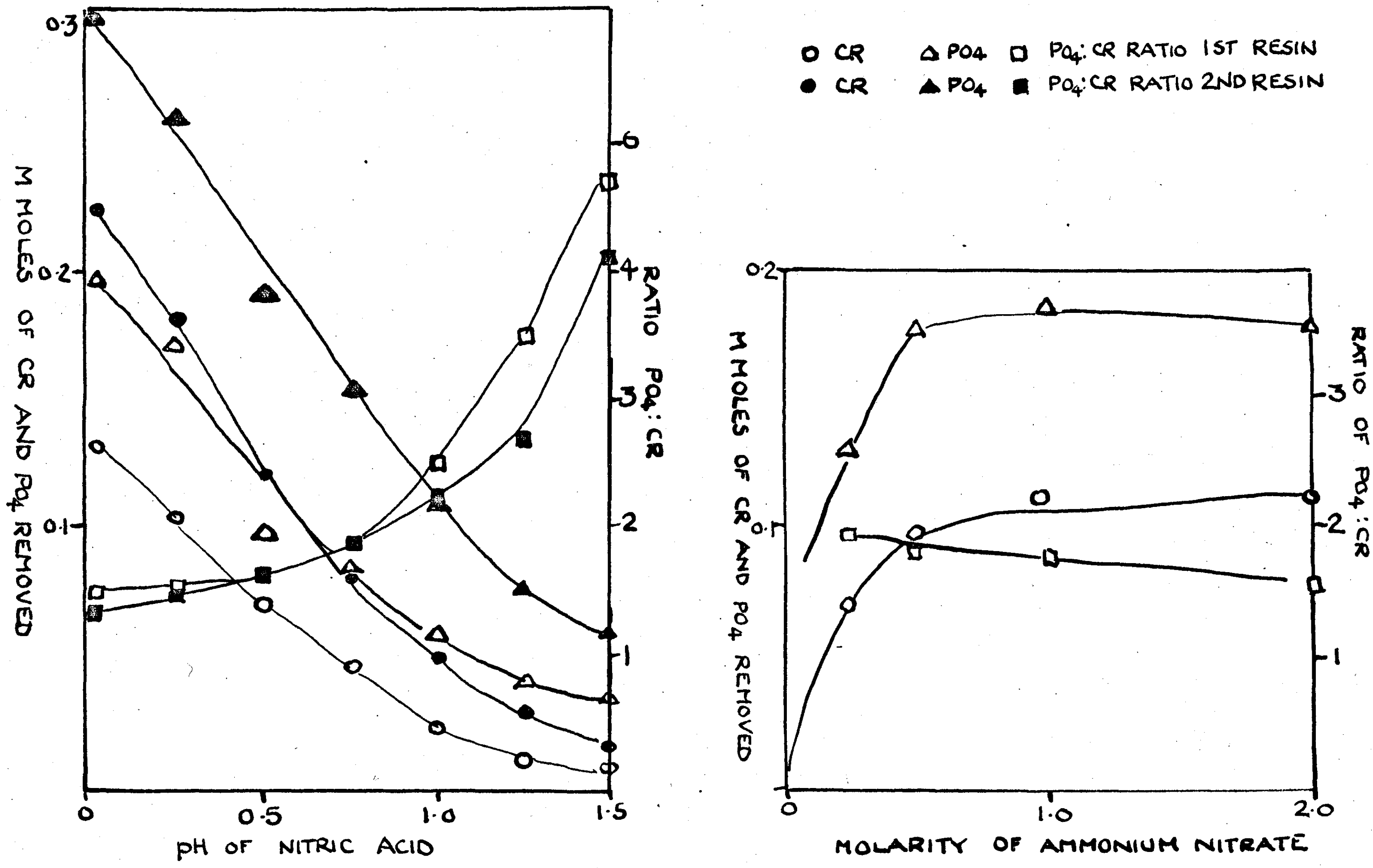
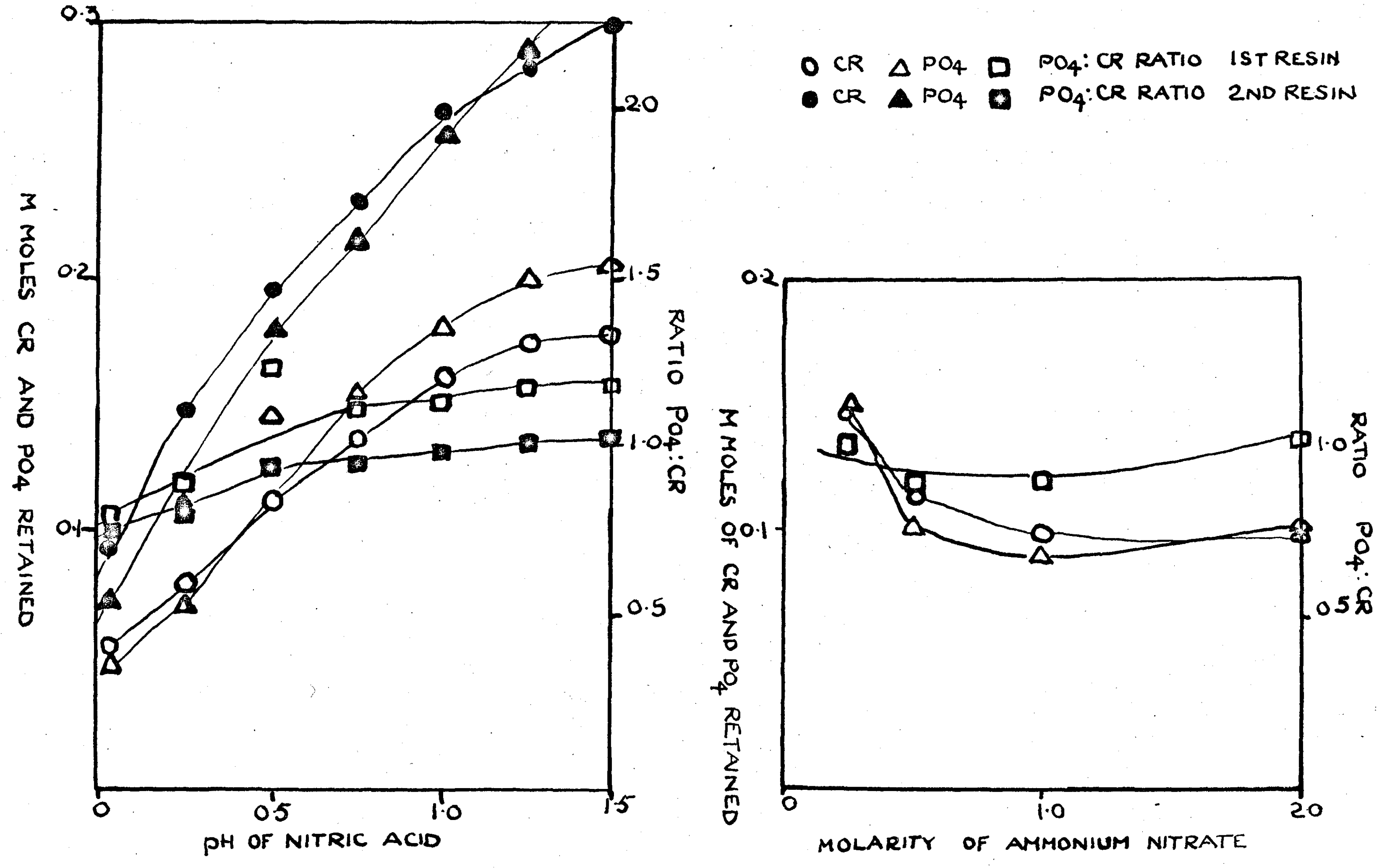


FIG 9 RETENTION OF CR AND PO4 ON ZEOKARB 225 WHEN TREATED WITH NITRIC ACID AND AMMONIUM NITRATE



Included on these graphs is a plot of the Cr:PO_4 ratio removed and retained at the different strengths of the solutions.

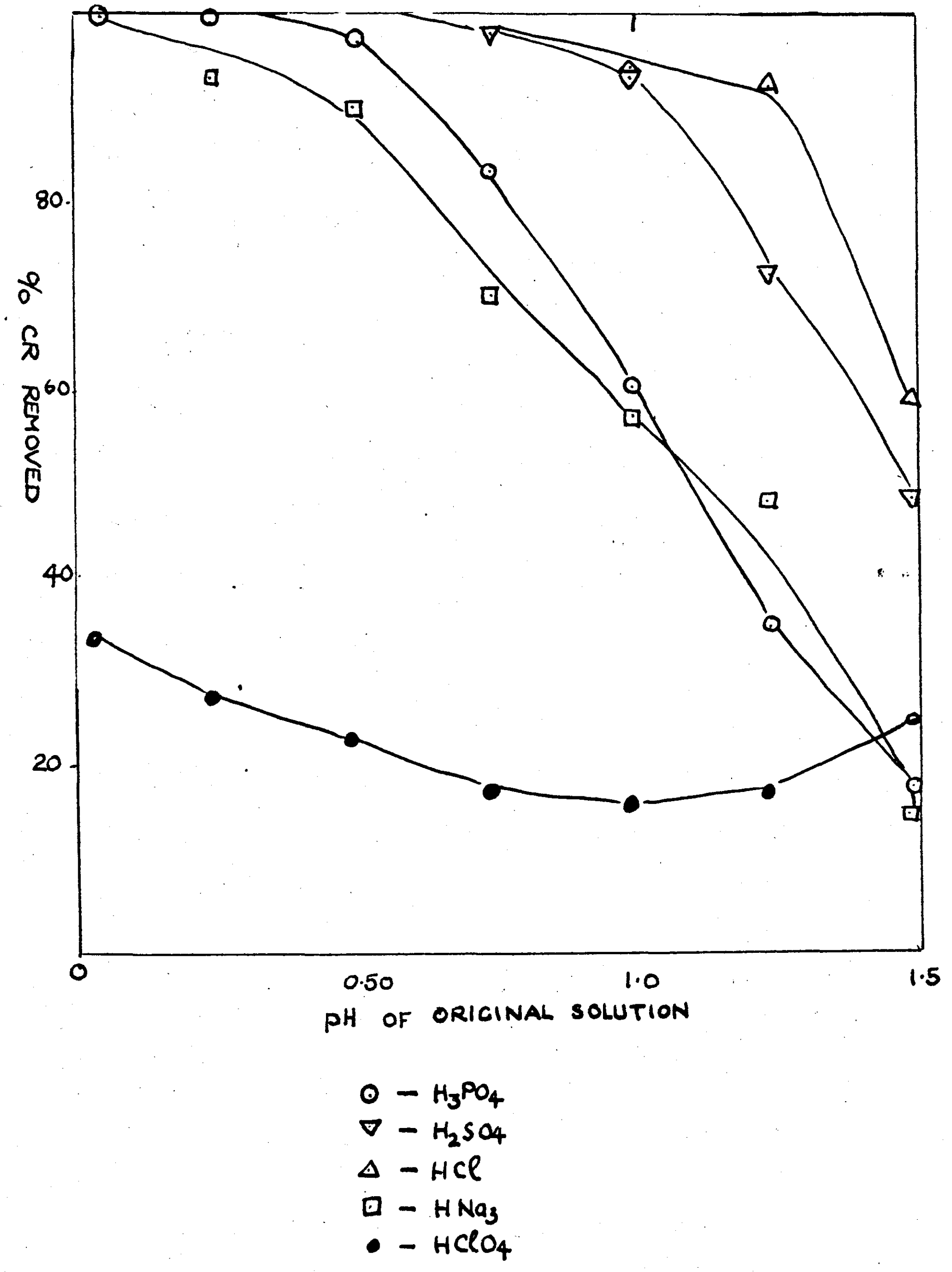
2. Desorption of Cr(111) species from De-acidite FF.

SERIES C.

The work in this section was carried out in order to gain a more complete picture of the system although the results obtained have not been applied in any way.

This series of experiments with the anion exchanger De-acidite FF was carried out in precisely the manner described for Series A(2) save that 1 gm. samples of De-acidite FF in the chromium (111) phosphate anionic complex form were used. The results are given in Table 14 on page 83 and a graph of results in Fig. 10.

FIG 10 THE REMOVAL OF $[\mathrm{CR(III)\ Phosphate}]^{a-}$ FROM DEACIDITE FF AFTER 7 DAYS



SECTION C.

BATCH EXPERIMENTS - (ii) SORPTION OF Cr(111) SPECIES

1. Sorption of $\left[Cr(H_2O)_6\right]^{3+}$ on Zeo Karb 225 (H form)

In the first set of sorption experiments a study of the rate of sorption of hexaäquo chromium (111) ions from an unaged chromium (111) - phosphoric acid solution was made with a resin of low cross-linking (i.e. high weight swelling) and with a resin of high cross-linking (i.e. low weight swelling).

½ gm. samples of the appropriate resin were weighed into clean dry conical flasks and 50 mls. of the solution were pipetted into each flask. The solution was then allowed to stand in contact with resin for the appropriate length of time - with occasional swirling to ensure a thorough mixing of the resin with the bulk of the solution. After the appropriate time of contact the resin was transferred in the usual way to a small column and the chromium content of the resin sample was determined after elution with nitric acid. Subsequently the resin capacity was also determined by passing a 1N solution of sodium sulphate (AnalaR) through the column and titrating the released acid with standard caustic soda.

The results are given in Table 15 on page 84.

2. Sorption of Cr phosphate cationic complexes from saturated solutions prepared by aging at 70° C. on Zeo Karb 225 (H form)

In this second set of sorption experiments the intention was to elucidate the cationic complexes sorbed on the resin by the method of Salmon (1). The solutions selected for study, in the first instance, were chromium (111) - phosphoric acid mixtures prepared in the usual manner and saturated with respect to chromium, i.e. working along the solubility isotherm of the phase diagram study at 70°. The composition of the various saturated solutions employed are given in Table 16 on page 85.

The initial work on the system by Jameson and Salmon (2) carried out at 40° indicated that there was a possibility that the resin was not completely converted to the complex ion form. In view of this indication two lines of investigation were decided upon :

(i) a study of the effect of varying the weight swelling of the resin.

(ii) a study of the effect of time of contact of the resin with the solution.

Each of these studies being carried out over a range of concentrations.

Furthermore, it was decided to use a resin of small particle size throughout, namely 50 - 100 mesh.

$\frac{1}{2}$ gm. samples of the appropriate Zeo Karb 225 resin in the Hydrogen form were weighed into clean dry conical flasks. 50 mls. of the fully aged hot solution were pipetted into each flask. The solution and resin remained in contact under the conditions of the experiment - either standing, with occasional swirling to ensure a thorough mixing of the resin with the bulk of the solution, or by shaking on a mechanical shaker - for the appropriate length of time.

At the conclusion of the experiment the resin was transferred in the usual way to a small column and then, after washing, the complex species were eluted with nitric acid. The effluent and washings were analysed for chromium and phosphate. Subsequently the resin capacity of each resin sample now fully converted to the H form was determined as outlined previously.

In the first set of Tables, namely 17 - 22, a record is given of the results obtained in studying the effect of varying the weight swelling of the resin for a constant time of contact.

In the second set of Tables, namely, 23 - 27, the results obtained in studying the effect of time of contact of solution and resin are given.

The graphical results which may be derived from these tables are deferred until the discussion of these batch studies, in Part 4, Section C on page 134.

From the results obtained in these series of experiments one of the features that is evident is that there is a change in ratio of chromium: phosphate on the resin with the time of contact of resin with solution. As is discussed on page 137, there are several factors which may account for this, namely :-

(i) Rate of diffusion of the various complexes.

(ii) Effect of the highly acid media within the resin initially on the complexes sorbed.

(iii) Changes in the solution within the time of the experiment.

Two further series of experiments were devised to test factors (ii) and (iii).

Firstly the sodium form of the resin was used in place of the hydrogen form. A blank experiment was carried out to find out the amount of conversion of sodium form to hydrogen form at the pH of the solution in contact with the resin.

Secondly a solution was aged in the normal fashion at 70° and then allowed to stand for a long period at room temperature before the normal procedure was adopted.

The results of these two series of experiments are recorded in Tables 28 and 29 on pages 97 and 98.

3. Sorption of chromium phosphate cationic complexes from unsaturated solutions of Zeo Karb 225 (H form)

(i) Solutions aged at 70°

In this third set of sorption experiments the technique applied was precisely similar to that outlined for the second set. The solutions of chromium (111) - phosphoric acid which were selected for study, however, were not saturated.

The first series of experiments was carried out with solutions of a constant chromium (111) content whilst the phosphate content was varied.

The second series of experiments was carried out with solutions of a constant phosphate content whilst the chromium (111) content was varied.

The composition of the solutions employed in this study are given in Table 30 on page 99.

The results of the batch sorption studies, carried out as outlined previously, are recorded in Tables 31 and 32, on pages 100 and 101.

(ii) Solutions aged at 100°C

A further series of experiments was carried out with solutions of a constant phosphate content whilst the chromium (111) content was varied. The solutions were aged by refluxing them for a period of at least 12 hours. The results of the batch sorption studies are recorded in Tables 33 on page 102.

4. Sorption of Chromium (111) from a '$2\frac{1}{2}$%' solution by De-acidite FF

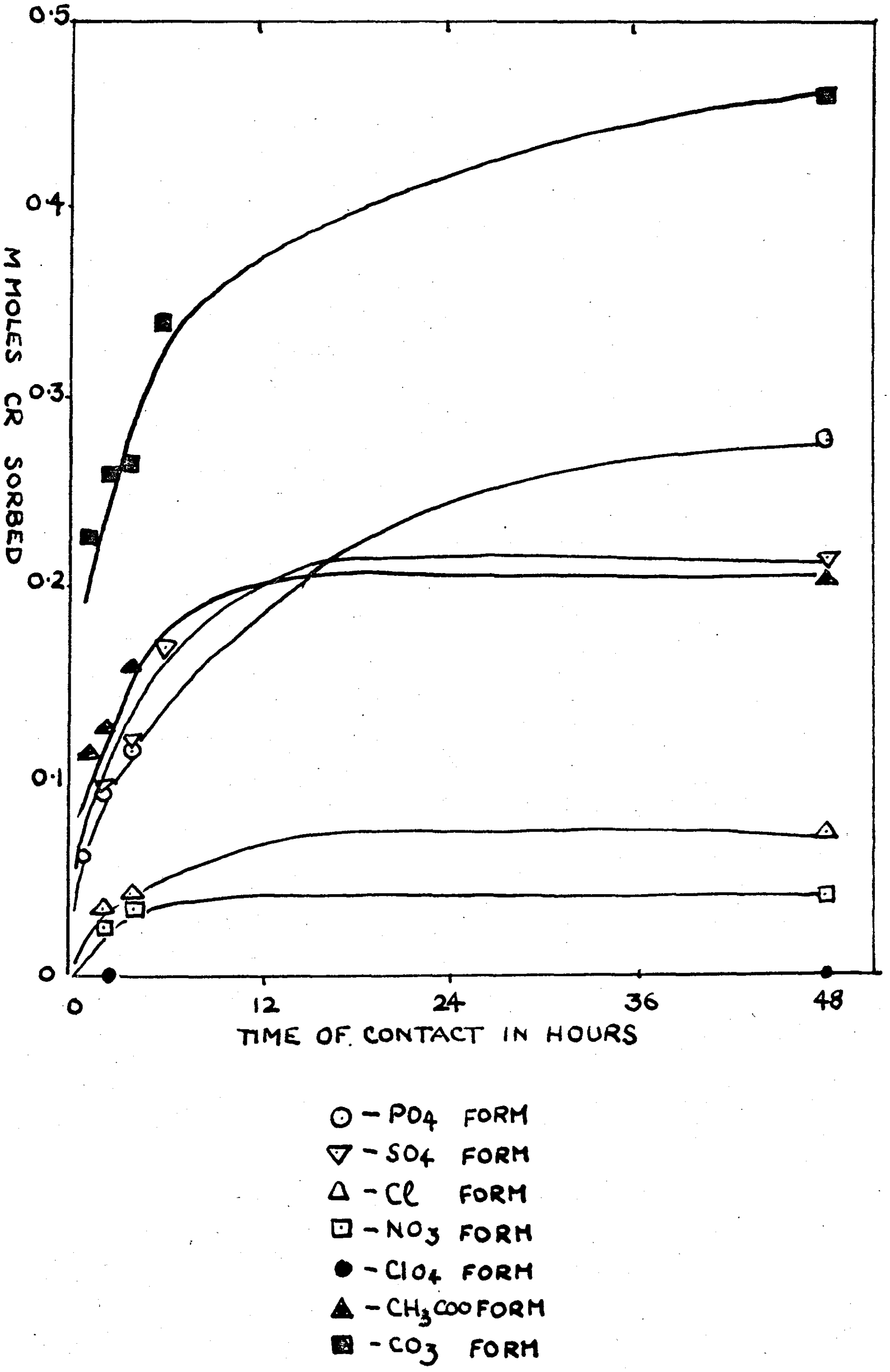
In the column experiments described in the next section, it was hoped to achieve a clean separation of the cationic, anionic, and neutral 'fractions' of a fully aged saturated solution by the passage of such a solution through, first a column of a cation exchanger, then a column of an anion exchanger and collecting the effluent from both columns after washing. By elution of each column separately and analysis of the two effluents and the initial washings, it was hoped to gain a knowledge of the %

chromium and % phosphate in the various forms.

