STUDIES OF SOME
QUADRIVALENT VANADIUM COMPOUNDS
IN AQUEOUS SOLUTION.

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by

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Summary.

Following a discussion of the orthophosphato complexes of metal ions and systems involving quadrivalent vanadium, studies are described in which ion-exchange, pH-titration, spectrophotometric, and magnetic methods were employed to investigate the complexes of the vanadyl ion in aqueous media. The data obtained from studies of vanadyl/phosphate solutions under acid conditions have been interpreted as showing the occurrence of the following complex-forming reactions:

\[
\begin{align*}
\text{VO}^{++} + \text{H}_2\text{PO}_4^- & \rightleftharpoons \text{VOHPO}_4^+ + \text{H}^+ \\
\text{VOHPO}_4^- + \text{H}_2\text{PO}_4^- & \rightleftharpoons \text{HVO(HPO}_4^- \text{)_2} \\
\text{HVO(HPO}_4^- \text{)_2} & \rightleftharpoons \text{VO(HPO}_4^- \text{)_2}^-- + \text{H}^+
\end{align*}
\]

and parallel reactions involving phosphoric acid molecules as reactant species. The properties of a green solid, which precipitated from vanadyl/phosphate solutions of low hydrogen ion concentration, are reported together with a postulated polymeric structure for this material. The structure involves the linking of vanadyl ions by hydroxyl and phosphate bridging groups. Evidence is also reported which shows that species containing quadrivalent vanadium in alkaline phosphate media are of a different nature to those formed in perchlorate media.

Studies of the vanadyl/thiocyanate system are described and the data obtained from these investigations are compared with those reported by other workers. Evidence is presented which shows that more than one thiocyanato vanadyl complex species co-exist in acid solutions, and that these are of low stability. The experimental data have been interpreted as showing that the species, VO(CNS)_4^--,
is formed in significant concentration in the solutions. It is shown that the absorption spectra of vanadyl/thiocyanate solutions may be considered to indicate that the thiocyanato ligands are coordinated to the vanadium ions through their nitrogen atoms.

Studies of the effects of hydrolysis on the absorption spectrum of the hydrated vanadyl ion are reported together with data which indicates that vanadyl ion forms complexes containing acetate, arsenate, bromide, chloride, oxalate and sulphate ligands.
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Notes of general relevance.

1. Unless stated to the contrary, it may be considered that vanadium is in the quadrivalent state in all vanadium-containing species and that phosphate species discussed are derived from orthophosphoric acid, $\text{H}_3\text{PO}_4$.

2. Solutions or systems containing vanadyl ion and an anion, which are not necessarily present in equivalent concentrations, are denoted as 'vanadyl/anion' solutions or systems.

3. Brackets, ( ), are used to denote the molar concentrations of species.

4. For the sake of clarity, water molecules co-ordinated to ions are omitted unless specifically required in the discussion.

5. When systems were required to attain equilibrium before analysis, one solution was analysed after standing for 7 days and a duplicate solution was analysed after 14 days. Since identical analytical data were obtained from duplicated, vanadyl-containing systems in this way, these systems may be considered to have attained equilibrium after standing for this period of time.

6. Experiments were carried out at room temperature, that is $20^\circ\text{C.} \pm 3^\circ$, unless stated to the contrary.
SECTION A.

INTRODUCTION, AND PURPOSE OF THE INVESTIGATIONS.
I. Introduction.

In recent years, the theory, underlying the constitution of inorganic compounds, has evolved rapidly from the classical concepts, which were widely held as a result of the first systematic study of complex compounds carried out by Werner. It is no longer justified to make the simple and arbitrary distinction between true salts, like sodium chloride, and complex salts, which involve predominantly covalent bonds between co-ordinated ligands and the central metal ion, such as hexammino cobaltic chloride. The development of modern experimental techniques, particularly physical techniques, has supplemented the older methods of approach, so that chemical species may now be studied in solution in such a way that the system under observation is not simultaneously destroyed. This has resulted in a revision of old, and often inadequate theories, with the result that complex formation has currently become accepted as a phenomenon occurring widely in solution.