However, preliminary column experiments were not very successful since it was found that the amount of chromium taken up on the anion exchanger varied considerably depending on whether the column was in the phosphate or the nitrate form. It was therefore decided to carry out the following series of experiments with the intention of finding a suitable <u>form</u> of the anion exchanger which would remove the anionic chromium (III) phosphate complexes rapidly whilst not causing their breakdown in any way.

Samples of De-acidite FF were prepared in the chloride, nitrate, sulphate, perchlorate, phosphate, acetate and bicarbonate forms. 1 gm. samples of resin were allowed to stand in contact with a fully aged solution for differing lengths of time. The results obtained are recorded in Table 34, and given graphically in Fig. 13.

FIG. 11 UPTAKE OF CR(III) FROM AN AGED SOLUTION BY DEACIDITE FF IN VARIOUS FORMS



SECTION D.

ION-EXCHANGE SEPARATIONS INTO CATIONIC, ANIONIC AND NEUTRAL COMPLEXES

1. Sorption using both Zeo Karb 225 and De-acidite FF.

In the first instance the intention was to achieve a separation into the cationic, anionic and neutral complexes which were present in the fully aged solutions investigated by batch studies. If the percentage of chromium in each class of complex were known and also the extent to which the phosphate was being utilised in complex formation, then from this knowledge over the range of solutions studied it should prove possible to make certain predictions relating to the mode of formation of the complexes.

Early attempts at achieving a chromatographic separation of the various cationic complexes involved the passage of a fully aged solution through a long column (1 x 50 cm.) of De-acidite FF, in the nitrate or sulphate form, prior to passage through a similar column of Zeo Karb 225 in the H form. It was found that the amount of chromium and phosphate sorbed on both columns and appearing in the washings from the columns on loading them varied considerably as the following factors were varied :

(a) The form of the anion exchanger

(b) The rate of passage of solution through the columns

(c) Even the order of passage seemed to have some effect on the results.

As a result of the batch studies as discussed in Section C (4), it is clear that any attempt to achieve a separation in this way would not be very valuable as in all probability one of two factors certainly would affect the balance of the anionic and neutral complexes. These two factors are :

(i) Chemical interaction between the anion exchanger in some forms and the solution passed through the column - resulting in more chromium being sorbed as anionic species than is in reality present in the solution.

(ii) Lack of sorption of the complex species on the anion exchanger in the other forms, resulting in a false value for the amount of neutral complexes.

As a result of these observations the experiments in this form were discontinued. Results of three or four of these experiments are recorded in Table 35 in order to illustrate the above discussion.

2. Sorption using Zeo Karb 225 only, i.e. separation of the cationic complexes from the other two classes present in a fully aged solution.

On the realisation that a chemical change of the anionic complexes was probably taking place on the passage of the solution through an anion exchange column or that incomplete sorption of the anionic species was taking place, it was decided to abandon the original intention and merely to differentiate between the cationic complexes and the rest.

The separation was achieved in the following manner. Two columns (25 x 2.5 cms.) containing about 15 gms. each of Zeo Karb 225 (H form) of 2% cross-linking were connected in series. An appropriate aliquot of the solution under investigation was pipetted undiluted on to the top of the first column and the columns were subsequently washed with 500 mls. of distilled water. The use of the second column was decided upon after it was observed that a certain proportion of the cationic complexes were held very lightly. It was found that a small portion of cationic chromium was retained in this way, which would otherwise have passed through and been analysed in the washings. When separation had been achieved in this way the cationic complexes were eluted from the column using 2N HNO_3 and employing the 'method of spurts'. Analysis of the chromium and phosphate content of both solutions was then carried out in the normal manner. The results are given in Tables 36a and b and indicate that the majority of the chromium is in the cationic form in most solutions. In addition, the impression gained in the earlier attempts at achieving a complete separation into the three classes of complex is that the rest of the chromium is in the form of anionic complexes, though it is difficult to be certain on this point.

SECTION E.

ION EXCHANGE CHROMATOGRAPHY

Ion Exchange Chromatography

In the previous section the separation of the complexes present in chromium (111)-phosphoric acid solutions into cationic and other components was discussed. In this section an account is given of the attempts made to separate the various cationic complexes present in these solutions and to determine their probable formulae. Mention is also made of the few attempts at elucidation of the anionic complexes present in the same solutions.

1. Early Work

The batch results involving the desorption of chromium (111) species (described in Section B.) led to the conclusion that hexaäquo chromium (111) ions should be separable from chromium (111)-phosphate complex cations since, say at pH 0.5, the % metal removed by nitric acid is 29.06 and 48.57 respectively where, in the first case, the resin is in the hexaäquo form and, secondly, where it is exclusively in the complex cation form. (See Genge and Salmon (3) for a discussion of the way in which the results of batch experiments may be applied to determining whether or not a column separation of macro-quantities should be possible). The first experiment which was carried out was an attempt to achieve this separation.

The column (10 in. x $\frac{1}{2}$ in.) was filled with $4\frac{1}{2}$% cross-linked Zeo Karb 225 in the H form in the normal way. The column was backwashed several times to ensure that the resin was evenly graded and settled properly. An artificial partially aged solution was prepared by mixing together equal volumes of a freshly prepared solution with a solution of equal strength that had been fully aged at 70°C. 10 mls. of this mixed solution was added dropwise to the top of the column. The level of the liquid in the column being maintained just above the level of the resin by adjustment of the side arm connected to the column. After the column had been loaded in this way it was thoroughly washed by passing through distilled water in a similar manner. The column was then eluted with 2N nitric acid. The effluent was collected in 10 ml. fractions and analysed for chromium in the usual manner. The results are given in Table 38 in conjunction with results obtained in the same column using a fully aged solution.

Having achieved a partial separation of hexaaquo chromium (111) and cationic chromium (111)-phosphate complexes, it was decided to carry out a similar experiment to see if there were a mixture of complexes present or only one. Accordingly 10 mls. of a fully aged solution were loaded on the same column and after washing the column was eluted with nitric acid of lower concentrations. The results are given in Table 39 and indicate that the cationic fraction from a fully aged solution could be separated into a number of bands, each representing one or more complex cations.

The next stage was the development of a technique of column operation in which separation of the bands was such as to allow identification of the different complexes by subsequent analysis of the effluent.

2. Ion exchange chromatography using step-wise elution

The first method of approach to the problem to the ion exchange chromatographic separations of the cationic complexes present in the system was to use step-wise elution as described in Part 1. on page 24.

The column design

In order to achieve as good a separation as possible, various column **arrangements were tried out.** The apparatus which gave the best results was accordingly adopted for all further work is described in this Section.

The column holding the ion exchange resin consisted of a burette which had a plug of glass wool introduced in the space between the 50 ml. mark and the glass tap. To the top of this column the outlet of a second balancing burette was connected via quill tubing to which was fitted a small glass tube in which a sintered disc had been sealed. For a diagram of the apparatus see Fig. 3B. The use of the balancing column was to ensure that the resin column could not run dry once the apparatus had been set up. The use of quill tubing was to cut down the dead volume of liquid above the resin bed. The use of the glass tube fitted with the sintered disc was ; (i) to trap any solid particles which might stray into the container and connecting tubes in the course of separation, (ii) to prevent the resin particles from flowing into the balancing column on back-washing the resin column. To the bottom of the first column a polythene tube was fitted which ran straight into the collecting vessel. The container holding the liquid to be passed through the column was a one litre aspirator fitted with a tap and delivery tube which was connected to the top of the balancing column. All connections were made with rubber bungs and with polythene tubing.

Using the columns

Two such sets of columns were arranged in series, that is, the exit tube from the first column of resin delivered directly into the second balancing column. After loading the columns arranged in this way, the exit tube was disconnected and each set treated separately. The first resin column was filled up to the zero mark with 4½% cross-linked Zeo Karb 225 in the H form and the second resin column was similarly loaded with 8% cross-linked De-acidite FF in the nitrate or sulphate form.

The columns were loaded as follows: Firstly, the level of liquid in both of the balancing columns was lowered so that the only water remaining in the apparatus was that in the quill tubing connections and directly above the resin columns, together with that occupying theinterstices of the resin columns themselves. Then a suitable aliquot of the fully aged solution was diluted up to 100 or 250 mls. in the container and allowed to pass through the apparatus at a rate of about 50 ml. per hour. Subsequently the columns were washed with distilled water in a similar manner.

After the passage of about one litre of distilled water, the two sets were disconnected and the final washing of each resin column was completed separately. Each column was then eluted using nitric acid of the appropriate concentration. As the chromatographic separation proceeded so the concentration of the nitric acid was increased by replacing the solution in the containing vessel by a fresh solution of higher concentration.

Results and problems

On this apparatus a number of chromatographic separations were tried using nitric acid as the eluting agent but two problems were encountered which made the results obtained almost impossible - except in a few isolated experiments - to interpret.

1. The first problem that was encountered was that on changing from one concentration to another, which was generally made after a complex had just been desorbed from the column (the judgment of this being made by eye), often there appeared at the base of the resin column a band where one had not been seen before. This led to the assumption that another complex had been found whereas, in fact, all that had been observed was that the previous complex had not been completely desorbed and that the passage of the more concentrated eluting agent 'sharpened up' the tail of this band. This problem was overcome to a certain extent by not

changing over to a more concentrated eluting solution so quickly.

2. The second problem that was encountered was more profound. Using nitric acid as the eluting agent it often proved impossible to place any meaning on the analyses of the various collected fractions of the effluent. The reason for this was that the Cr : PO_4 ratio, especially in the early fractions, was often such that no interpretation could be given to the results at all. Four chromatograms showed this behaviour most markedly - the results of one are given as an example in Table 40.

As far as the results of other chromatograms are concerned, those which appear to be reliable are given in an abbreviated form in Table 41.

3. Ion exchange chromatography using gradient elution

In using step-wise elution and nitric acid as the eluting agent, two problems seemed to render the results difficult or impossible to interpret in spite of the fact that a clear separation of the complexes appeared to have been made. These problems have already been stated and a discussion of the so-called phosphate drift is given in Part 4, Section B, on page 129.

To try to overcome these problems, the following approach was decided upon :-

(i) To use gradient elution in place of step-wise elution.

(ii) To use ammonium nitrate solution as the eluting agent initially and followed by an ammonium nitrate-nitric acid mixture.

(iii) To add to the previously prepared column in the H form a slurry of resin in the complex form.

The use of gradient elution

A discussion of gradient elution has already been given in Part 1, Section C and a figure of the apparatus was shown in Fig. 3A.

The resin that was used in the experiments described under this head was 2% cross-linked Zeo Karb 225 in the H form and the column used was a burette set up similarly to that described in the section on step-wise elution, except that, in order to cut out as much as possible of the volume of liquid above the resin column, the balancing column was dispensed with. The delivery tube extended in the burette to just above the initial level of the resin.

The advantage of gradient elution was that the first problem which was encountered with the step-wise elution technique was eradicated (namely the appearance of spurious bands). By having a continuously increasing concentration of the eluting agent, not only was this problem eliminated but the bands of the complex were kept sharper and the tailing effect was considerably reduced. This ensured a clearer separation of the bands and the results of the analyses were accordingly more trustworthy. The only necessity in this method was to choose C_1 (the initial concentration of the reservoir) and V_0 (the volume of the mixing chamber) so that a clear separation of the complexes was achieved.

The use of ammonium nitrate as an eluting agent

In the batch experiments described in Section B on page 54 and discussed in Part 4, Section B on page 131, one of the reasons for the so-called 'phosphate drift' could be that the complexes sorbed on the resin undergo breakdown brought about by the high acid concentration, and this breakdown results in release of phosphate ions. The results of the batch experiments indicate that with ammonium nitrate this effect is considerably reduced. In the elution of the more lightly held complexes, ammonium nitrate alone was used, but after these had been eluted a mixture of ammonium nitrate-nitric acid was used as the eluting agent. The reason for this change over was in order to facilitate the estimation of chromium, the determination of which appeared to be difficult in the presence of a large excess of ammonium nitrate. To achieve the change over, the apparatus was designed with two reservoirs, each connected separately to the mixing chamber, and fitted with a screw clip. The first reservoir contained ammonium nitrate solution (usually 0.66 M) and the contents of this were allowed to flow into the mixing chamber first. At the chosen time the screw clip of this reservoir was closed and that belonging to the second reservoir was opened. The second reservoir contained ammonium nitrate at the same concentration together with nitric acid (usually 2 M or 4 M). In this way it was hoped to reduce the phosphate drift to a minimum by keeping the breakdown of the complexes as low as possible.

The use of a slurry added to the ion-exchange column

The previously prepared column was loaded in the following way:- to the fully aged solution which was to be investigated was added a half gram or smaller oven-dried sample of 2% cross-linked Zeo Karb 225 in the H form. This mixture was shaken for two hours on a mechanical shaker and then the resin was separated from the solution by transferring it to a sintered glass crucible and thoroughly washed with distilled water under pressure. The resin was then transferred, as a slurry, to the top of the column in the H form where it was allowed to settle as a compact band. This technique was employed since there are probably two reasons why abnormal $Cr:PO_4$ ratios were encountered in the earlier work. The first is the actual phosphate drift due to the breakdown of some of the complexes sorbed on the resin, due to the environment in which they are, and second that it is possible for unionized phosphoric acid to be retained in the resin phase even on prolonged washing. Obviously the possibility of this happening is reduced considerably if the resin sample in the complex form, and washed free from phosphate, is loaded directly to the top of the carefully prepared column in the H form.

The variation of concentration

The theoretical expression derived to give the concentration in the mixing chamber after a volume V mls. had flowed out was :

$$\frac{C_o - C_1}{C - C_1} = e^{V/V_o} \qquad \ldots\ldots\ldots\ldots \quad (1)$$

See page 25. The theoretical values of the concentration in the mixing chamber after different volumes had passed out of that chamber are given in Table 43 for the two values of V_o which were used in the experiments and for the different values of C_1 which were used. From work carried out by Bissett, (4), it has been shown that the experimental curve of concentration against volume delivered follows the theoretical curve almost exactly and accordingly that was not verified in the series of experiments described here.

Results

A number of experiments were carried out and an outline of the results is given in Tables 42a and b. The solutions selected were those of constant P_2O_5 concentration with varying values of Cr_2O_3 content. It was felt that those would furnish the most information.

PART 3

SECTION F.

TABULAR RESULTS

TABLE 8

Phase Diagram Study of the Cr_2O_3 - P_2O_5 - H_2O System at 70°

Solution			Solid	
ρ	% Cr_2O_3	% P_2O_5	% Cr_2O_3	% P_2O_5
1.002	0.09	1.07	7.32	9.77
1.013	0.24	2.24	7.90	11.55
1.022	0.48	2.90	8.15	12.28 *
1.049	1.43	5.37	9.43	15.08
1.061	1.87	6.62	7.75	13.49 *
1.085	2.39	8.71	10.27	17.65
1.100	3.28	9.43	7.87	14.70 *
1.103	3.17	9.92	13.29	21.73
1.120	3.92	10.49	-	-
1.155	5.44	13.18	6.76	14.03
1.180	6.36	14.36	15.50	24.90 *
-	8.61	17.23	9.76	18.67 *
1.265	9.09	17.93	17.36	27.72
-	6.46	14.13	13.25	22.50

* Denotes experiments carried out after allowing samples to stand at 70° for 12 weeks

TABLE 9

Desorption of $\left[Cr(111)(H_2O)_6\right]^{3+}$ from metal form Zeo Karb 225

pH of	% Cr removed from resin by				
Solution	H_3PO_4	H_2SO_4	HCl	HNO_3	$HClO_4$
1.50	0.99	0.00	0.32	0.00	-
1.25	4.19	3.55	1.97	0.82	-
1.04	-	-	-	-	2.48
1.00	7.81	17.59	2.50	6.16	-
0.87	12.68	-	-	-	-
0.75	15.05	25.03	15.40	12.52	-
0.60	24.54	-	-	-	-
0.54	-	-	-	-	16.30
0.50	26.02	42.22	31.36	29.06	-
0.25	39.76	67.49	62.04	58.44	-
0.08	-	-	-	-	41.66
0.05	46.59	86.18	92.11	89.60	-

½ gm. resin 20 - 50 mesh size 8% cross-linked.

50 mls. of acid of the appropriate pH. 7 days standing.

TABLE 10

Desorption of [Cr(111) phosphate]$^{x+}$ from Zeo Karb 225

pH of Solution	% Cr removed from resin by				
	H_3PO_4	H_2SO_4	HCl	HNO_3	$HClO_4$
1.50	11.81	7.16	7.47	6.66	8.75
1.25	15.99	13.63	11.92	5.61	13.58
1.00	22.69	18.97	15.83	16.38	19.43
0.75	41.00	44.75	29.11	30.70	28.07
0.50	55.40	65.97	51.80	48.57	37.59
0.25	69.38	82.08	75.38	79.17	54.08
0.05	76.77	100.00	97.44	98.88	58.03

½ gm. resin 20 - 50 mesh size 8% cross-linked

50 mls. of solution of acid. 7 days standing.

Resin treated with a solution containing :

7.5% P_2O_5

1.25% Cr_2O_3

91.25% H_2O

Temperature of aging : 70°C

Time of aging : 4 days.

TABLE 11

Desorption of Chromium and Phosphate from Zeo Karb 225 by Nitric Acid

	pH of HNO_3	m/moles Cr	m/moles PO_4	% Cr	% PO_4	Ratio
Removed	1.50	0.007	0.033	3.8	14.0	1:4.71
	1.25	0.011	0.038	5.9	16.0	1:3.45
	1.00	0.023	0.058	12.5	24.5	1:2.52
	0.75	0.046	0.085	25.2	35.8	1:1.85
	0.50	0.069	0.097	37.9	53.5	1:1.41
	0.25	0.104	0.168	57.2	70.7	1:1.63
	0.03	0.130	0.196	71.2	82.7	1:1.51
Retained	1.50	0.175	0.204	96.2	86.0	1:1.17
	1.25	0.171	0.200	94.1	84.0	1:1.17
	1.00	0.159	0.179	87.5	75.5	1:1.13
	0.75	0.136	0.153	74.8	64.3	1:1.12
	0.50	0.113	0.140	62.1	46.5	1:1.23
	0.25	0.078	0.070	42.8	29.3	1:0.89
	0.03	0.053	0.041	28.9	17.4	1:0.79

$\frac{1}{2}$ g.m. samples 50 - 100 mesh Water Regain 0.43

Pretreatment of resin - shaken for $1\frac{1}{2}$ hours with solution containing :

2.5% P_2O_5 0.3% Cr_2O_3 97.2% H_2O

Content of resin Cr 0.124 moles/equiv. i.e. 0.182 m.moles.

PO_4 0.162 moles/equiv. i.e. 0.238 m.moles.

Ratio of Cr : PO_4 on resin 1:1.30

TABLE 12

Desorption of Chromium and Phosphate from Zeo Karb 225 by Nitric Acid

	pH of HNO_3	m/moles Cr	m/moles PO_4	% Cr	% PO_4	Ratio
Removed	1.50	0.015	0.061	4.64	16.6	1:4.10
	1.25	0.029	0.078	9.1	21.3	1:2.69
	1.00	0.050	0.110	15.9	30.7	1:2.20
	0.75	0.083	0.155	26.2	42.2	1:1.89
	0.50	0.120	0.190	38.2	51.6	1:1.58
	0.25	0.177	0.258	56.1	70.3	1:1.46
	0.03	0.224	0.298	71.1	81.2	1:1.33
Retained	1.50	0.300	0.307	95.4	83.4	1:1.02
	1.25	0.286	0.289	90.9	78.7	1:1.01
	1.00	0.265	0.258	84.1	69.3	1:0.97
	0.75	0.232	0.213	73.8	57.8	1:0.92
	0.50	0.194	0.178	61.8	48.4	1:0.92
	0.25	0.138	0.109	43.9	29.7	1:0.79
	0.03	0.093	0.069	28.9	18.8	1:0.75

$\frac{1}{2}$ gm. samples 50 - 100 mesh Water Regain 0.43

Pretreatment of resin - stood for 7 days with solution containing :

2.5% P_2O_5 0.3% Cr_2O_3 97.2% H_2O

Content of resin Cr 0.240 moles/equiv. i.e.0.315 m.moles.

PO_4 0.280 moles/equiv. i.e.0.368 m.moles.

Ratio of Cr:PO_4 1:1.17

TABLE 13

Desorption of Chromium and Phosphate from Zeo Karb 225 by Ammonium Nitrate

	molarity	pH	m.moles Cr	M.moles PO_4	% Cr	% PO_4	Ratio Cr : PO_4
Removed	0.25	2.03	0.068	0.131	32.7	47.8	1 : 1.92
	0.50	1.97	0.094	0.173	45.0	63.4	1 : 1.84
	1.00	1.98	0.112	0.186	53.3	68.0	1 : 1.66
	2.00	1.98	0.113	0.173	53.7	63.0	1 : 1.53
Retained	0.25	2.03	0.142	0.143	67.3	52.2	1 : 1.00
	0.50	1.97	0.116	0.101	55.0	36.7	1 : 0.87
	1.00	1.98	0.098	0.088	46.7	32.0	1 : 0.90
	2.00	1.98	0.097	0.101	46.3	36.8	1 : 1.04

$\frac{1}{2}$ gm. samples 50 - 100 mesh Water regain 0.43

Pretreatment of resin - shaken for two hours with solution containing :

2.5% P_2O_5. 0.3% Cr_2O_3. 97.2% H_2O

Content of resin Cr 0.154 moles/equiv. i.e. 0.210 m.moles

PO_4 0.201 moles/equiv. i.e. 0.274 m.moles.

Ratio of Cr : PO_4 is 1 : 1.31

TABLE 14

Desorption of [Cr (111) phosphate]$^{a-}$ from De-acidite FF

pH of solution	% Cr removed from resin by				
	H_3PO_4	H_2SO_4	HCl	HNO_3	$HClO_4$
1.50	17.76	48.67	59.40	15.40	24.43
1.25	34.79	72.45	92.50	48.59	17.05
1.00	60.48	92.87	94.10	57.14	16.05
0.75	83.64	98.20	97.50	70.24	17.40
0.50	97.53	99.30	100.00	90.20	23.08
0.25	100.00	100.00	100.00	93.27	27.11
0.05	100.00	100.00	100.00	100.00	33.80

1 gm. resin 20 - 50 mesh size 8% cross-linked

50 mls. solution 7 days standing.

Resin treated with a solution containing 7.5% P_2O_5

1.25% Cr_2O_3

91.25% H_2O

Temperature of aging : 70°C

Time of aging : 4 days

TABLE 15

Sorption of $[Cr(H_2O)_6]^{3+}$ on Zeo Karb 225 (H form)

Resin	time of contact	m.moles Cr sorbed	m equivs. per ½ gm. resin	moles/equiv.	% saturation
1	7 mins.	0.4117	1.29	0.319	95.8
1	15 mins.	0.4040	1.26	0.319	95.8
1	30 mins.	0.4057	1.27	0.320	96.1
1	1 hour	0.3955	1.25	0.320	96.1
1	2 hours	0.3986	1.25	0.319	95.8
1	4 hours	0.4176	1.26	0.331	99.4
2	1 hour	0.3685	1.36	0.271	81.4
2	2 hours	0.3709	1.32	0.281	84.4
2	4 hours	0.3786	1.32	0.287	86.2
2	8 hours	0.3886	1.31	0.297	89.2

50 mls. solution containing 5% P_2O_5

0.5% Cr_2O_3

94.5% H_2O

Resin 1 40 - 100 mesh ½ gm. samples Weight swelling 1.98

Resin 2 50 - 100 mesh ½ gm. samples Weight swelling 0.43

TABLE 16

Composition of the saturated Cr(111) - phosphoric acid mixtures aged at 70° employed in the ion-exchange studies.

solution	% Cr_2O_3	% P_2O_5	% H_2O	[Cr] moles/1000gm	[PO_4] moles/1000 gm.	[PO_4]/[Cr]
"2½"	0.3	2.5	97.2	0.039	0.352	8.98
"5"	1.0	5.0	94.0	0.132	0.704	5.34
"7½"	2.0	7.5	90.5	0.263	1.056	4.01
"10"	3.5	10.0	86.5	0.488	1.408	2.89
"12½"	5.0	12.5	82.5	0.658	1.761	2.68
"15"	7.0	15.0	78.0	0.921	2.113	2.29

TABLE 16A

Weight swelling of resin compared with Nominal % of cross-linking

Weight Swelling	% Cross-linking
22.0	½%
11.1	1%
5.4	2%
1.95	4½%
1.97	4½%(ii)
1.1	8%
0.43	20%

In all cases mesh size is 50 - 100 except 4½% (ii) which is 40 - 100.

TABLE 17

Sorption of Chromium (111) and Phosphate from a "15%" solution by Zeo Karb 225 (H form)

% cross-linking	m.moles Cr found	m.moles PO_4 found	Resin capacity	moles/ equiv.Cr	moles/ equiv.PO_4	Ratio Cr : PO_4
4½%(ii)	1.143	1.593	1.345	0.850	1.184	1 : 1.39
20	0.148	0.203	1.376	0.108	0.148	1 : 1.37

Temperature of aging 70°C. Time of aging 4 days.

Weight of resin 0.500 gm. Volume of solution 50 mls.

Time of contact of solution with resin : 2 hours.

TABLE 18

Sorption of Chromium (111) and Phosphate from a "12½%" solution by Zeo Karb 225 (H form).

½ cross-linking	m.moles Cr found	m.moles PO_4 found	Resin capacity	moles/ equiv.Cr	moles/ equiv.PO_4	Ratio Cr : PO_4
½	1.243	1.970	0.893	1.392	2.207	1 : 1.58*
1	2.196	3.266	1.701	1.291	1.920	1 : 1.49
2	2.054	2.926	1.703	1.206	1.718	1 : 1.42
4½	1.547	2.180	1.851	0.835	1.177	1 : 1.40
8	0.887	1.218	1.992	0.445	0.611	1 : 1.37
20	0.126	0.171	1.404	0.090	0.122	1 : 1.35

Temperature of aging 70°C. Time of aging 4 days.

Weight of resin 0.500 gm.

Volume of solution 50 mls. pH of solution 1.12.

Time of contact of solution with resin : 2 hours.

* approx. 0.25 gm. of resin used.

TABLE 19

Sorption of Chromium (111) and Phosphate from a "10%" solution by Zeo Karb 225 (H form)

% cross-linking	m.moles Cr found	m.moles PO_4 found	Resin capacity	moles/ equiv.Cr	moles/ equiv.PO_4	Ratio Cr : PO_4
½	1.414	1.723	0.892	1.586	1.932	1 : 1.22*
1	2.475	2.890	1.698	1.457	1.702	1 : 1.17
2	2.208	2.761	1.706	1.295	1.619	1 : 1.25
4½	1.627	2.139	1.854	0.877	1.154	1 : 1.32
8	1.030	1.432	1.634	0.630	0.876	1 : 1.39
20	0.128	0.176	1.430	0.090	0.123	1 : 1.37

Temperature of aging 70°C. Time of aging : 4 days.

Weight of resin 0.500 gm.

Volume of solution 50 mls. pH of solution 1.12.

Time of contact of solution with resin : 2 hours.

* approx. 0.25 gm. of resin used.

TABLE 20

Sorption of Chromium (111) and Phosphate from a "$7\frac{1}{2}$%" solution by Zeo Karb 225 (H form)

% cross-linking	m.moles Cr. found	m.moles PO_4 found	Resin capacity	moles/ equiv.Cr	moles/ equiv.PO_4	Ratio Cr : PO_4
$\frac{1}{2}$	0.790	0.981	0.889	0.889	1.104	1 : 1.12*
1	1.524	1.918	1.734	0.879	1.106	1 : 1.14
2	1.492	2.001	1.824	0.818	1.097	1 : 1.22
$4\frac{1}{2}$	1.272	1.649	1.861	0.684	0.886	1 : 1.30
8	0.861	1.155	2.003	0.430	0.576	1 : 1.34
20	0.111	0.165	1.434	0.077	0.115	1 : 1.49

Temperature of aging : 70°C. Time of aging : 4 days.

Weight of resin : 0.500 gm.

Volume of solution : 50 mls. pH of solution 1.12

Time of contact of solution with resin : 2 hours.

* approx. 0.25 gm. of resin used.

TABLE 21

Sorption of Chromium (111) and Phosphate from a "5%" solution by Zeo Karb 225 (H form)

% cross-linking	m.moles Cr.found	m.moles PO_4 found	Resin cap. m.equivs./½ gm.	Moles/ equiv.Cr	Moles/ equiv.PO_4	Ratio Cr : PO_4
½	0.615	0.866	0.858	0.717	1.008	1 : 1.41*
1	1.163	1.583	1.658	0.701	0.995	1 : 1.36
2	1.312	1.747	1.725	0.760	1.013	1 : 1.33
4½	1.143	1.577	1.825	0.626	0.864	1 : 1.38
8	0.878	1.199	1.965	0.447	0.610	1 : 1.37
20	0.130	0.188	1.428	0.091	0.132	1 : 1.45

Temperature of aging : 70°C. Time of aging : 4 days.

Weight of resin : 0.500 gm.

Volume of solution : 50 mls. pH of solution 1.19

Time of contact of solution with resin : 2 hours.

* approx. 0.25 gm. of resin used.

TABLE 22

Sorption of Chromium (111) and Phosphate from "$2\frac{1}{2}$%" solution by Zeo Karb 225 (H form)

% cross-linking	m.moles Cr.found	m.moles PO_4 found	Resin cap. m.equivs./$\frac{1}{2}$ gm.	moles/ equiv.Cr	moles/ equiv.PO_4	Ratio Cr : PO_4
$\frac{1}{2}$	0.372	0.520	0.95	0.394	0.551	1 : 1.40*
1	0.652	0.920	1.54	0.424	0.597	1 : 1.41
2	0.790	1.126	1.81	0.436	0.621	1 : 1.43
$4\frac{1}{2}$	0.696	0.920	1.88	0.370	0.489	1 : 1.32
8	0.470	0.646	2.05	0.229	0.315	1 : 1.37
20	0.080	0.106	1.36	0.059	0.077	1 : 1.32

Temperature of aging : 70°C. Time of aging : 4 days.

Weight of resin : 0.500 gms.

Volume of solution : 50 mls. pH of solution 1.35

Time of contact of solution with resin : 2 hours.

* 0.25 gm. of resin used.

TABLE 23

Sorption of Chromium (111) and Phosphate from a "$2\frac{1}{2}$%" solution by Zeo Karb 225 (H form)

Time of contact	% cross-linking	m.moles Cr.found	m.moles PO_4 found	Resin Capacity	moles/ equiv.Cr.	moles/ equiv.PO_4	Ratio Cr : PO_4
1 hour	$\frac{1}{2}$	0.358	0.504	0.96	0.374	0.526	1 : 1.41 *
standing	1	0.310	0.445	0.68	0.456	0.655	1 : 1.43
"	2	0.799	1.123	1.99	0.401	0.563	1 : 1.41
"	$4\frac{1}{2}$	0.583	0.799	1.85	0.315	0.431	1 : 1.37
"	8	0.366	0.477	2.06	0.177	0.231	1 : 1.31
"	20	0.065	0.085	1.36	0.048	0.063	1 : 1.31
1 hour	$\frac{1}{2}$	0.379	0.523	0.92	0.413	0.569	1 : 1.38 *
shaking	1	0.591	0.814	1.51	0.391	0.466	1 : 1.38
"	2	0.796	1.063	1.98	0.401	0.536	1 : 1.34
"	$4\frac{1}{2}$	0.834	1.126	1.88	0.443	0.599	1 : 1.35
"	8	0.622	0.792	2.03	0.306	0.390	1 : 1.27
"	20	0.162	0.198	1.37	0.118	0.135	1 : 1.22

Temperature of aging : 70°C. Time of aging : 4 days.

Weight of resin : 0.500 g.

Volume of solution : 50 mls.

* 0.25 gm. resin used.

TABLE 24

Sorption of Chromium (111) and Phosphate from a "2½%" solution by Zeo Karb 225 (H form)

Time of contact	% cross-linking	m.moles Cr.found	m.moles PO_4 found	Resin Capacity	moles/ equiv.Cr	moles/ equiv.PO_4	Ratio Cr : PO_4
4 hours	1	0.362	0.504	0.76	0.475	0.661	1 : 1.39
"	2	0.882	1.221	1.99	0.444	0.614	1 : 1.38
"	4½	0.783	1.024	1.87	0.419	0.548	1 : 1.31
"	4½(ii)	0.483	0.669	1.37	0.354	0.490	1 : 1.38
"	8	0.515	0.698	2.01	0.257	0.348	1 : 1.36
"	20	0.113	0.147	1.37	0.076	0.107	1 : 1.31
8 hours	½	0.413	0.562	0.95	0.432	0.592	1 : 1.36*
"	1	0.375	0.532	0.76	0.493	0.700	1 : 1.42
"	2	0.888	1.226	1.99	0.446	0.615	1 : 1.38
"	4½(ii)	0.594	0.808	1.28	0.464	0.628	1 : 1.36
"	8	0.529	0.718	2.06	0.256	0.348	1 : 1.36
"	20	0.124	0.162	1.37	0.091	0.118	1 : 1.31

Temperature of aging : 70°C   Time of aging : 4 days.

Weight of resin : 0.500 g.

Volume of solution : 50 mls.

* approx. 0.25 g. resin.

TABLE 25

Sorption of Chromium (111) and Phosphate from a "$2\frac{1}{2}$%" solution by Zeo Karb 225 (H form)

Time of contact	% cross-linking	m.moles Cr.found	m.moles PO_4 found	Resin capacity	moles/ equiv.Cr	moles/ equiv.PO_4	Ratio Cr : PO_4
16 hours	20	0.152	0.203	1.38	0.111	0.147	1 : 1.33
24 hours	20	0.160	0.209	1.35	0.118	0.155	1 : 1.30
7 days	1	0.770	0.965	1.53	0.504	0.631	1 : 1.25
"	2	0.999	1.168	1.99	0.502	0.587	1 : 1.17
"	$4\frac{1}{2}$	1.056	1.246	1.87	0.565	0.661	1 : 1.18
"	8	0.953	1.153	2.06	0.462	0.559	1 : 1.21
"	20	0.339	0.396	1.35	0.250	0.293	1 : 1.17

Temperature of aging : 70°C. Time of aging : 4 days.

Weight of resin : 0.500 g.

Volume of solution : 50 mls.

TABLE 26

Sorption of Chromium (111) and Phosphate from solutions by Zeo Karb 225 (H form)

Time of contact	solution	m.moles Cr found	m.moles PO_4 found	Resin capacity	moles/ equiv.Cr	moles/ equiv.PO_4	Ratio Cr : PO_4
1 hour	"5%"	0.621	0.951	1.26	0.493	0.756	1 : 1.53
"	"7½%"	0.873	1.201	1.34	0.650	0.895	1 : 1.38
"	"10%"	1.040	1.440	1.33	0.780	1.080	1 : 1.38
"	"15%"	1.073	1.482	1.35	0.793	1.102	1 : 1.38
5 hours	"5%"	0.738	1.102	1.26	0.586	0.875	1 : 1.49
4 hours	"7½%"	0.891	1.271	1.35	0.662	0.943	1 : 1.43
"	"10%"	1.078	1.508	1.35	0.798	1.117	1 : 1.40
"	"15%"	1.158	1.662	1.34	0.862	1.238	1 : 1.44
8 hours	"5%"	0.785	1.119	1.27	0.617	0.880	1 : 1.42
"	"7½%"	0.956	1.311	1.36	0.706	0.968	1 : 1.37
"	"10%"	1.104	1.524	1.34	0.825	1.139	1 : 1.38
"	"15%"	1.170	1.662	1.34	0.870	1.237	1 : 1.42

Temperature of aging : 70°C. Time of aging : 4 days.

Weight of resin : 0.500 g.

Volume of solution : 50 mls.

Cross-linking of resin : 4½% (ii)

TABLE 27

Sorption of Chromium (111) and Phosphate from solutions by Zeo Karb 225 (H form)

Time of contact	Solution	m.moles Cr found	m.moles PO_4 found	Resin capacity	moles/ equiv.Cr	moles equiv.PO_4	Ratio Cr : PO_4
7 days	"2½%"	0.697	0.875	1.28	0.545	0.684	1 : 1.25
14 days	"2½%"	0.767	0.917	1.28	0.598	0.715	1 : 1.19
7 days	"5%"	0.836	0.996	1.28	0.652	0.777	1 : 1.19
14 days	"5%"	0.900	1.057	1.28	0.704	0.827	1 : 1.17
7 days	"7½%"	1.017	1.261	1.34	0.761	0.943	1 : 1.24
7 days	"10%"	1.219	1.482	1.35	0.904	1.099	1 : 1.22
7 days	"15%"	1.336	1.684	1.35	0.990	1.248	1 : 1.26
1 hour shaking	"7½%"	0.960	1.303	1.35	0.710	0.963	1 : 1.36
"	"10%"	1.083	1.477	1.38	0.785	1.071	1 : 1.36
"	"15%"	1.109	1.606	1.35	0.821	1.193	1 : 1.45

Temperature of aging : 70°C. Time of aging : 4 days

Weight of resin ; 0.500 g.

Volume of solution : 50 mls.

Cross-linking of resin : 4½%(ii)

TABLE 28a

Sorption of Chromium (111) and Phosphate from a "2½%" solution by Zeo Karb 225 (Na form)

Time of contact	% cross-linking	m.moles Cr. found	m.moles PO_4 found	Resin capacity	moles/equiv.Cr	moles/equiv.PO_4	Ratio Cr : PO_4
2 hours	4½	0.578	0.798	2.06	0.281	0.388	1 : 1.38
"	20	0.081	0.112	1.62	0.050	0.069	1 : 1.38
8 hours	4½	0.665	0.940	2.06	0.323	0.457	1 : 1.41
"	20	0.126	0.161	1.63	0.078	0.099	1 : 1.27

Weight of resin : 0.500 g.

Volume of solution : 50 mls. pH of solution : 1.31

TABLE 28b

Conversion of Zeo Karb 225 (Na form) to H form by Phosphoric Acid at pH 1.31.

Time of contact	% cross-linking	Resin* Capacity	H ion* Capacity	% Conversion of Na → H.
2 hours	4½	1.90	1.145	60.4
"	20	1.60	0.898	55.7
8 hours	4½	1.89	1.151	61.1
"	20	1.58	0.936	59.4

* in m.equivs./per ½ gm.

TABLE 29

Sorption of Chromium (111) and Phosphate from a "$2\frac{1}{2}\%$" solution after standing with Zeo Karb 225 (H form).

Time of contact	% cross-linking	m.moles Cr found	m.moles PO_4 found	Resin capacity	moles/ equiv.Cr	moles/ equiv.PO_4	Ratio Cr : PO_4
1 hour	$4\frac{1}{2}$	0.465	0.687	1.87	0.248	0.366	1 : 1.48
2 hours	$4\frac{1}{2}$	0.519	0.756	1.81	0.287	0.418	1 : 1.46
4 hours	$4\frac{1}{2}$	0.668	0.950	1.89	0.354	0.503	1 : 1.42
8 hours	$4\frac{1}{2}$	0.724	1.018	1.88	0.385	0.540	1 : 1.41
2 hours	20	0.090	0.138	1.34	0.067	0.103	1 : 1.53

Temperature of aging : 70°C. Time of aging : 4 days.

Temperature of standing : Room Temperature

Time of standing : 5 weeks.

Weight of resin : 0.500g.

Volume of solution : 50 mls.

TABLE 30

Composition of the unsaturated Chromium (111) and Phosphoric Acid mixtures aged at 70° and 100°C. employed in the ion exchange studies.

Solution	%Cr_2O_3	%P_2O_5	%H_2O	[Cr] moles/1000gm.	[PO_4] moles/1000gm.	[PO_4]/[Cr]
1-5	0.3	5.0	94.7	0.039	0.704	17.96
1-10	0.3	10.0	89.7	0.039	1.408	35.90
1-15	0.3	15.0	84.7	0.039	2.113	53.88
5-15	1.5	15.0	83.5	0.196	2.113	10.78
10-15	3.0	15.0	82.0	0.392	2.113	5.39
15-15	4.5	15.0	80.5	0.588	2.113	3.59
20-15	6.0	15.0	79.0	0.784	2.113	2.69

TABLE 31

Sorption of Chromium (111) and Phosphate from solutions of constant Cr_2O_3 content by Zeo Karb 225 (H form)

% cross-linking	solution	m.moles Cr found	m.moles PO_4 found	Resin capacity	moles/equiv.Cr	moles/equiv.PO_4	Ratio Cr : PO_4
1	1-5	0.424	0.600	1.71	0.248	0.351	1 : 1.42
4½	1-5	0.404	0.590	1.87	0.216	0.316	1 : 1.46
20	1-5	0.073	0.088	1.46	0.050	0.060	1 : 1.20
1	1-10	0.151	0.235	1.71	0.089	0.138	1 : 1.55
4½	1-10	0.174	0.275	1.82	0.096	0.151	1 : 1.58
20	1-10	0.038	0.044	1.46	0.026	0.030	1 : 1.17
1	1-15	0.066	0.118	1.73	0.038	0.068	1 : 1.80
4½	1-15	0.098	0.139	1.82	0.054	0.076	1 : 1.40
20	1-15	0.020	0.025	1.41	0.014	0.018	1 : 1.25

Temperature of aging of solution : 70°C

Time of aging : 4 days.

Weight of resin : 0.500 g.

Volume of solutions : 50 mls.

Time of contact of solutions with resin : 2 hours standing

TABLE 32

Sorption of Chromium (111) and Phosphate from solutions of constant P_2O_5 content by Zeo Karb 225 (H form)

% cross-linking	Solution	m.moles Cr.found	m.moles PO_4 found	Resin capacity	moles/ equiv.Cr	moles/ equiv.PO_4	Ratio Cr : PO_4
4½	5-15	0.435	0.724	1.90	0.229	0.381	1 : 1.66
8	5-15	0.352	0.515	2.00	0.176	0.257	1 : 1.47
4½	10-15	0.800	1.204	1.85	0.433	0.651	1 : 1.50
8	10-15	0.632	0.909	2.02	0.313	0.451	1 : 1.44
4½	15-15	1.132	1.611	1.90	0.596	0.848	1 : 1.42
8	15-15	0.856	1.218	1.98	0.432	0.615	1 : 1.42
4½	20-14	1.521	2.036	1.90	0.801	1.073	1 : 1.34
8	20-15	1.018	1.363	1.99	0.510	0.683	1 : 1.34

Temperature of aging : 70°C. Time of aging : 4 days

Weight of resin : 0.500 g.

Volume of solution : 50 mls.

Time of contact of solutions with resin : 2 hours standing.

TABLE 33

Sorption of Chromium (111) and Phosphate from solutions of constant P_2O_5 content by Zeo Karb 225 (H form)

% cross-linking	Solution	m.moles Cr.found	m.moles PO_4 found	Resin capacity	moles/ equiv.Cr	moles/ equiv. PO_4	Ratio Cr : PO_4
2	5-15	0.514	0.844	1.78	0.288	0.474	1 : 1.64
* 2 (wash)	5-15	0.087	0.232	1.78	0.049	0.130	1 : 2.67
8	5-15	0.342	0.504	1.94	0.176	0.260	1 : 1.47
2	10-15	0.847	1.334	1.74	0.486	0.765	1 : 1.58
* 2 (wash)	10-15	0.146	0.313	1.74	0.084	0.179	1 : 2.15
8	10-15	0.629	0.926	1.95	0.323	0.475	1 : 1.47
2	15-15	1.262	1.979	1.83	0.689	1.081	1 : 1.57
* 2 (wash)	15-15	1.234	0.512	1.83	0.128	0.280	1 : 2.19
2	20-15	2.091	2.816	1.72	1.212	1.633	1 : 1.35
* 2 (wash)	20-15	0.231	0.756	1.72	0.134	0.438	1 : 3.27
8	20-15	1.007	1.377	1.97	0.511	0.698	1 : 1.37
* 8 (wash)	20-15	0.082	0.206	1.97	0.042	0.104	1 : 2.51

Temperature of aging : 101°C. Time of aging : 12 hours

Weight of resin : 0.500 g.

Volume of solution : 50 mls.

Time of contact of solutions with resin : 2 hours standing.

*denotes some chromium species removed on washing. Washings collected and analysed.

TABLE 34

Sorption of Chromium (111) from a 2½% solution by De-acidite FF.

Form of resin	m. moles of Cr sorbed after a time of contact of					
	½	1	2	4	6	48 hours
ClO_4	-	-	0.000	-	-	0.000
NO_3	-	-	0.026	0.033	-	0.042
Cl	-	-	0.034	0.041	-	0.073
PO_4	-	0.062	0.094	0.116	-	0.282
SO_4	-	-	0.099	0.120	0.172	0.215
CH_3COO	-	0.114	0.127	0.159	-	0.205
CO_3	0.215	0.226	0.264	0.267	0.338	0.463

Temperature of aging : 70°C. Time of aging : 4 days.

Weight of resin : 1.000 g.

Mesh size : 20 - 50.

Cross-linking : 8%

TABLE 35

Separation of cationic, anionic and neutral complexes

	Cationic		Anionic		Neutral		Total	
Expt. No.	m.moles Cr found	m.moles PO_4 found	m.moles Cr found	m.moles PO_4 found	m.moles Cr fnd.	* m.moles PO_4 fnd.	m.moles Cr fnd.	m.moles PO_4 fnd.
I	2.65	4.01	0.72	6.91	0.45	22.31	3.82	33.23
II	3.17	5.30	0.42	3.87	0.16	23.93	3.75	33.10
III	2.30	3.78	0.21	6.00	0.51	22.29	3.02	32.07
IV	2.19	3.61	0.35	6.26	0.39	20.28	2.93	30.15

* Owing to the vast excess of phosphate, most of it appears in the effluent although it is anionic.

EXPT.I 25 ml. portion of the fully aged solution diluted eight times and loaded at the rate of 100 mls. per hour in the order of cation exchange column first, anion exchange column second. Anion Exchanger in the nitrate form.

EXPT.II 25 ml. portion of the same aged solution diluted 10 times and loaded at 50 mls./hour. Same order of column arrangement. Anion Exchanger in the sulphate form.

EXPT.III and IV Approximately equal volumes of aged solution were shaken with excess De-acidite FF in the bicarbonate form for 5 minutes and 1 hour respectively. The remaining solution and washings being passed through the cation exchange column.

TABLE 36a

Separation of Cationic Complexes only from fully aged solutions at 70°C.

	Cationic		In Solution		Total	
Solution No.	m.moles Cr found	m.moles PO_4 found	m.moles Cr found	m.moles PO_4 found	m.moles Cr found	m.moles PO_4 found
2½	0.302	0.493	0.097	3.425	0.399	3.917
5	1.039	1.712	0.328	6.271	1.368	7.983
7½	1.061	1.746	0.318	4.451	1.379	6.197
10	2.219	3.611	0.378	4.698	2.596	8.300
12½	1.254	2.016	0.247	2.465	1.500	4.481
1-5	0.263	0.465	0.131	5.501	0.394	5.966
1-10	0.174	0.361	0.174	12.299	0.349	12.660
1-15	0.170	0.354	0.264	24.116	0.434	24.470
5-15	0.598	1.127	0.487	11.540	1.086	12.666
10-15	1.252	2.275	0.919	10.687	2.171	12.962
15-15	2.480	4.453	0.845	9.578	3.325	14.031
20-15	3.935	6.249	0.708	7.499	4.643	13.748

TABLE 36b

Separation of Cationic Complexes from fully aged solutions at 70°C.(ii)

	Cationic		Resin	Remainder	Initial soln.
Solution	% Cr	% PO_4	$[PO_4]/[Cr]$	$[PO_4]/[Cr]$	$[PO_4]/[Cr]$
Saturated					
2½	75.6	12.6	1.63	35.1	8.98
5	76.0	21.5	1.65	19.1	5.34
7½	77.0	28.2	1.65	14.0	4.01
10	85.5	43.5	1.63	12.4	2.89
12½	83.6	45.0	1.61	10.0	2.68
Unsaturated					
1-15	39.3	1.5	2.08	91.3	53.88
1-10	50.0	2.9	2.07	70.7	35.90
1-5	66.7	7.8	1.77	42.0	17.96
5.15	55.1	8.9	1.88	23.7	10.78
10-15	57.7	17.6	1.82	11.6	5.39
15-15	74.6	31.7	1.80	11.3	3.59
20-15	84.8	45.5	1.59	10.6	2.69

TABLE 37a

Separation of Cationic Complexes from fully aged solutions at 100°C.

	Cationic		In Solution		Total	
Solution	m.moles Cr found	m.moles PO_4 found	m.moles Cr found	m.moles PO_4 found	m.moles Cr found	m.moles PO_4 found
5-15	0.623	1.273	0.439	11.550	1.063	12.860
10-15	1.923	3.617	0.343	9.402	2.266	13.019
15-15	2.606	4.443	0.677	9.796	3.283	14.239
20-15	1.514	2.601	0.238	2.681	1.752	5.281

TABLE 37b

	Cationic		Resin	Remainder	Initial soln.
Solution	% Cr	% PO_4	$[PO_4]/[Cr]$	$[PO_4]/[Cr]$	$[PO_4]/[Cr]$
5-15	58.6	10.2	2.04	26.3	10.78
10-15	84.9	27.8	1.88	27.4	5.39
15-15	79.4	31.2	1.70	14.5	3.59
20-15	86.4	49.3	1.72	11.3	2.69

TABLE 38

Ion Exchange Chromatography (i) Separation of mixed unaged and fully aged solution (70°C)

Fully aged solution		Mixed solution	
10 ml.fractions No.	m.moles Cr found	10 ml.fractions No.	m.moles Cr found
1	0.00	1	0.00
2	0.00	2	0.00
3	0.02	3	0.01
4	0.40	4	0.24
5	0.67	5	0.56
6	0.46	6	0.28
7	0.25	7	0.27
8	0.16	8	0.28
9	0.07	9	0.38
10	0.05	10	0.47
11	0.04	11	0.20
12	0.03	12	0.14
13	0.02	13	0.11
14	0.02	14	0.08
15	0.02	15	0.04
16	0.01	16	0.02
17	0.01	17	0.02
18	0.01	18	-

Composition of Solution.

$\%P_2O_5$	7.5
$\%Cr_2O_3$	1.25
$\%H_2O$	91.25

4½% cross-linked Zeo Karb 225 (H form). Column size 2 x 25 cms.

Eluting agent 2M HNO_3

TABLE 39

Ion Exchange Chromatography (ii) Separation of complexes from fully aged solution aged at 70°C.

10 ml. fraction No.	m.moles Cr found x 10	10 ml. fraction No.	m.moles Cr found x 10
1	0.01	16	0.19
2	0.03	17	0.24
3	0.10	18	0.22
4	0.23	19	0.23
5	0.31	20	0.48
6	0.91	21	0.60
7	2.16	22	1.05
8	2.84	23	0.97
9	2.60	24	0.82
10	1.45	25	0.71
11	0.89	26	0.30
12	0.63	27	0.28
13	0.39	28	0.22
14	0.30	29	0.17
15	0.20	30	0.15

1st separation achieved. 4½% cross-linked Zeo Karb 225 (H form).

Column size 2 x 25 cms. Eluting agent 0.25 pH HNO_3.

Volume of solution taken : 20 mls.

Composition of solution : 7.5% P_2O_5 1.25% Cr_2O_3 91.25% H_2O.

TABLE 40

Ion Exchange Chromatography (iii) Illustration of "phosphate drift" using a fully aged solution at 70°C.

100 ml.fraction	strength of eluting agent	m.moles Cr found	m.moles PO_4 found	Ratio Cr : PO_4
1	pH 1	0.003	0.577	1 :192.3
2	"	0.015	0.160	1 : 10.7
3	"	0.015	0.215	1 : 14.3
4	"	0.046	0.162	1 : 3.5
5	"	0.034	0.110	1 : 3.2
6	"	0.002	0.278	1 :139.0
7	pH 0.5	0.030	0.177	1 : 5.9
8	"	0.083	0.248	1 : 3.0
9	"	0.036	0.294	1 : 8.2
10	pH 0.25	0.189	0.343	1 : 1.81
11	0.64N	0.732	1.177	1 : 1.61
12	0.64N	0.156	0.277	1 : 1.78
13	0.80N	0.101	0.372	1 : 3.68
14	0.96N	0.240	0.665	1 : 2.77
15	1.92N	0.460	0.626	1 : 1.36
16	1.92N	1.112	1.240	1 : 1.12
17	1.92N	1.277	1.075	1.19: 1
18	1.92N	0.482	0.504	1 : 1.05
19	3.84N	0.713	0.646	1.10: 1
20	3.84N	0.604	0.503	1.20: 1

4½% cross-linked Zeo Karb 225 (H form). Column size 1.2 x 50 cms.

Eluting agent HNO_3 Composition of solution 7.5% P_2O_5

1.25% Cr_2O_3

5 mls. solution used

91.25% H_2O

Column washed free of phosphate.

TABLE 41

Ion Exchange Chromatography (iv) Chromatograms. Early results from

Fraction 250 ml. No.	Complex No.	Strength of eluting agent	m.moles Cr found	m.moles PO_4 found	Ratio Cr : PO_4
1 and 2	Cat 1	pH 1	0.287	0.638	1 : 2.2
3	Cat 2	pH 0.25	0.143	0.156	1 : 1.09
5	Cat 3	pH 0.25	0.301	0.355	1 : 1.18
6	Cat 4	2M	1.095	0.719	1.52 : 1
7 and 8	Cat 4	3M	0.553	0.353	1.57 : 1
3	An 1	pH 0.5	0.132	0.253	1 : 1.92
4	An 2	2M	0.422	0.510	1 : 1.21

4½% cross-linked Zeo Karb 225 (H form).

Column size 1.2 x 50 cms.

Eluting agent HNO_3 Composition of solution :

7.5% P_2O_5 1.25% Cr_2O_3 91.25% H_2O

25 mls. solution used. Rate of flow 50-55 mls. per hour.

Solution subsequently passed through De-acidite FF (SO_4 form)

TABLE 42a

Ion Exchange Chromatography - Gradient elution.

Elucidation of Complexes (i)

Solution taken	Complexes in order of elution	Vo*	C_1*		m.moles Cr found	m.moles PO_4 found	Ratio Cr : PO_4
			NH_4NO_3	HNO_3			
1 - 15	C 1	500 mls	1 N	-	0.054	0.109	1 : 2.02
5 - 15	C 1	575 "	0.66 N	-	0.196	0.406	1 : 2.07
	C 2	"	0.66 N	-	0.077	0.111	1 : 1.45
	C 3	"	0.66 N	4 N	0.065	0.088	1 : 1.36
10 - 15	C 1	580 "	0.66 N	-	0.182	0.364	1 : 2.00
	C 2	"	0.66 N	-	0.138	0.201	1 : 1.46
	C 3	"	0.66 N	-	0.112	0.156	1 : 1.38
	C 4	"	0.66 N	4 N	0.049	0.060	1 : 1.22
	C 7	"	-	8 M	0.101	0.051	1.99 : 1

2% cross-linked Zeo Karb 225 (H form). Column size 1.2 x 33 cms.

Eluting agents (i) NH_4NO_3. (ii) NH_4NO_3, HNO_3 mixture.

Results are given only of the main portion of the eluted complex.

½ gm. samples of resin shaken with 10 gms. of fully aged solution for 2 hours, washed phosphate free on a sintered glass crucible and loaded as a slurry on to the prepared column in the H form.

* See equation on page 27.

TABLE 42b

Ion Exchange Chromatography - Gradient elution.

Elucidation of Complexes (ii)

Solution taken	Complexes in order of elution	Vo*	C_1		m.moles Cr found	m.moles PO_4 found	Ratio Cr : PO_4
			NH_4NO_3	HNO_3			
15 - 15	C 1	580 mls	0.66N	-	0.073	0.179	1 : 2.47
"	C 2	"	0.66N	-	0.071	0.102	1 : 1.45
"	C 3	"	0.66N	-	0.038	0.050	1 : 1.33
"	C 4	"	0.66N	4N	0.106	-	1 : 1.25$^+$
"	C 5	"	0.66N	4N	0.144	0.160	1.: 1.12
"	C 6	"	0.66N	4N	0.150	0.152	1 : 1.01
20 - 15	C 1	580 mls	0.66N	-	0.032	0.064	1 : 1.99
"	C 2	"	0.66N	-	0.087	0.140	1 : 1.61
"	C 3	"	0.66N	-	0.026	0.035	1 : 1.33
"	C 4	"	0.66N	4N	DID	NOT	APPEAR
"	C 5	"	0.66N	4N	0.258	0.295	1 : 1.14
"	C 6	"	0.66N	4N	0.177	0.178	1 : 1

As for Table 42a

+ by inference.

TABLE 43

Ion Exchange Chromatography - Gradient elution.

Calculated Values of concentration

Vo mls	Volume delivered	C when C_1 = 0.66	C when C_1 = 1.0N	C when C_1 = 4.0N
500	62.5 mls.	0.075	0.113	0.452
"	125 mls.	0.146	0.221	0.88
"	250 mls.	0.260	0.394	1.58
"	375 mls.	0.348	0.528	2.11
"	500 mls.	0.417	0.632	2.53
"	625 mls.	0.471	0.713	2.85
"	750 mls.	0.513	0.777	3.11
"	1000 mls.	0.571	0.865	3.46
600	60 mls.	0.059	0.092	0.368
"	120 mls.	0.120	0.181	0.724
"	240 mls.	0.220	0.330	1.32
"	360 mls.	0.300	0.450	1.78
"	540 mls.	0.391	0.593	2.37
"	750 mls.	0.471	0.713	2.85
"	900 mls.	0.513	0.777	3.11
"	1200 mls.	0.571	0.865	3.46

SECTION G.

BIBLIOGRAPHY OF PART 3.

(1) Salmon, Revs. Pure Appl. Chem., 1956, 6, 24.

(2) Jameson and Salmon, J.C.S., 1955, 360.

(3) Genge and Salmon, J.C.S., 1957, 256.

(4) Bissett, 1959, unpublished work.

PART 4

DISCUSSION OF RESULTS

SECTION A.

PHASE DIAGRAM RESULTS

The chromium (111) phosphoric acid system at 70°C. has been studied for the range of solutions extending up to 66% of phosphoric oxide, i.e. in that region of the system readily studied by the use of AnalaR syrupy phosphoric acid. Samples containing more than 20% (approximately) consistently assumed a gel-like appearance and subsequent filtration resulted in the isolation of one phase only.

Comparing the results of the phase diagram at 70°C. with those obtained by Jameson and Salmon (1) for the same system at 40°C. (See Figs.5 and 12), it may be seen that the system is completely altered.

The solid phase over the range for which results have been obtained is a light green amorphous flocculent precipitate.

The parallel tie lines could be due to one or more of the following reasons :

(1) Metastable equilibria.

(2) Solid-solutions formation.

(3) Occurrence of a solid phase $Cr_2O_3 . P_2O_5 \, x \, H_2O$ which has adsorbed more or less phosphoric acid according to the composition of the liquid phase.

(4) The solid phase is acting as an ion-exchange material.

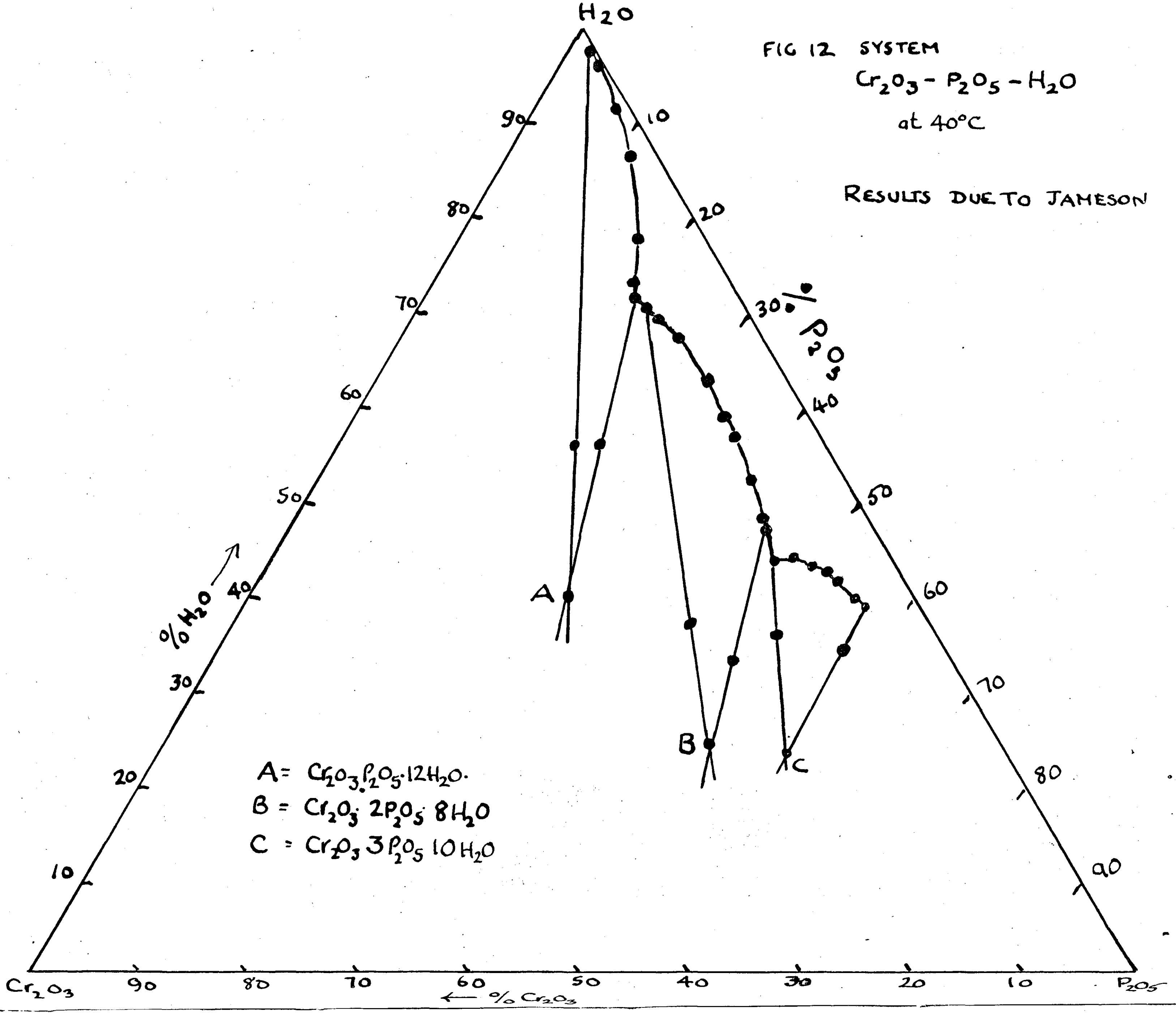


FIG 12 SYSTEM $Cr_2O_3 - P_2O_5 - H_2O$ at 40°C

RESULTS DUE TO JAMESON

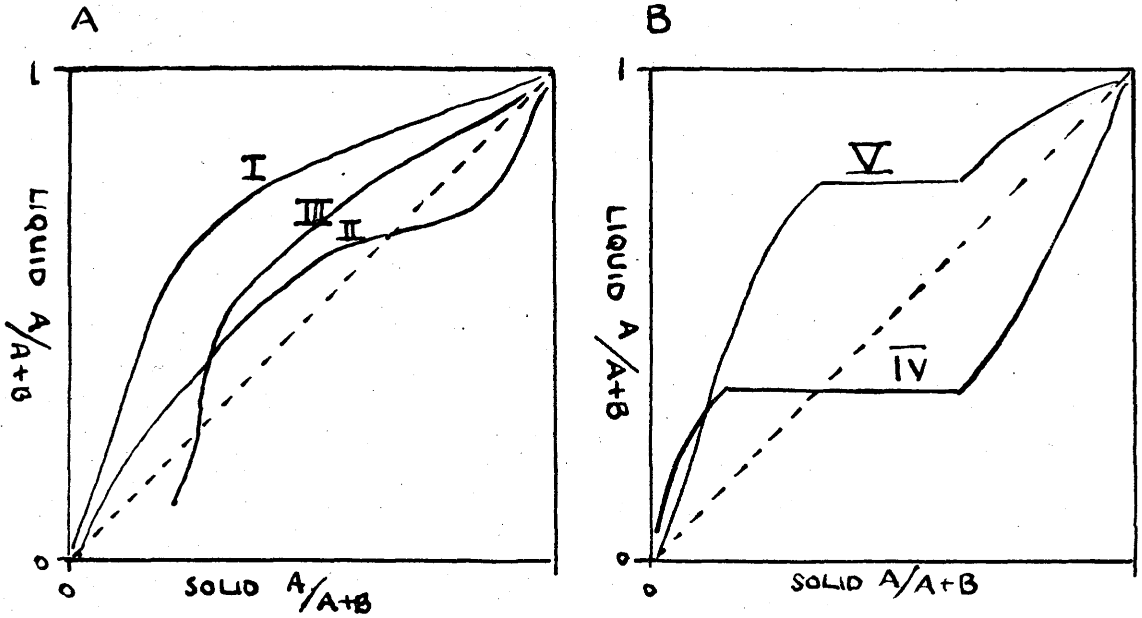
(1) The system is metastable.

In the system Fe_2O_3. P_2O_5. H_2O at 25°C Cameron and Bell (2), Carter and Hartshorne (3) and Salmon(4) found similar tie lines which persisted up to 20% of phosphoric oxide but later work by Jameson and Salmon (5) showed that such tie lines were but one of a number of stages that the system went through before stable equilibrium was attained. However, the time taken to reach equilibrium at 25°C. was some 10 - 15 weeks after the experiment was commenced. In the present work the suspensions were stirred frequently and it might be assumed that at 70°C. equilibrium would be reached much more rapidly. The fact that two series of tubes, analysed after widely differing periods, gave similar results and a smooth solubility isotherm must be interpreted as implying that equilibrium had in fact been attained.

(2) The formation of solid solutions between the green tertiary phosphate and one or more acid components.

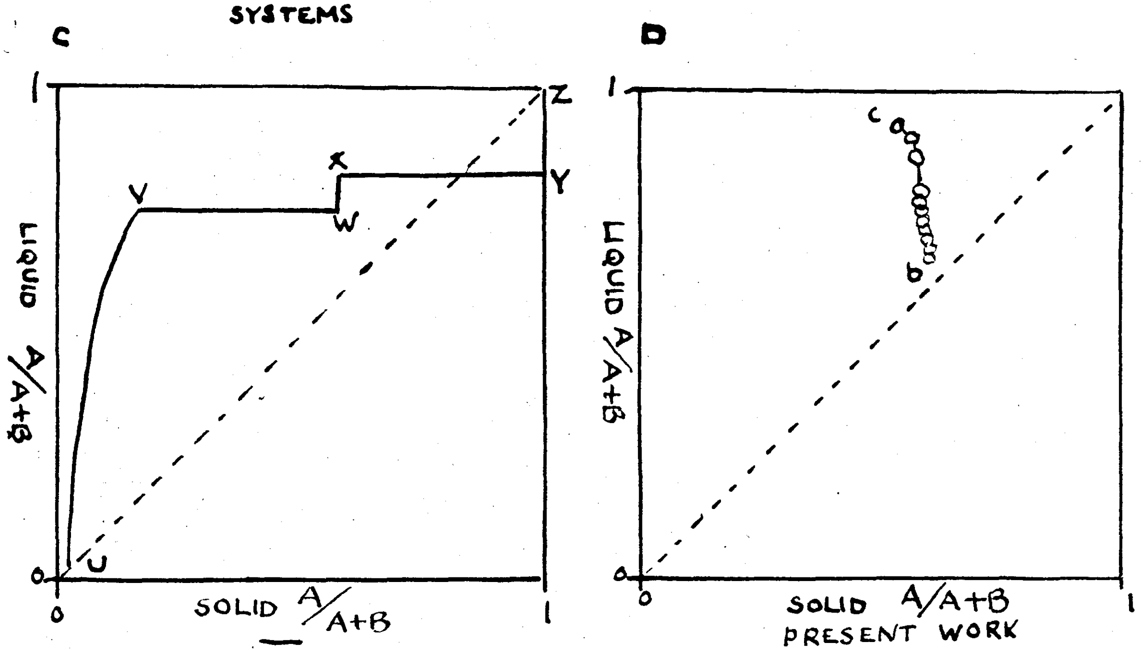
The system has parallel tie lines between the limits of 1 : 1 and 1 : 1.5 for the mole ratio $Cr_2O_3 : P_2O_5$ and over this range the solid phase does not correspond to any stoichiometric compound. Solid solutions have been classified by Roozeboom (6) as being of five different types where the system consists of two salts and water. Three of the five types are concerned with complete miscibility of the solid components and the other two refer to systems in which the miscibility is incomplete and in which there are always two series of solid solutions. He distinguishes between each of the five by means of the so-called "Roozeboom" diagram, which is a plot

FIG 13 ROOZEBOOM DIAGRAMS FOR DIFFERENT TERNARY SYSTEMS



COMPLETELY MISCIBLE SYSTEMS

INCOMPLETELY MISCIBLE SYSTEMS



TYPE VI

PRESENT WORK

A = P_2O_5

B = Cr_2O_3

of the % A in liquid (ignoring water content,(i.e. $\frac{A}{A + B}$ x 100%)where A and B are the two salts concerned) against % A in solid. Figs.13A and B give the Roozeboom diagram for each of the five types of solid solutions and the curve bc in Fig. 13D gives the diagram for the present results where we have B= Cr_2O_3 A = P_2O_5. These results indicate that the present system can not be described in this way.

(3) That a solid phase $Cr_2O_3 \cdot P_2O_5 \times H_2O$ has adsorbed more or less phosphoric acid according to the composition of the liquid phase.

A sixth type of solid solution not included in the above classification has been described by Ricci (7) in which the solid solution is of varying composition with the varying composition of the liquid with which it is in equilibrium. When plotted on a Roozeboom diagram it has the shape as indicated in curve uvw xyz in Fig.13C. Thus while the present results have a certain resemblance to this sixth type of solid solution, it does not appear to be the complete explanation. Carter and Hartshorne (3) interpret the parallel tie line system in the $Fe_2O_3.P_2O_5.$ H_2O system by assuming that the compound $Fe_2O_3P_2O_5.x\ H_2O$ adsorbed more or less acid according to the concentration in the liquid phase. If such adsorption is pictured as being physical it would depend on the surface area of the solid and it is difficult to see how this would consistently lead to parallel tie lines.

(4) The system is acting as an ion-exchange material

Jameson and Salmon (5) interpreted the parallel tie lines of the

$Fe_2O_3.P_2O_5.H_2O$ system at 25°C. as being due to the fact that $H_6[Fe(PO_4)_3]$, which separated out initially, acted as a cation exchanger, That, as the composition of the liquid in contact with the solid changed so the hydrogen ions could be exchanged for ferric ions or for complex ferric phosphate cations.

The present system could be interpreted in a similar manner. The ratio of $Cr_2O_3 : P_2O_5$ i.e. of $Cr : PO_4$ in the present system of the solid materials lies between 1 : 1 and 1 : 1.5 and an exchange process using the complexes which have already been isolated could be envisaged as follows :

$$[Cr\,HPO_4]_3\,[Cr(PO_4)_2] \rightleftharpoons [Cr(H_2PO_4)]_3\,[Cr(PO_4)_2]_2$$

$Cr: PO_4$ 4 : 5 5 : 7

$$\rightleftharpoons [Cr(H_2PO_4)_2]_3\,[Cr(PO_4)_2]$$

1 : 2

or possibly :

$$[Cr(HPO_4)_3]_3\,[Cr(HPO_4)_3] \rightleftharpoons [Cr(H_2PO_4)]_3\,[Cr(HPO_4)_3]_2$$

2 : 3 5 : 9

$$\rightleftharpoons [Cr(H_2PO_4)_2]_3\,[Cr(HPO_4)_3]$$

4 : 9

The ratio of $Cr : PO_4$ in the solid phase being influenced by there being present a mixture of the possible cations in conjunction with the anions $[Cr(PO_4)_2]^{3-}$ and $[Cr(HPO_4)_3]^{3-}$.

But there seem to be two good reasons why this explanation is probably not completely correct.

(i) The marked difference in the nature of the phase diagram at 40°C. and at 70°C. probably implies that the possible solid phases as suggested for the system at 40°C. are not those that exist at 70°.

(ii) The knowledge that the ion exchange data at 70° infers the existence of other complexes apart from the simple mononuclear ones used in the above picture.

A recent note by Kraus and Phillips (8) suggested that the precipitate resulting from the addition of phosphoric acid to a zirconium (IV) solution when dried and ground up showed certain cation exchange properties. Since that time a number of papers have appeared suggesting that on the one hand a number of hydrous oxides show exchange properties, e.g. Kraus and Phillips (9), Amphlett, McDonald and Redman (10) and Anderson (11). Among the oxides investigated by these workers were those of zirconium, thorium, tin (IV) and titanium (IV) and those of certain tervalent metals, notably chromium, iron, and aluminium. On the other hand certain phosphates and tungstates have also been investigated by Amphlett, McDonald and Redman (12) and these have been shown to behave in a similar fashion to weakly acidic polyfunctional cation exchangers. The solid material was prepared by the addition of phosphoric acid to a zirconium (IV) solution, drying the precipitate, grinding, and sieving. After treatment in this way the material was quite stable. No investigation of the structure of these phosphates was made but it was suggested that the solid material consisted of zirconium atoms linked by bridging oxygen atoms. To the zirconium atoms acid phosphate groups were attached and these had replaceable H ions for cation exchange. As it was suspected that the solid material in the present system was behaving as an ion exchanger, it was decided to test this suspicion in a semi-quantitative manner. The results are given in the accompanying table.

TABLE 44

Behaviour of solid material from phase diagram study at 70°C. as an ion exchanger.

Treated with a dilute solution of AnalaR chrome alum.

	Cr sorbed	initial pH	Final pH of soln.
Sample 1	0.014 m/moles	3.37	2.87
Sample 2	0.046 m/moles	3.44	1.94

Sample 2 was subsequently treated with nitric acid (pH 1.5).

It was observed that $[Cr(H_2O)_6]^{3+}$ was desorbed.

Finally Sample 2 was treated with 250 ml. 0.1M NaCl.

The released H ions were titrated with standard NaOH.

Capacity of Sample 2 = 0.18 m.moles ∴ moles/equiv.chromium = 0.25.

In both samples no phosphate was detected in the effluent.

In the present system any explanation must account for :

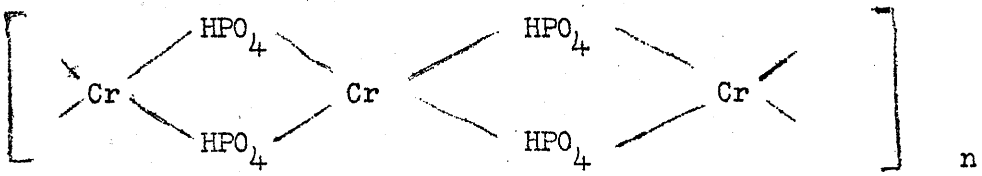
(i) The undoubted ion-exchange character of the solid.

(ii) The completely different phase diagram results at 70°C, when compared with those obtained at 40°C.

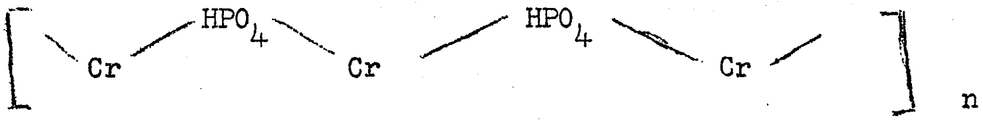
The behaviour of some ter- and tetra-valent metal hydroxides and hydrous oxides and of some phosphates and tungstates of tetravalent metals as ion exchangers would suggest that the present system is similar.

It is suggested that the solid material is a polymeric network of one of the following types :

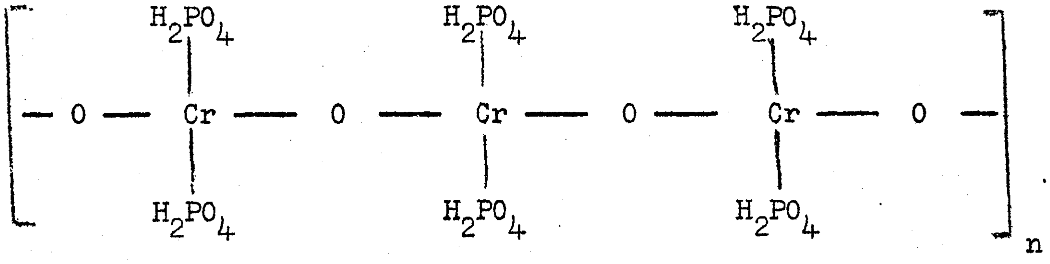
Type 1.



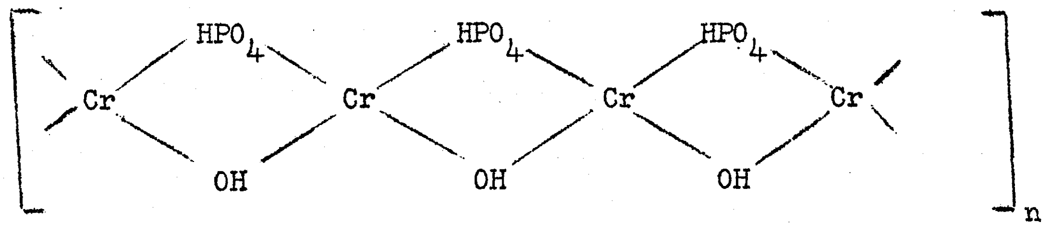
Type 2.



Type 3.



Type 4.



in which the hydrogens of the acid phosphate groups are replaceable by other cations, and in which the chains may easily be branched to build up a three-dimensional network. The terminal groups would probably be $-H_2PO_4$ groups.

In deciding whether any one of these types is the most likely to occur, there are two further factors to be borne in mind :

(i) Chromium (111) does not form basic compounds of the type Cr OX except under near neutral or alkaline conditions and under the influence of high temperatures. On the other hand Zr(IV), Hf(IV), and Bi(111) all form well known series of oxy compounds where the probable structure in the solid state involves oxygen bridging. It seems unlikely that there is an exact parallel between the structure of the solid material isolated under the present conditions and that suggested for the zirconium and hafnium phosphate material by Amphlett et al (12).

(ii) If, as will be discussed more fully later, there is a connection between the structure of complexes found in a saturated solution in contact with the solid material, then the cationic complexes which have so far been isolated and identified in the present study would tend to support the structure as being either Type 1 or Type 2. As there is a predominance of cationic complexes, it would also, on the same grounds, suggest that Types 3 and 4 were unlikely since they could only be envisaged as giving rise to neutral or anionic complexes.

The conclusions which may be drawn as to the nature of the solid phase isolated at 70°C. are that the material is behaving as an ion exchange material and its probable structure belongs either to Type 1 or Type 2.

SECTION B.

BATCH ION EXCHANGE STUDIES

(i) Desorption of Cr(111) Species

Discussion of Series A (i) and A (ii)

In Part 1, Section C a brief discussion of the significance of batch ion exchange studies in which the metal form of the resin is allowed to equilibriate with different acids at different pH values was given.
It is possible to compare in a semiquantitative manner the extent to which complex formation in solution occurs between the metal cation and the anion of the acid. In a set of experiments at a given pH and involving a series of acids it follows that the anion concentration is reasonably constant - since in the range of pH values under consideration the ionisation of all acids, even di- and tri- basic, may be represented to a first approximation as :

$$HA \rightleftharpoons H^+ + A^- \qquad \text{------} \qquad (1)$$

Taking this equilibrium in conjunction with the other equilibria in the system acid - metal form resin - namely :-

$$\overline{Cr^{3+}} + 3H^+ \rightleftharpoons Cr^{3+} + \overline{3H^+} \qquad \text{------} \qquad (2)$$

$$Cr^{3+} + pA^{x-} \rightleftharpoons \left[Cr\ A_p\right]^{y-} \qquad \text{------} \qquad (3)$$

it may be deduced that at a given pH value any increase in the amount of metal removed from the resin at equilibrium as compared with the amount removed by an acid whose anion is known not to complex to any significant extent with the metal, is a reflection of the tendency of A to form complexes with chromium (111) ions at that pH.

The first conclusion that may be drawn from the experiments in which the hexaaquo chromium (111) form of the resin was in contact with various acids at different pH values is that at low pH's some complexing is occurring between $[Cr(H_2O)_6]^{3+}$ ions and each of the three acids, sulphuric, nitric and hydrochloric but that little is taking place with phosphoric acid,as the curve follows closely to that of perchloric acid where it is known that little or no complexing is occurring. In addition it was observed that the solution remained violet in colour. This result is opposite to what might be expected until it is recalled that the attainment of equilibrium in the system chromium (111) - phosphoric acid at 25°C. is very slow. Thus the time of contact of seven days of the metal form of the resin with phosphoric acid is too short to allow the system to come to equilibrium.

Plane and Taube (13) make the observation in studies of the kinetics in the system $[Cr(H_2O)_6]^{3+} - H_2O$ that the provision of an anion in which electron transfer is possible accelerates the rate of exchange of bound aquo groups and presumably also complex formation. A similar system to the present one is that of chromium (111) - arsenic acid and this has been studied at 25°C. It is a system in which electron transfer is very likely and in fact complex formation takes place rapidly in solution.

Whilst the complexing power of arsenic acid is lower than phosphoric acid, the results give a guide as to the amount of complexing to be expected with chromium (111) - phosphoric acid at 25°C at equilibrium - a further indication that this is so is provided by the similarity of the results at 70°C. The results due to Lukaszewski, Salmon and the author (14) are given in the following table.

TABLE 45

Desorption of $[Cr(H_2O)_6]^{3+}$ from metal form Zeo Karb 225 by phosphoric and arsenic acids

	H_3AsO_4		H_3PO_4	
	pH	%Cr removed	pH	%Cr removed
25°C	0.02	72.5	0.01	54.6
	0.28	68.0	0.24	42.0
	0.53	66.9	0.36	36.0
	0.82	50.5	0.50	32.4
	1.00	36.0	0.76	15.0
	1.30	11.5	0.92	9.5
	1.50	6.0	1.27	0.0
70°C	0.02	82.5	0.02	90.0
	0.28	76.5	0.06	87.5
	0.54	70.3	0.28	78.5
	0.82	58.0	0.50	73.5
	1.00	31.5	0.76	56.5
	1.25	6.5	0.84	49.0
	1.44	2.9	1.00	30.0
	1.92	0.0	1.10	17.5
			1.27	3.5

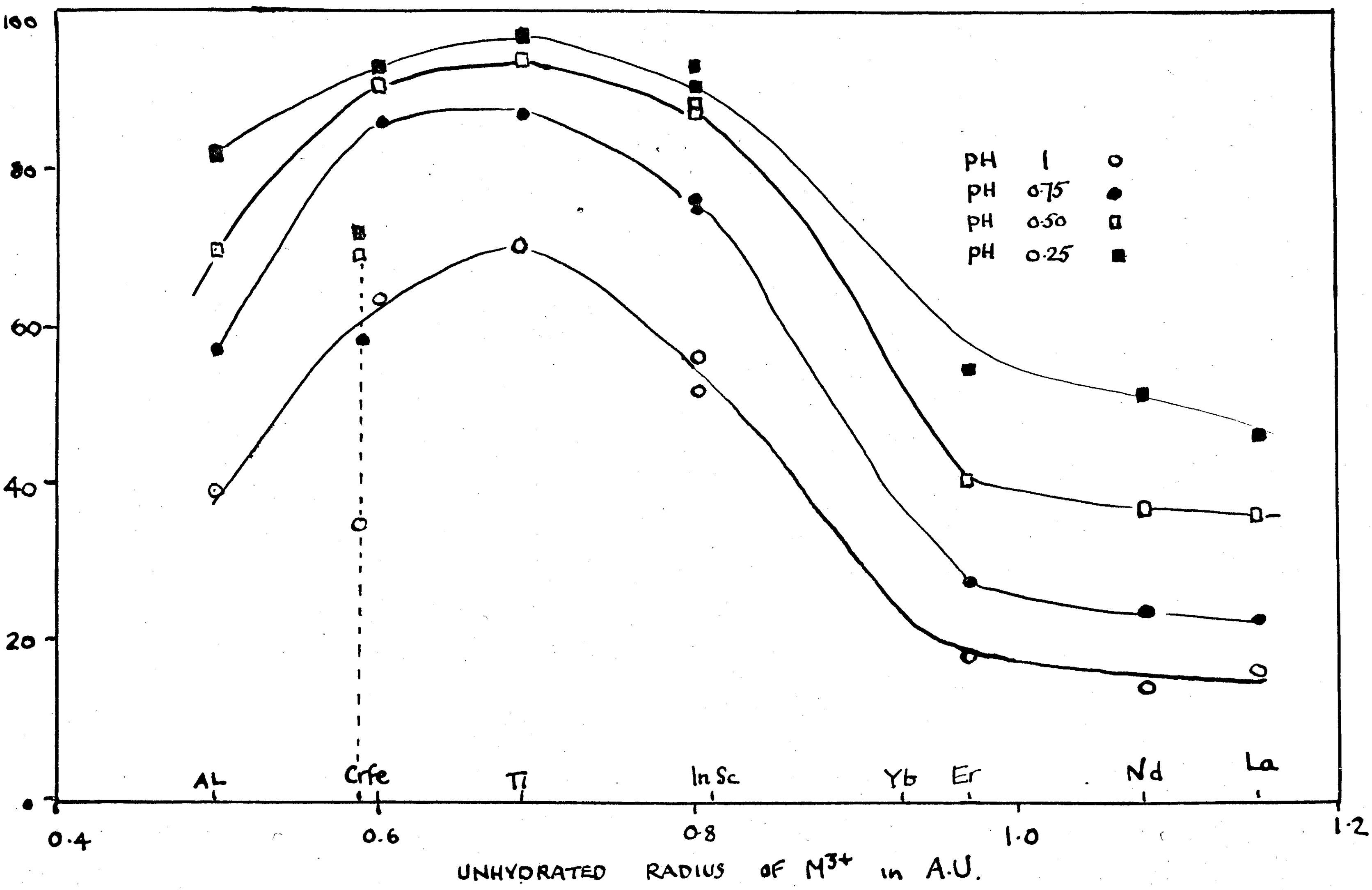
From the table it is possible to predict that the probable % Cr that would be removed from the resin under equilibrium conditions at room temperature by phosphoric acid would be some 2% greater than the amount removed by arsenic acid under similar condition. Thus for the pH values 0.25, 0.50, 0.75, 1.00, the predicted values for the % removal of chromium (111) from the resin are 72%, 69½%. 58% and 34½% respectively. If these results are plotted along with the results for other tervalent metals on the graph of unhydrated ionic radius (A°) against % metal removed at equilibrium (Genge and Salmon (15)), it is seen (Fig.14) that the results for chromium (111) do not fit into the picture at all.

It is possible to explain this as follows :

(i) In this paper Genge and Salmon (15) state that the metals considered are those which are likely to form complexes by use of outer d orbitals, that is, by sp^3d^2 hybridisation but in the case of chromium, it is to be expected that the bonding involved will use inner d orbitals, that is, by $d\gamma^2sp^3$ hybridisation, since these are readily available - Cr^{3+} having an electronic configuration of $3d_\varepsilon^3$ and spin pairing being unnecessary.

(ii)The fact that chromium does not readily form a trischelate complex with phosphate but only a bischelate (Jameson and Salmon (1)) is in contrast to the behaviour of aluminium and iron (111) which both readily form trischelates (see Jameson and Salmon (5) and (16)) probably exerts an additional effect.

FIG 14 THE REMOVAL OF VARIOUS METALS FROM ZEOKARB 225 WITH PHOSPHORIC ACID SHOWING THE ANOMALOUS POSITION OF CR



The second conclusion that may be drawn relates to a comparison of the results of series A(1) and A(2). If a comparison is made not of the complexing power of the anions of the acids used but between the relative affinities of $\left[Cr(H_2O)_6\right]^{3+}$ and $\left[Cr(phos)\right]^{x+}$ for the resin, it is easy to see that the chromium complexes are held much less strongly, e.g. for nitric acid at pH 0.75 the % metal removed in the case of the hexaaquo form of the resin is 12.5% whilst for the complex form of the resin the figure is 30.7%. As has been suggested in Part 3, Section E, this difference in affinity may be utilised in the separation of the chromium (111) complex cations from hexaäquo chromium (111) ions and a description has been given of this achievement.

Discussion of Series B.

In Part 3, Section C a description was given of the batch studies on chromium-phosphate form of the cation exchanger with nitric acid and ammonium nitrate. The reason for carrying out this series of experiments was outlined briefly. This was to investigate one possible mechanism of the phenomenon referred to as phosphate drift and to see whether the problems associated with it could be overcome in any way.

The phenomenon was observed in the early attempts at achieving a chromatographic separation of the cationic complexes. It was found that on eluting the partially loaded column with dilute nitric acid, there occurred a surge of phosphate so that in the early stages of the chromatographic development there was always a large excess of phosphate over that which could be expected to be found in a cationic complex with chromium. This could only be interpreted as being free phosphate which was not complexed. It was also found that the later complexes to be eluted were held very tenaciously by the resin and that the Cr : PO_4 ratio was high, that is, little phosphate appeared to be associated with the chromium.

The phenomenon could presumably arise from one or the other or both of the following ways :

(1) The aged solution with which a column is loaded consists of anionic and cationic complexes together with phosphate ions and unionized phosphoric acid. It is possible not only for the cationic complexes to be sorbed on the column of Zeo Karb in the H form but also for any unionized phosphoric acid to be held in the resin by Van der Waal's forces. Similar effects have been described by Davies and Owen (17) and Reichenberg and Wall (18) for organic compounds and in particular for organic acids of comparable strength to that of phosphoric acid. In any two phases in contact with one another, there will always be a distribution of an unionized soluble compound between the two phases - in general favouring one phase more than the other. It seems likely that unionized phosphoric acid will tend to be held in the resin phase rather than in the liquid in contact with it. Also, as the resin immediately below the zone that is sorbing the cationic complexes is in the H form, the equilibrium concentration of the ionized phosphoric acid will be very much lower than

in the external solution (i.e. the acid is behaving essentially as a non-electrolyte).

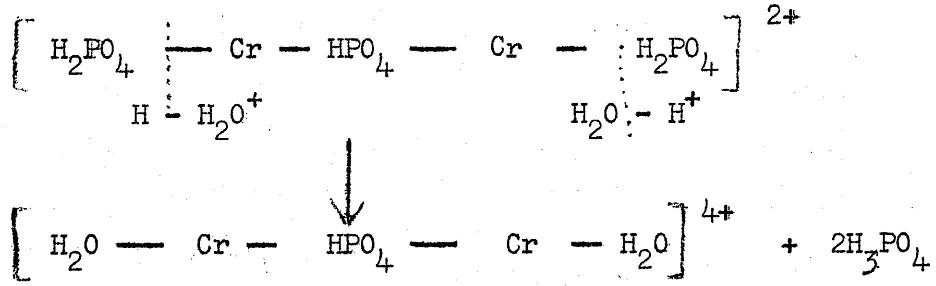
That this effect is operating in the column work is apparent by the improvement in results which was achieved when the cationic complexes were sorbed on the resin as in a batch experiment and then this resin, thoroughly washed, was loaded as a slurry on to the top of the column of Zeo Karb 225 already in the H form.

(2) The second way in which the phosphate drift might be interpreted is that certain of the complexes are not resistant to attack by H^+ ions and either in the resin phase or in the solution used to elute the resin the complexes are broken down to a certain extent. Initially with the resin in the H form, the concentration in the resin beads is of the order of 5N in acid, so that as the cationic complexes begin to enter they are encountering an extremely acidic medium, and even when 4/5ths resin has been converted to the complex form, the acidity is still of the order of 1N.

It is possible to picture the breakdown of a complex of the type :

$$\left[H_2PO_4 — Cr — HPO_4 — Cr — H_2PO_4 \right]^{2+}$$

(which is the probable structure of one of the complexes found in the present system) as follows :



$$\begin{array}{c} \left[\underset{H\,\vdots\,-\,H_2O^{+}}{H_2PO_4\,\vdots}— Cr — HPO_4 — Cr — \underset{H_2O\,\vdots\,-\,H^{+}}{\vdots\,H_2PO_4} \right]^{2+} \\ \downarrow \\ \left[H_2O — Cr — HPO_4 — Cr — H_2O \right]^{4+} + 2H_3PO_4 \end{array}$$

The undissociated H_3PO_4 would be held in the resin as explained in mechanism (1) above, and on subsequent elution on a column would appear associated with the most lightly held complex. In a batch experiment the phosphate would come off under equilibrium conditions and the ratio of PO_4 : Cr in the solution in equilibrium with the resin would be high. The batch studies that were carried out with the complex form of the resin and nitric acid of different pH values show that at a pH of 1.5 the ratio of PO_4 : Cr eluted is greater than 4 : 1. At higher acidity more of the cationic complexes are desorbed and consequently the ratio of PO_4 : Cr falls. However, it is of interest to note that the increment $[PO_4] - [Cr]$ is approximately constant for each set of experiments, indicating that the effect is probably uniform over the range of pH's studied.

TABLE 46

1st set		2nd set	
pH	$[PO_4] - [Cr]$		$[PO_4] - [Cr]$
1.50	0.026		0.046
1.25	0.027		0.049
1.00	0.035		0.060
0.75	0.039		0.072
0.50	0.028		0.070
0.25	0.064		0.081
0.03	0.036		0.074

On the other hand the retention figures show that the ratio of PO_4 : Cr falls to around 0.75 : 1 or 3 : 4, which would suggest that the complex remaining sorbed on the column is of the type:

$$\left[H_2O - Cr - HPO_4 - Cr - HPO_4 - Cr - HPO_4 - Cr - H_2O \right]^{6+}$$

or alternatively the complexes remaining on the column could be a mixture of two or more of the type:

$$\left[H_2O - Cr - HPO_4 - Cr - H_2O \right]^{4+} \quad \text{together with} \quad \left[Cr - H_2PO_4 \right]^{2+}$$

The conclusion that may be drawn from these results is that at least some breakdown of complexes is occurring, probably under the influence of the H ions in solution. If this is in fact the case, then equilibrium batch studies with a solution of a salt rather than an acid should show a significant difference. The studies with ammonium nitrate show that this is so. The ratio of PO_4 : Cr in the solution at equilibrium is at most 1.92 : 1 and from other work it is known that the least strongly held complex in all the solutions studied has the ratio Cr : PO_4 of 1 : 2, i.e., it is $\left[Cr\ (H_2PO_4)_2 \right]^{+}$. Thus the ratio is at least a likely one. The ratio of PO_4 : Cr of the retained portion of the sorbed complexes at equilibrium is about 1 : 1 - allowing for the experimental difficulties of the analysis of chromium in the presence of a large amount of ammonium nitrate. Thus the inference which may be drawn is that the phosphate drift is attributable in part to the action of H ions from the solution effecting some breakdown of one or more of the complex species sorbed on the resin. These results make clear why no really useful data could be gained from the chromatographic separation of complex species on a column of Zeo Karb 225 using nitric acid as the eluting agent.

SECTION C

BATCH ION EXCHANGE STUDIES

(ii) Sorption of Cr(111) Species

From saturated solutions prepared by aging at 70°C.

Jameson and Salmon (1) commented on the fact that care was needed in the interpretation of the results of batch studies on cationic complexes from chromium (111) - phosphoric acid solutions aged at 40°C. Among the reasons quoted are the following :

(1) The complexes were often difficult to remove from the resin - once sorbed.

(2) The time of aging of the solution seemed to exert a marked effect on the uptake of chromium ahd phosphate on the resin.

(3) The probability that the size of the complexes prevents occupancy of all the available exchange sites in the resin beads.

(4) The time of contact of the solution with the resin affects the amount of chromium and phosphate sorbed.

(1) and (2) have already been discussed and the present work in the main was carried out at 70°C. so that fully aged solutions could be used more readily.

Discussion on factor (3)

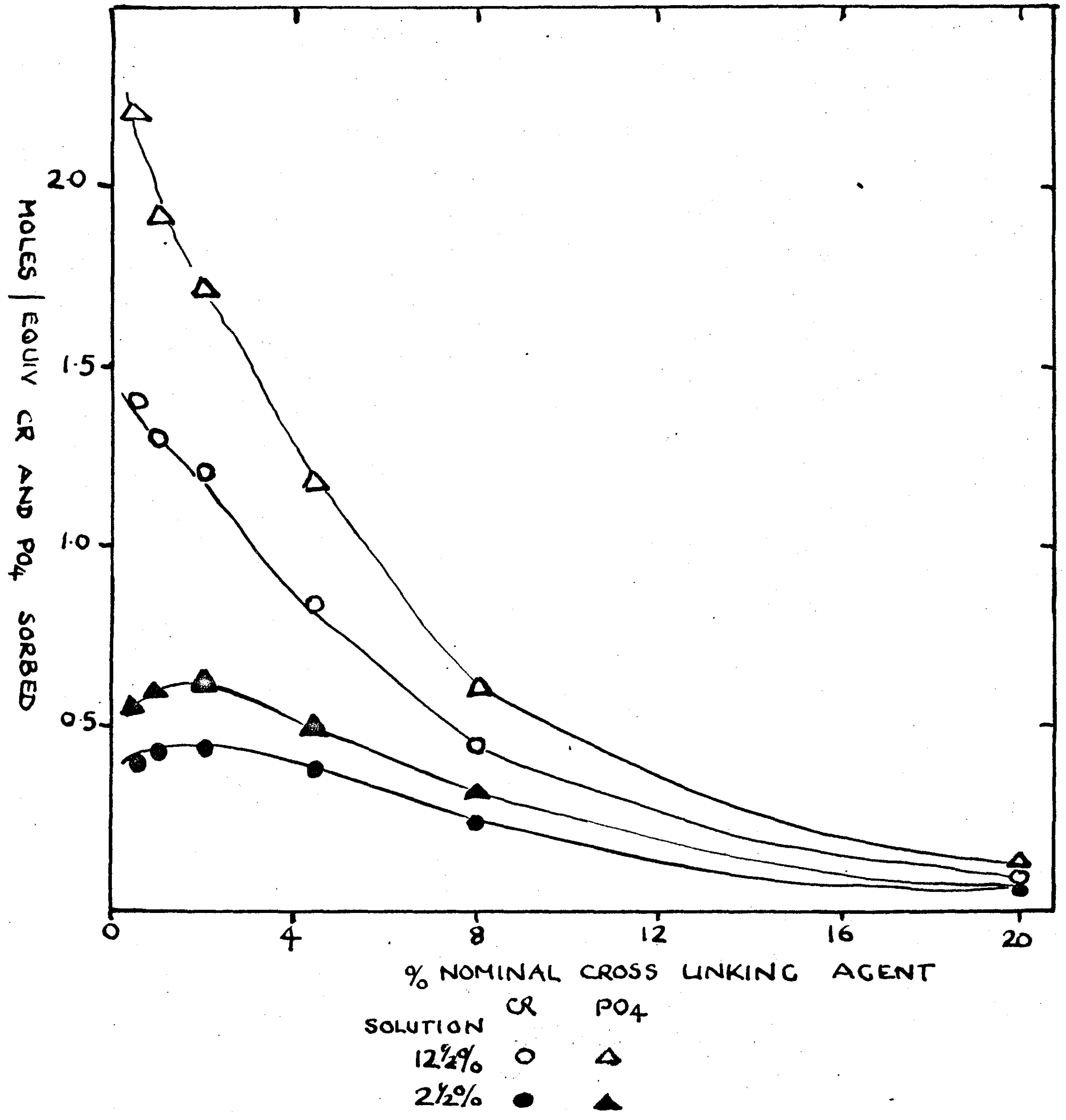
If, as seemed probable, some steric effects are coming into play, then using resins of varying degrees of cross-linking should result in the uptake of varying amounts of chromium and phosphate. If a number of complexes are involved, then the ratio of chromium : phosphate in the resin will vary also. Taking the results of Tables 17 - 22, in which a range of resins were allowed to come in contact with saturated solutions containing from 2½% - 15% P_2O_5 for two hours, it will be seen (see Fig. 15) that as the degree of cross-linking increases so there is a marked fall in the amount of chromium and phosphate taken up per equivalent of exchanger The amount taken up on a 20% cross-linked resin is only some 10% or less of that which is sorbed on the ½, 1, or 2% cross-linked resin.

A comparison of the figures given in these tables and relevant figures from later tables indicate that the following points are noteworthy.

(1) The amount of chromium and phosphate sorbed on the resin falls markedly with increase in cross-linking (or corresponding decrease in weight swelling), indicating an ionic sieve effect. The figures for the uptake of $\left[Cr(H_2O)_6\right]^{3+}$ as given in Table 15 indicate that, whilst there is some ionic sieve effect even for the simple hexaäquo ion, nevertheless the extent to which the complex ions are excluded is such as to indicate that the ions involved are relatively large.

(2) The amount sorbed on the lightly cross-linked resin is considerably less for the solutions containing less P_2O_5 and correspondingly lower amounts of chromium. The most likely reason for this is not that the complexes in the more dilute solutions are larger but that the charge on the ions has a general tendency to be higher as the pH is higher.(If the complex has +1 charge then at saturation 1 mole/equiv. will be sorbed,

FIG 15 UPTAKE OF CR AND PO4 FROM AGED SOLUTIONS BY ZEOKARB OF DIFFERENT CROSS LINKING



for a complex having a charge of +2 at saturation 0.5 mole/equiv. will be sorbed, etc.) The other possible reason is that the effective 'pressure' of the ions is less. The actual concentration of cationic complexes in the more dilute solutions is known (see e.g. Tables 36a and b) to be considerably lower than in the more concentrated solutions, and at equilibrium one would expect a smaller amount to be sorbed.

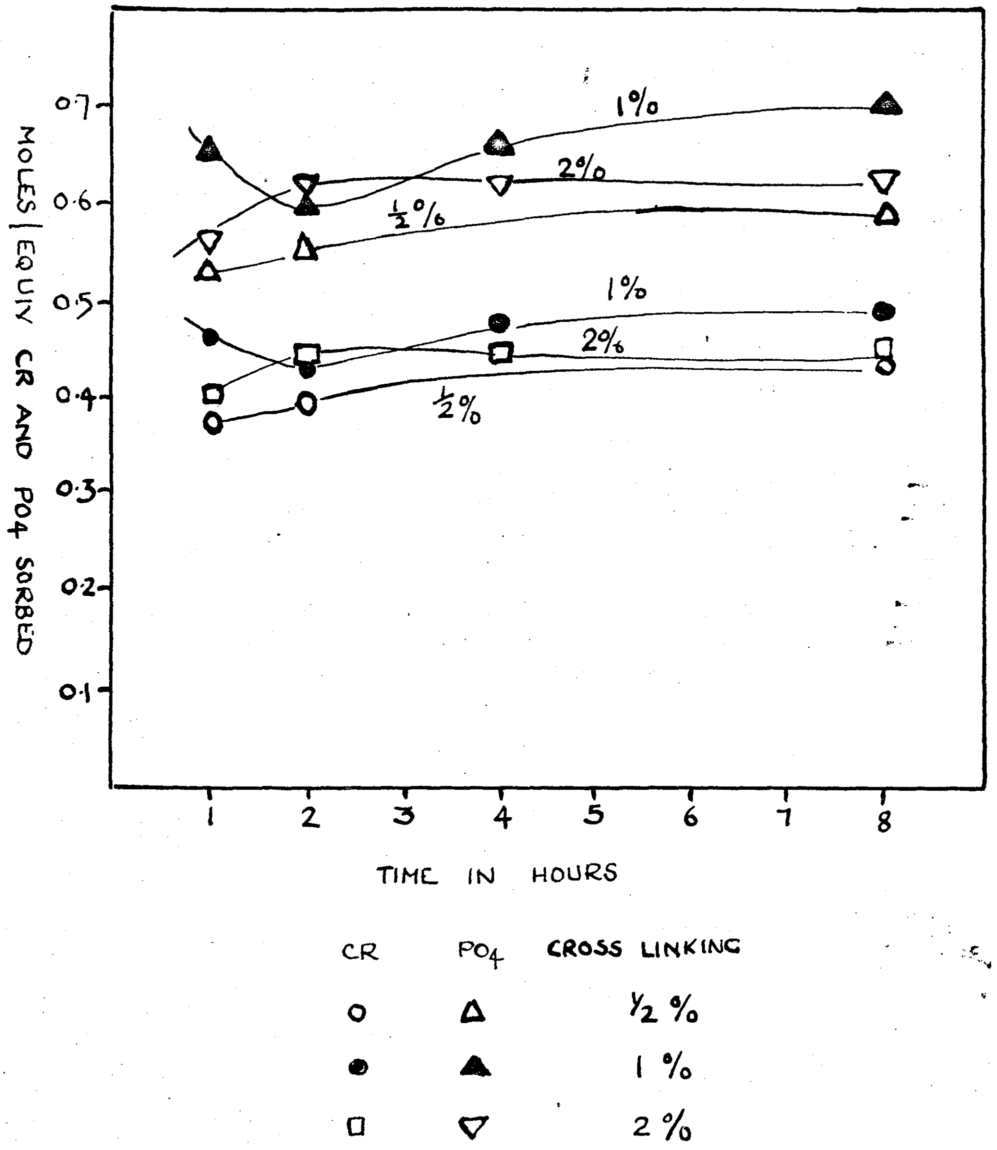
(3) The ratios of Cr : PO_4 are also given in the results but it is hard to discern any significant trend in the ratios with increase in cross-linking. The values for those resins which take up very little chromium and phosphate are of necessity not very accurate and probably are not more accurate than 0.1 unit. If anything, it appears that for the 12½% and 15% P_2O_5 solutions, there is a fall in the ratio of Cr : PO_4 with increased cross-linking whilst for the other saturated solutions, the ratio tends to rise with increase in cross-linking.

(4) In certain of the results for the ½% and the 1% cross-linked resins (see Fig. 16 for one example), the amount of chromium and phosphate sorbed is less per equivalent than the amount sorbed on the 2% cross-linked resin. This fall in uptake is probably due to the fact that all the exchange sites are not used since they are not in close enough proximity for them all to be utilised by a large ion having a number of charged centres.

Discussion on factor (4)

In order to discuss the effects of varying the time of contact of resin with fully aged solutions, the experiments carried out may be conveniently divided as follows :

FIG 16 COMPARISON OF UPTAKE OF CR AND PO_4 ON RESINS OF ½, 1, 2% CROSS LINKING



(1) Consideration of one selected solution with one selected resin for varying periods of time.

(2) Consideration of one selected solution with different resins for varying periods of time.

(3) Consideration of different solutions with one selected resin for varying periods of time.

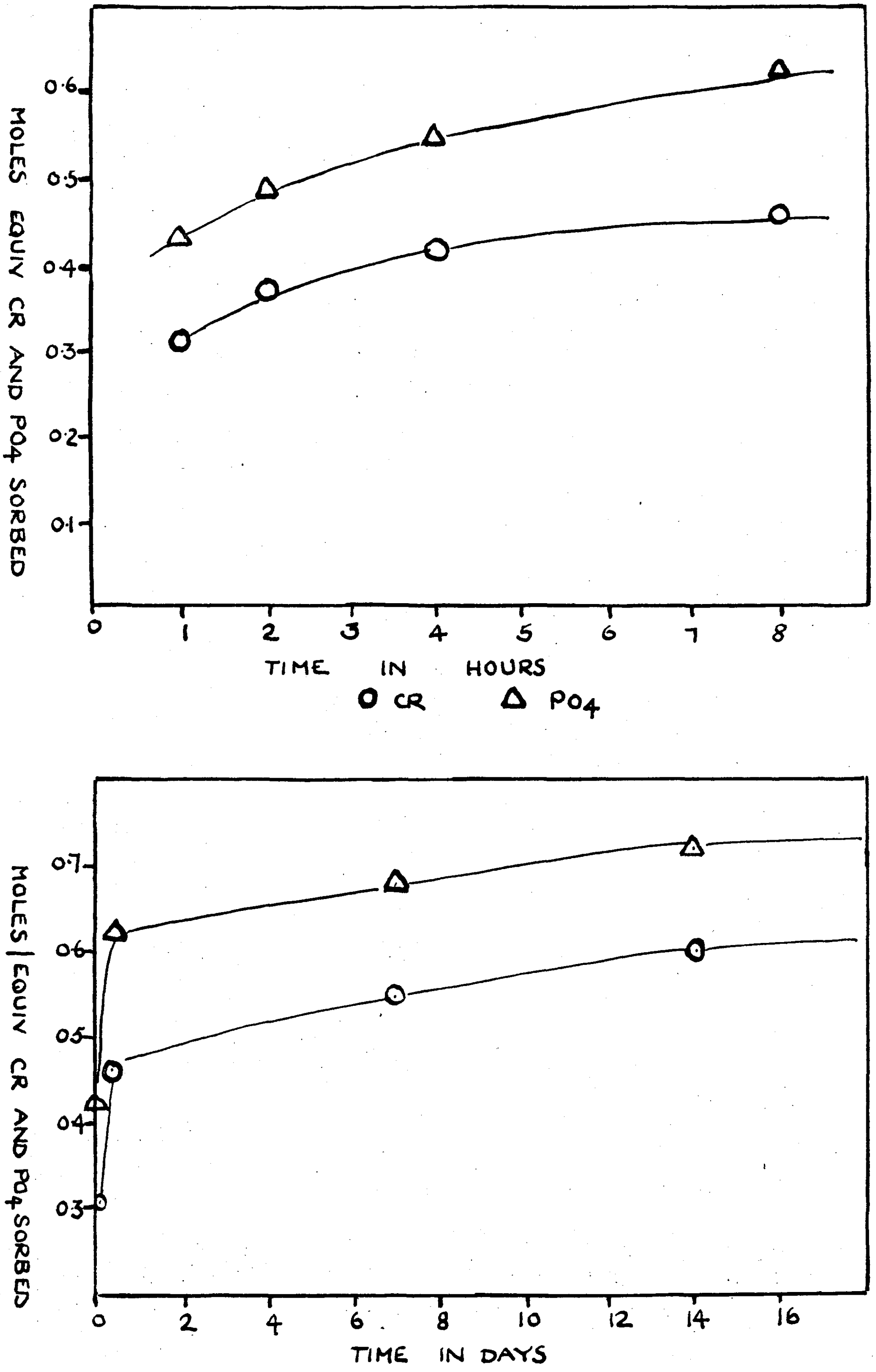
(1) To illustrate the effect of varying the time of contact, the behaviour of the 2½% P_2O_5. 0.3% Cr_2O_3 solution with the 4½% cross-linked resin will be taken, but exactly similar results are found with resins of different cross-linking and with different solutions.

The graph (see Fig. 17) of the sorption of chromium and phosphate with time shows a steady increase in the amount taken up with time. The shape of the curve is such to indicate that the ions being sorbed are large and that entry is slow. Even after seven days it is by no means certain that uptake is complete, for standing the solution in contact with the resin for fourteen days results in a further 7% increase in the amount sorbed. Whilst the amount of chromium and phosphate on the resin is increasing with time, the ratio of PO_4 : Cr passes through a maximum around 2 - 4 hours of contact and then subsequently falls.

There are two possible explanations to account for these results.

(a) That there are a number of different cationic complexes and that they, on account of their size, are sorbed slowly and at different rates. This probably accounts for the variation in ratio of PO_4 : Cr with

FIG 17 UPTAKE OF CR AND PO_4 ON ZEOKARB 225 ($4\frac{1}{2}$% DVB)
FROM A $2\frac{1}{2}$% SOLUTION
FULLY AGED



time. If the complexes are polynuclear and of the type $\left[H_2PO_4 - (Cr - HPO_4)_{n-1} - Cr - H_2PO_4\right]^{n+}$ as seems possible from the chromatographic work, then presumably the greater n is the more difficulty the complex encounters in entering the resin. When n is large the ratio PO_4 : Cr approaches 1 : 1. If such complexes are sorbed with difficulty a fall in the ratio of PO_4 : Cr with time from the initial value corresponding to the sorption of the smaller complexes would be predicted and is in fact the observed behaviour.

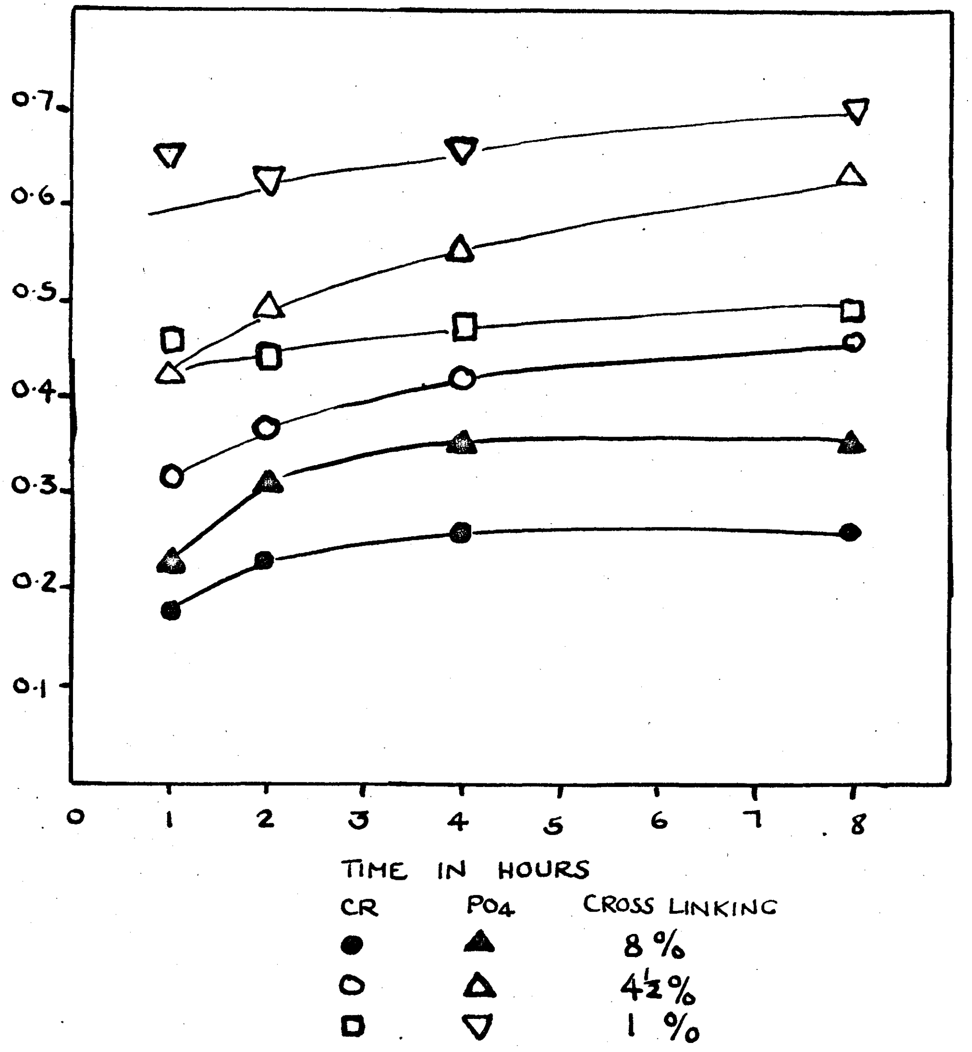
(b) A probable second explanation which may be as important as the first is that the complexes are undergoing breakdown on contact with the resin at room temperature and that as they are breaking down into smaller units, these units may penetrate the more readily into the resin beads. Consequently the results obtained after a considerable time of contact have little relation to the actual species present in solution. This mechanism has already been discussed in the previous section and if due to the acid concentration in the resin, then it would appear possible to reduce the effect by utilizing the sodium form of the resin. However, as may be seen from the results in Table 28b, the % conversion of the sodium form resin to H form in contact with phosphoric acid of the same pH as the fully aged saturated solution is somewhat over 50% and accordingly little would be gained from the use of sodium form resin as the concentration in the resin would still be of the order of 2N. The results with the sodium form resin in Table 28a show no significant difference from those carried out using hydrogen form resin.

(2) If the explanations given above are substantially correct, then it would be expected that as the cross-linking of the resin goes down, so not only would the total amount sorbed increase but also the rate of uptake would be greater and the resin would appear more saturated more rapidly, and the reverse would be true for a resin of a higher degree of cross-linking. In Fig.18 a comparison is made of the 1%, 4½% and 8% cross-linked resins for the 2½% solution, and this is found to be the case.
(3) Further considerations of the results in which the different saturated solutions were studied confirm all the discussion given above.

In similar systems of other tervalent metals and phosphoric acid it has proved possible to interpret the results of the batch experiments in such a way as to postulate a number of likely complexes. However, it does not appear easy to interpret the results in the present system by the method of Salmon (19) The possibility of a fairly large number of complexes of similar type existing in solution and all being sorbed, as well as the possibility of breakdown of certain complexes, makes the application of the expression which may be derived of considerable difficulty, and it may only be applied to those results where equilibrium or pseudo-equilibrium is reached quickly.

Salmon (19) has developed an expression for interpreting the results of batch studies in which the resin is equilibriated with fairly concentrated solutions. This may be derived as follows :

FIG 18. UPTAKE OF CR AND PO4 ON ZEOKARB 225 FROM A 2½% FULLY AGED SOLUTION



Let moles of Cr sorbed per equiv. of exchanger $= N_M$

moles of PO_4 sorbed per equiv. of exchanger $= N_A$

If the resin is saturated with M^{3+} moles per equiv. $= 0.33$.

Assume that the complex sorbed

$$\left[M_y H_x(PO_4)_z \right]^{(3(y-z) + x)+}$$ together with free Cr^{3+} ions.

For 1 equiv. of exchanger

Thus the moles of free metal sorbed

$$= N_M - {}^{y}/_{z}\, N_A$$

∴ equivs. of free metal sorbed

$$= 3\,(N_M - {}^{y}/_{z}\, N_A)$$

and the moles of complex sorbed.

$$= {}^{1}/_{z}\, N_A$$

∴ equivs. of complex sorbed

$$= {}^{1}/_{z}\, N_A \left[3(y-z) + x \right]$$

∴ since total equiv. sorbed = 1 we have

$$\therefore 1 = 3\,(N_M - {}^{y}/_{z}\, N_A) + \frac{1}{z}\, N_A\,(3\,(y-z) + x) \quad \ldots.\ (1)$$

$$\therefore 1 = 3\,N_M + 3N_A \left(\frac{x - z}{z} \right)$$

In the case of fully aged solutions no free Cr^{3+} is present and thus equation 1 reduces to :

$$1 = \frac{1}{z}\, N_A \left[3(y-z) + x \right] \quad \ldots..\ (2)$$

and since $\frac{N_A}{z} = \frac{N_M}{y}$

we have

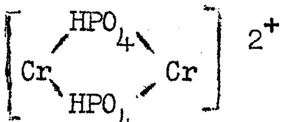
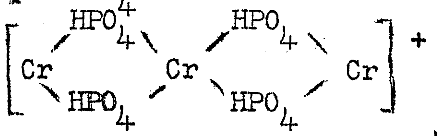
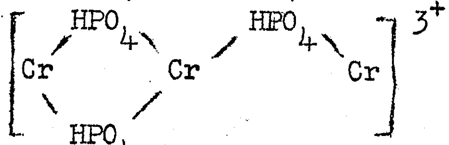
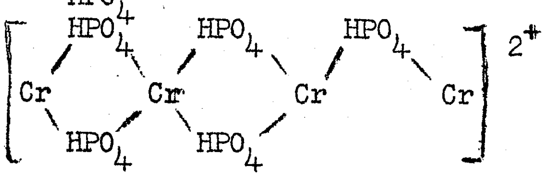
$$1 = N_A \left[\frac{3(y-z) + x}{z} \right] = N_M \left[\frac{3(y-z) + x}{y} \right]$$

Consequently we may derive the following table for some of the most likely complexes as found from the chromatographic separations.

Further discussion of the application of those expressions is deferred until after the consideration of the chromatographic separations that have so far been achieved.

TABLE 47

Moles of chromium and phosphate per equivalent of resin sorbed for various complexes

Complex	y	x	z	moles M/equiv.	moles PO_4/equiv.
				$\frac{y}{3(y-z)+x}$	$\frac{z}{3(y-z)+x}$
$[Cr(HPO_4)]^{+}$	1	1	1	1	1
$[Cr(H_2PO_4)]^{2+}$	1	2	1	0.5	0.5
$[Cr(H_2PO_4)_2]^{+}$	1	4	2	1	2
$[Cr - HPO_4 - Cr]^{4+}$	2	1	1	0.5	0.25
$[Cr - PO_4 - Cr]^{3+}$	2	0	1	0.66	0.33
$[Cr - HPO_4 - Cr - H_2PO_4]^{3+}$	2	3	2	0.66	0.66
$[Cr - HPO_4 - Cr - HPO_4]^{2+}$	2	2	2	1	1
$[Cr - PO_4 - Cr - HPO_4]^{+}$	2	1	2	2	2
$[H_2PO_4 - Cr - HPO_4 - Cr - H_2PO_4]^{2+}$	2	5	3	1	1.5
$[HPO_4 - Cr - HPO_4 - Cr - H_2PO_4]^{+}$	2	4	3	2	3
$[H_2PO_4 -(Cr - HPO_4)_{n-1} - Cr-H_2PO_4]^{n+}$	n	n+3	n+1	1	$\frac{n+1}{n}$
	2	2	2	1	1
	3	4	4	3	4
	3	3	3	1	1
	4	5	5	2	2.5

From unsaturated solutions

Two series of experiments were carried out, namely with a constant amount of Cr_2O_3 and varying P_2O_5 and with a constant amount of P_2O_5 and increasing Cr_2O_3.

(1) Discussion of results obtained in which solutions containing a constant amount of Cr_2O_3 were used.

The results given in Table 31 ' must be interpreted along with the results of the column experiments in which the % of cationic chromium and phosphate was determined. In these experiments the amount of chromium in the cationic form decreases with increasing P_2O_5 concentration and consequently in the parallel batch studies it is to be expected that there will be a fall in the amount taken out of solution by the resin as is in fact observed. Furthermore, the results of the column experiments indicate that the PO_4 : Cr ratio increases from 1.6 —— 2.1 as the solution increases in P_2O_5 concentration. This increase in ratio is mirrored in the batch experiments where a similar increase is observed for the more lightly cross-linked resin. For the more closely cross-linked resin the amount of chromium and phosphate sorbed is so small as to render the ratio inaccurate.

(2) (a) Discussion of results obtained in which solutions containing a constant amount of P_2O_5 were used - solutions aged at 70°C.

Similar considerations apply here as were applied in (1) above. From the column experiments (see Table 36a) in which % cationic chromium ahd phosphate was determined, it may be seen that as the amount of chromium in solution rises so the % of cationic complexes also increases while the ratio of PO_4 : Cr falls. The batch experiments show similar behaviour. A more detailed discussion of the complexes present is deferred to the discussion on the chromatographic separations since these solutions have been fully investigated in this way.

(b) - solutions aged at 100°C

A comparison of the results obtained at the two temperatures indicates that the system is substantially the same at both temperatures (cf. Tables 32 and 33) in that the amount sorbed and the PO_4 : Cr ratio is about the same in both cases and behaviour is exactly similar in the other effects which have been examined.

Discussion of Anion exchange results

The effect of varying times of contact of a 2½% P_2O_5.0.3% Cr_2O_3 solution aged at 70° with De-acidite FF in various forms was also studied (see Table 34 and Fig.11). The results that have been obtained may be divided into two classes :

(1) The resin in the ClO_4^-, NO_3^-, Cl^-, CH_3COO^-, SO_4^{--} forms.

(2) The resin in the PO_4 or HCO_3^- form.

(1) The first group are those in which the amount of chromium sorbed reaches, for each form of the resin, a constant value before 48 hours elapsed. The difference between these final values is probably a measure of the differing affinities of the ions for the resin as compared with the

mixture of anionic chromium phosphate complexes and phosphate.

(2) The second group are those in which the amount of chromium sorbed is still increasing after 48 hours. The reason for this appears to lie in the fact that there is a certain amount of interaction taking place between the anionic chromium complexes that are being sorbed and either PO_4 or HCO_3, i.e. that reactions of the following type are occurring :

$$\text{(a)} \quad y\ An^{m-} + \left[Cr(PO_4)_2\right]^{3-} \rightleftharpoons \left[Cr\ (An)_y\right]^{n-} + 2\ PO_4^{3-}$$

$$\text{(b)} \quad z\ An^{m-} + \left[Cr(PO_4)_2\right]^{3-} \rightleftharpoons \left[Cr\ (An)_z(PO_4)\right]^{x-} + PO_4^{3-}$$

and that consequently more chromium is being sorbed. These results indicate that in column experiments where separation into anionic and cationic complexes is attempted, neither PO_4 nor HCO_3 form of the anion exchange resin should be used.

The results of the uptake of anionic chromium on the perchlorate form of the resin are rather odd on comparison with those obtained when similar chromium species sorbed on a resin sample are allowed to stand with $HClO_4$ of differing pHs for a similar period. The zero uptake of chromium into De-acidite FF in ClO_4 form is acceptable since the affinity of ClO_4 for the resin is high, but accordingly it would be imagined that $HClO_4$ would be particularly effective in removing similar species from the resin. A possible explanation that this is not the case lies not in a consideration of the relative affinities of the ions involved but on an ionic sieve effect. It is well known that ClO_4^- form of the resin has undergone considerable shrinkage due to the high affinity that ClO_4 has for the resin and in consequence large ions, such as $[Cr(PO_4)_2]^{3-}$ would find it hard to penetrate the resin bead. On the other hand, when the reverse process is being considered it may be pictured that ClO_4 ions readily enter the resin bead and near the surface rapid exchange ensues and then with partial conversion to the ClO_4^- form shrinkage occurs and effectively locks in the remaining $[Cr(PO_4)_2]^{3-}$ ions.

SECTION D.

ION EXCHANGE SEPARATIONS

The discussion is concerned only with the results obtained using Zeo Karb columns, i.e. the experiments in which the cationic complexes were separated from the rest of the solution.

The results may best be discussed under two heads :

(1) The experiments with saturated solutions.

(2) The experiments with unsaturated solutions.

(1) From the results given in Tables 36a and b, it will be seen that the ratio of PO_4/Cr on the resin remains fairly constant, 1.63 ± 0.02 for the saturated solutions, whilst the PO_4/Cr ratio of the original solutions varies between 8.98 and 2.68. The figures of the column separations may be compared with those obtained on comparable batch experiments - those where the resin was in contact with the solution for some two hours.

TABLE 48

Comparison of ratios from batch and column experiments

Solution *	Column PO_4/Cr	Batch PO_4/Cr
2½	1.63	1.43
5	1.65	1.33
7½	1.65	1.22
10	1.63	1.25
12½	1.61	1.42

*See Table 16 for meaning of description

The results of the batch experiments give a consistently lower ratio and this is probably explained as follows :-

(a) The column experiments will effectively sorb all the cationic complexes present in the solution whilst the batch experiments would tend to favour the complexes that are held more strongly - which as has been already commented on will almost certainly have a lower PO_4/Cr value.

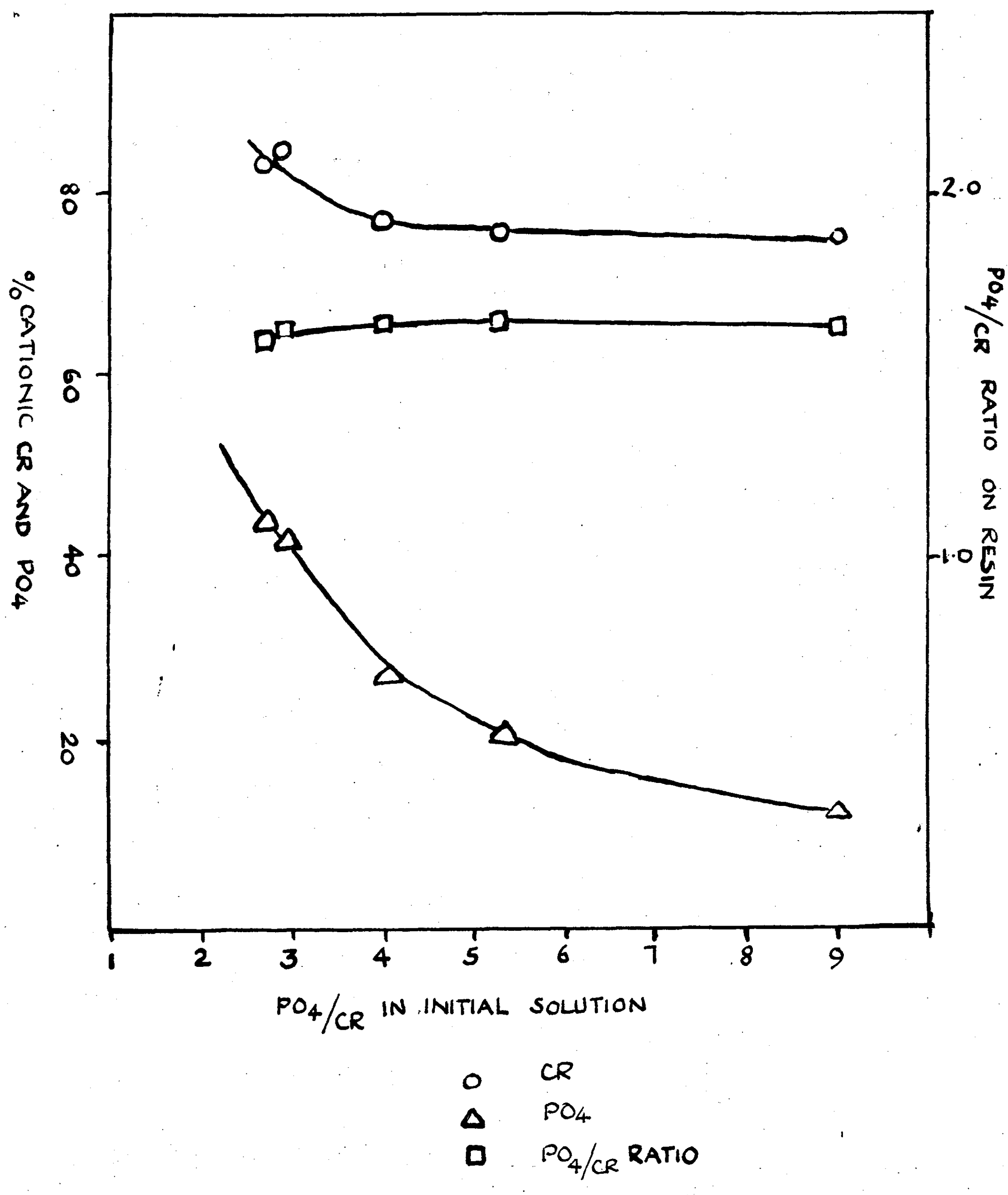
(b) That there is the possibility, as was observed in certain experiments, see especially Table 33 of a lightly held complex such as $\left[Cr(H_2PO_4)_2\right]^+$ being washed off the resin in a batch experiment.

(c) That in the column experiment undissociated phosphoric acid is being sorbed along with the complex cations and that the PO_4/Cr value is therefore higher than the true value.

The significant feature of the results of these column experiments is that the ratio of PO_4 : Cr of the cationic complexes is approximately the same in all the solutions and this would lead to the suggestion that the study of the saturated solutions might not be the most profitable line of investigation, since these solutions probably contain the same complexes but in greater concentration as the concentrations of the saturated solutions increase.

The second feature is that as the PO_4/Cr value falls in the original solution so the amount of chromium and phosphate that is present in a cationic form increases. It is of interest to note that there is a very high amount of cationic phosphate, up to 45% in the more concentrated saturated solutions. (See Fig. 19).

FIG 19 % CATIONIC CR AND PO_4 FOUND IN FULLY AGED SOLUTIONS



(2) Taking the results given in Tables 36a and b for the unsaturated solutions, it may be seen that whilst the amount of chromium and phosphate present as cationic complexes follows a similar trend to that outlined above, nevertheless the behaviour of the PO_4/Cr value is different. In the case of the saturated solutions the PO_4/Cr value of the cationic species is approximately constant but in the case of the unsaturated solutions, the value varies considerably, in fact between 2.08 - 1.59. These figures may be compared with corresponding values obtained from the batch studies in the following Table :

TABLE 49

Comparison of ratios from batch and column experiments

Solution *	Column PO_4/Cr	Batch PO_4/Cr
1 - 5	1.77	1.42
1 - 10	2.07	1.55
1 - 15	2.08	1.80
5 - 15	1.88	1.66
10 - 15	1.82	1.50
15 - 15	1.80	1.42
20 - 15	1.59	1.34

* See Table 30 for meaning of description

Once again the PO_4/Cr values of the comparable batch experiments are lower but the trend in the values follows closely that found from the column experiments. It is obvious from the results using 1 - 15 and 1 - 10 solutions that a certain amount of free phosphate is being sorbed on the column under the conditions of the experiments and is not being washed off.

The result of the column experiment on the 1 - 15 solution indicates clearly that the only complex present is one in which the ratio of $Cr : PO_4$ is 1 : 2 and as this is a cationic complex it can only have the formula $\left[H_2PO_4 - Cr - H_2PO_4\right]^+$.

SECTION E.

ION EXCHANGE CHROMATOGRAPHY

Taking the results given in Tables 42a and b, the presence of complexes with the most probable ratios may be tabulated in the following way. The complexes are listed in order of elution, i.e. C 1 first and C 2 next and so on down to C 7.

TABLE 50

Appearance of complexes in solutions of constant P_2O_5 concentration

Complex	Ratio PO_4/Cr	solutions in order of increasing Cr concn.				
		1 - 15	5 - 15	10 - 15	15 - 15	20 - 15
C 1	2	✓	✓	✓	✓	✓
C 2	1.5		✓	✓	✓	✓
C 3	1.33		✓	✓	✓	✓
C 4	1.25			✓	✓	-
C 5	1.12				✓	✓
C 6	1.0				✓	✓
C 7	0.5			✓		

The structures of C1 and C 7 must be $\left[H_2PO_4 - Cr - H_2PO_4\right]^{+}$ and $\left[Cr - HPO_4 - Cr\right]^{4+}$ and presumably the other complexes must be intermediate in character and in charge. C 7 it will be noticed was the result of treating the column with 8N acid and is probably a breakdown product of a complex with a higher PO_4/Cr value.

These results along with those of the ion exchange separations indicate that as the chromium content increases whilst the phosphate concentration remains constant so

(a) The % cationic chromium increases.

(b) The number of complexes rises and that the PO_4/Cr value falls with the succeeding complexes.

(c) That the overall PO_4/Cr value falls as the PO_4/Cr value of the solution falls.

The probable structures of the complexes must be consistent with those already postulated, must be of equal or intermediate charge, and must fit into the probable mechanism of formation.

In the light of the foregoing, it is possible to draw up the following table of probable structures for the complexes :

TABLE 51

Probable structures of complexes found in solutions of constant P_2O_5 concentration.

Complex	PO_4/Cr value	Probable structures
C 1	2	$[H_2PO_4 - Cr - H_2PO_4]^{+}$
C 2	1.5	$[H_2PO_4 - Cr - HPO_4 - Cr - H_2PO_4]^{2+}$
C 3	1.33	$[H_2PO_4 - (Cr - HPO_4)_2 - Cr - H_2PO_4]^{3+}$
C 4	1.25	$[H_2PO_4 - (Cr - HPO_4)_3 - Cr - H_2PO_4]^{4+}$
C 5	1.12	$[H_2PO_4 - (Cr - HPO_4)_6 - Cr - H_2PO_4]^{7+}$
C 6	1.0	$[H_2PO_4 - Cr - HPO_4 - Cr]^{3+}$
C 7	0.5	$[Cr - HPO_4 - Cr]^{4+}$

In the case of C 2, C 3, C 4, C 5 the charge may be reduced by one, or two units by the loss of a hydrogen from one or both of the terminal acid phosphate groups, and of more units of charge if the hydrogen ions are lost from the bridging phosphates.

These structures and the results of this section are all in accord with the results of the batch experiments but indicate that it would be difficult to use the approach of Salmon (19) in trying to interpret the batch results de novo.

SECTION F

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PART 5

CONCLUSIONS

SECTION A.

GENERAL DISCUSSION AND CONCLUSIONS

One of the earliest observations in the present work is the rather remarkable increase in the rate of aging between the temperatures which have been studied. If it is assumed that the initial formation of a complex involves a slow step followed by a chain reaction, an equation of the type as the first stage would be most probable.

$$[Cr(H_2O)_6]^{3+} + \text{Phosphate} \xrightarrow{\text{slow}} [Cr(H_2O)_5]^{3+}$$

$$\xrightarrow{\text{rapid}} [Cr(H_2O)_5 \ H_2PO_4]^{2+} \qquad \text{——} \ (1)$$

In chemical reactions in general we have the following relationship for rates of reaction at temperatures t and t + 10.

$$\frac{K_{t + 10}}{K_t} \simeq 2 \text{ or } 3 \qquad \text{where } K = \text{rate constant.}$$

Whilst the present work has not provided the appropriate data, the time of aging is an indication of the rate constant and the figures between 40°C. and 70°C. show that a reasonable time of aging, based on the data at 40°C., would predict a time of something between 3 - 13 days at 70°C. where 3 is the lowest limit by putting a very unusually high figure for the ratio of $K_{t + 10} / K_t$. However, the work of Plane and Taube (1) on the exchange of H_2O with $[Cr(H_2O)_6]^{3+}$ indicates that there is a large temperature increment. They consider that the slow step in the exchange to be :

$$\left[Cr(H_2O)_6\right]^{3+} \xrightarrow{slow} \left[Cr(H_2O)_5\right]^{3+} \xrightarrow[H_2O^*]{rapid} \left[Cr(H_2O)_5\ H_2O^*\right]^{3+}$$

and so the present figures may be reasonable, on the other hand it might be inferred that two routes of aging are possible, the one favoured at low temperatures, and the other at higher temperatures. In any case the presence of phosphoric acid is likely to be of considerable importance in the deducing of a possible mechanism of formation of complexes, and its behaviour with temperature is of considerable interest.

It has been shown by Harned and Embree (2) that the ionization constants of a number of acids conformed to a general empirical equation as far as their behaviour with respect to temperature was concerned.

The ionisation constant k.. for an acid at temperature t°C. is expressed as :

$$\log k_t = \log k_m + f\ (t - \theta) \quad \text{———} \quad (2)$$

where k_m = max. value of the ionization constant which occurs at temperature θ .

$f\ (t - \theta)$ is a function of temperature.

Within the range of $t - \theta = \pm 75$ degrees the equation may best be written :

$$\log k_t = \log k_m - 5.0 \times 10^{-5}\ (t - \theta)^2 \quad \text{——} \quad (3)$$

Nims (3) applied this equation to the experimentally determined values of k_1 for H_3PO_4.

Equation (3) for k_1 for H_3PO_4 becomes

$$\log k_t = - 2.0304 - 5 \times 10^{-5}\ (t + 18)^2 \quad \text{———} \quad (4)$$

and showed that k_t (obs) was very close to k_t (calc) in the range of 0 - 50°. Consequently this equation may be applied with confidence up to a temperature of 93°C. in order to calculate pk_1 values for H_3PO_4 for higher temperatures than pK_1 has been measured.

temp.	pk_1
50°C.	2.260
70°C.	2.428
100°C.	2.728

Similarly the expression for k_2 has been calculated. For k_2 the expression becomes :

$$\log k_{2t} = -7.1888 - 5.0 \times 10^{-5} (t - 43.1)^2 \quad \ldots\ldots. (5)$$

and it is possible to calculate similar values of pk_2

temp.	pk_2
50°C.	7.191
70°C.	7.220
100°C.	7.363

So above the temperature of 43.1°C. both k_1 and k_2 for phosphoric acid are decreasing - that is, it is becoming a weaker acid. Thus it is clear that above 43°C. a somewhat different 'climate' exists in the system chromium (111) - phosphoric acid.

It seems reasonable to suppose that this accounts for the entirely different behaviour of the system at 25° and 40°C. to that observed at 70°C. and 100°C.

In the light of the foregoing and of the results so far obtained in the present study, it is possible to postulate the following mechanism for the formation of the various complexes :

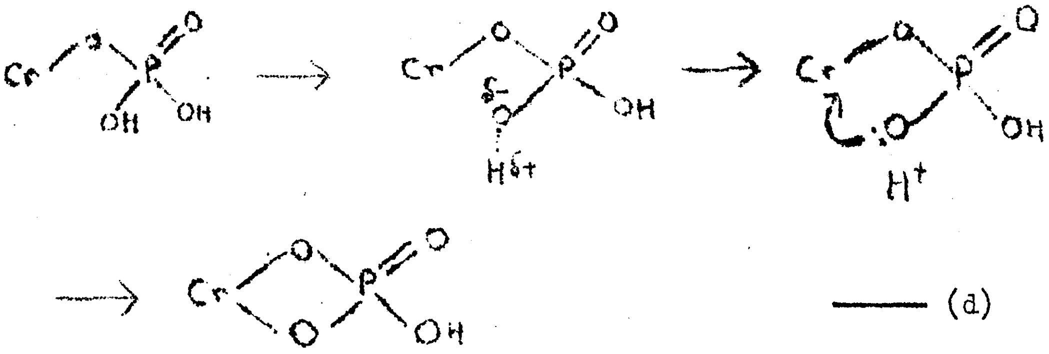
$$\left[Cr(H_2O)_6\right]^{3+} \xrightarrow{\text{slow}} \left[Cr(H_2O)_5\right]^{3+} \quad \text{——} \quad (a)$$

$$\left[Cr(H_2O)_5\right]^{3+} + H_2PO_4^{-} \xrightarrow{\text{rapid}} \left[CrH_2PO_4(H_2O)_5\right]^{2+} \quad \text{——} \quad (b)$$

The third step is of considerable interest, it is obvious that the preferred structure of phosphate bonded to chromium is as a monodentate ligand and consequently we have :

$$\left[Cr(H_2PO_4)\right]^{2+} + H_2PO_4^{-} \longrightarrow \left[Cr(H_2PO_4)_2\right]^{+} \quad \text{——} \quad (c)$$

rather than or as well as



—— (d)

both c and d involve the loss of a second molecule of water from the chromium cation which, since the absorption peaks of the complex are shifted towards the infra red - implying that the ligand groups are held less firmly than in the aquo complex, will not be such a slow step as (a); but presumably (c) is favoured since the formation of a stable four-membered ring depends on the unhydrated ionic radius of chromium (see Genge and

Salmon (4)), and the electronegativity of the metal ion, and the availability of suitable orbitals. It appears from their work that the use of inner d orbitals in formation of d^2sp^3 hybrid orbitals is not helpful in the formation of a highly polar linkage as pictured above.

Further complexes may be formed by suitable elimination reactions of the type :

$$\left[H_2PO_4 \text{ — } Cr \text{ — } H_2PO_4\right]^+ \quad \left[H_2PO_4 \text{ — } Cr \text{ — } H_2PO_4\right]^+$$

$$\downarrow$$

$$\left[H_2PO_4 \text{ — } Cr \text{ — } HPO_4 \text{ — } Cr \text{ — } H_2PO_4\right]^{2+} + H_3PO_4 \text{ — } \quad (e)$$

where the elements of phosphoric acid are split out by a process of elimination similar to that described as -olation by Bjerrum (5) and others in the formation of polynuclear complexes of chromium involving hydroxyl bridging.

It is easy to picture the build up of complexes in solution utilizing this concept of elimination of phosphoric acid between complexes (which might be termed phospho-olation). As the concentration increases so the process repeats itself to give chain complexes of the type so far postulated. When the solution becomes saturated, these polynuclear complexes form a basis for the actual structure of the solid material which is present in contact with the saturated solution. Thus there would be units of the type :

$$\left[- Cr \text{ — } HPO_4 \text{ — } Cr \text{ — } HPO_4 \text{ — } Cr -\right]$$

present in the solid phase, and this would account satisfactorily for the behaviour of the material as found in the present work.

The concept of -olation has been applied to :

(a) solid materials

(b) colloidal particles

(c) non-colloidal aggregates in solution

by a number of workers, e.g. Ewing (6) and the school of Thomas (7). They have suggested that the behaviour of hydrous oxides in each of these three states may be best explained in terms of an -olation concept.

The work of the school of Sillen (8) and the postulation of the structure of polynuclear complexes of metal hydroxides based on a 'core and links' theory owes its origin in thought at least to the ideas of -olation.

The present work suggests that the concept is of wider application under suitable conditions.

Summary of Conclusions

The major difference between the chromium (111) - phosphoric acid system at 0° - 40°C. and 70° - 100°C. is the appearance of polynuclear complexes. These have not been noted in the previous work of Jameson and Salmon (9) at 0°C and 40°C.

At a constant P_2O_5 concentration and at low chromium content the first cationic complex that is formed is a simple mononuclear one of PO_4 : Cr ratio of 2 : 1. As the chromium concentration rises so the overall PO_4 : Cr ratio of the cationic complexes falls and various polynuclear species appear (see Table 51) probably formed by elimination reactions of the type indicated in equation (e). From the chromatographic work it is clearly the polynuclear complexes which are susceptible to breakdown into smaller units by H^+ ions.

Table 52 correlates the results of the work in the system chromium (111) - phosphoric acid for the different temperatures so far obtained.

TABLE 52

Cationic complexes found in the chromium (111) - phosphoric acid system.

0°C.	40°C.	70°C.
$[\mathrm{Cr(H_2O)_6}]^{3+}$	$[\mathrm{Cr(H_2PO_4)_2}]^{+}$ $[\mathrm{Cr\ HPO_4}]^{2+}$	$[\mathrm{Cr(H_2PO_4)_2}]^{+}$ $[\mathrm{H_2PO_4 - (Cr\text{-}HPO_4)_{n-1} - Cr - H_2PO_4}]^{n+}$ n = 1,2,3 and 6 $[\mathrm{Cr - HPO_4 - Cr}]^{4+}$ $[\mathrm{Cr - HPO_4 - Cr - H_2PO_4}]^{3+}$

SECTION B

POSSIBLE EXTENSIONS

There are three main fields which suggest themselves as leading on from this work.

(1) A correlation of ion-exchange chromatographic results and batch experiment results.

(2) A fuller investigation of the present system at lower and higher temperatures and at higher concentrations.

(3) An investigation as to whether the concept is of wider application.

(1) One of the more disappointing features of the present work was the inability to interpret, other than in general terms, the results of the batch experiments in which complex chromium (111) species were sorbed on the resin. It would therefore be useful taking the known batch and column results and developing expressions which could be applied to batch studies of other similar systems, where the complexes are not sufficiently stable as to permit chromatographic separation.

(2) Whilst a number of points have become clearer in the investigation of the present system, there is obviously a great deal of work which could profitably be done at lower temperatures - particularly the chromatographic technique could be applied more widely now that the initial problems of achieving satisfactory separations have been overcome.
A possible way in which the length of time of aging could be reduced would be by the use of a small amount of added chromous salt. Plane

and Taube (1) have commented on the increase in rate of reaction in the system $\left[Cr(H_2O)_6\right]^{3+}$ - H_2O on the introduction of chromous ions inter alia.

(3) The postulation of the concept of phospho-olation suggests that it should be of wider application than just the present system, and it would be useful to examine such systems as ferric (111) - phosphoric acid and aluminium (111) - phosphoric acid at 70°C. or higher. Again, if the concept is general then other oxy ligands besides hydroxide and phosphate should show similar behaviour. The most obvious system to investigate would be something like chromium (111) - arsenic acid in the first instance.

SECTION C

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