The wave-mechanical treatment of bonding orbitals, and the approximations embodied in the crystal-field and ligand-field theories, have considerably promoted the understanding of complex compounds. These have resulted in a greater possibility of the explanation of the stereochemistry of such compounds from data derived, for example, from spectrophotometric and magnetic studies. Considering metal ions in aqueous solution, since it is unreasonable to consider electron pairing, and hybridisation of orbitals to take place only on the addition of a suitable complexing agent, most 'simple' ions are currently considered to be complexes in which the co-ordination sites around the central ion are occupied by water.
molecules. Thus, the 'simple' chromic ion, for example, is considered to be complexed by six water molecules. Other complex species are formed from such aquated ions by the replacement of the aquo ligands with new ligand groups at the co-ordination sites around the central metal ion. Complexes formed in this manner are usually characterised by the same mode of hybridisation of orbitals as the original hydrated ion. However, the new ligand can, in some instances, depending on its size, structure, and polarisability, change the hybridisation of the orbitals of the metal ion. Thus, the hexaquo ferric ion, which is characterised by $d^{2}sp^{3}$ hybridisation, may give rise to both hexacyano- and tetrachloro ferric ions, which are characterised by $d^{2}sp^{3}$ and $sp^{3}$ hybridisation respectively.

Since ligands in the co-ordination sphere are bonded to the central ion by the overlap of bonding orbitals, the extent of the overlap in the bonds formed will be reflected in the energy levels of these orbitals and in the properties of the complex which are associated with the electrons localised around the central metal ion. Thus, when ligands co-ordinated to the central ion are replaced, the properties of the central ion are modified. With a suitable interpretation, therefore, the changes of these properties may be used to study the nature of the bonds formed between the central metal ion and its ligand groups, and of the complex species as a whole.

N.Bjerrum has shown that replacement of co-ordinated water molecules in a hydrated ion by other ligand groups takes place in a step-wise manner (121,122). This may be illustrated by the stability constants and other data compiled by various workers for complexes in aqueous solution in which metal ions are complexed by phosphate ligands. Gosselin and Coghlan, in a study of the 1:1
complexes of the calcium ion, have shown that complexes formed by the co-ordination of condensed phosphate groups are more stable than those containing orthophosphate ligands (1). This, together with many other factors concerning phosphate systems, has been discussed by Van Wazer and Callis (2). However, complexes with orthophosphate ligands are still of importance. The stability of these complexes depends to a considerable extent upon the charge and size of the metal ion to which the ligands are co-ordinated. Thus, Smith and Alberty have shown that very weak 1 : 1 complexes are formed between orthophosphate species and lithium, sodium, and potassium ions (3). Other workers have shown that the divalent ions of magnesium, calcium, strontium, and manganese form 1 : 1 complexes containing monohydrogen phosphate ligands which are only slightly enhanced in stability (4). The slight tendency of the divalent ions generally to complex with orthophosphate species was confirmed by the pH-titration and ion-exchange work performed by Holroyd and Salmon (5). From the wide variety of divalent ions studied, they demonstrated that only the manganous ion forms orthophosphato complexes to any great extent. However, tervalent ions have been shown to form orthophosphate complexes of moderate stability. Bjerrum and Dahm have reported mononuclear complexes of the aluminium ion containing up to three orthophosphate ligands (6). Bismuth, indium, chromic, and ferric ions, and some cations of the rare-earth metals, also have a moderate tendency to form such complexes, while the indium ion has been shown to accommodate up to three monohydrogen phosphate ligands (5,7-15). Of the tervalent cations, the titanium ion has the greatest tendency to complex with orthophosphate species, although the number and nature of the ligand groups accommodated by the ion still remains obscure (16). The quadrivalent thorium ion has been shown to form complexes containing
one or two dihydrogen phosphate ligands, but due to its larger size, the complexes formed are of low stability (17). Everest and Salmon have also reported the formation of a phosphato complex containing quadrivalent germanium (18).

The investigations summarised above have shown that monohydrogen phosphate ions have a greater tendency to complex with metal ions than dihydrogen phosphate ions. Furthermore, a maximum of three monohydrogen phosphate ions appear to be accommodated by metal ions characterised by a maximum co-ordination number of six. Now, West, Schulze, Duc-Mange, and other workers have shown that the orthophosphate group has a tetrahedral structure, with double bonds between the phosphorus and oxygen atoms contributing to the stability of the configuration (19-23). Thus, the most stable type of phosphate complexes may be expected to involve a four-membered chelate ring of the following type:

Furthermore, the greatest stability of such a chelate ring would be achieved by obtaining maximum overlap of the $sp^3$ hybridised bonding orbitals of the oxygen atoms with the bonding orbitals of the central metal ion. Thus, the size of the metal ion, and configuration of its complexes are of considerable importance in determining the stability of chelate phosphato species. Genge and Salmon have shown that the optimum unhydrated ionic radius for the formation of an orthophosphate chelate ring with tervalent metal ions is 0.7 Å. (16). They assumed that such complexes have octahedral configurations involving outer d-orbitals of the metal ions in hybridisation. Furthermore, their calculations have shown that the
formation of chelate rings with orthophosphate species will inevitably distort the natural bond angles in the complexes. This may well account for the relatively low stabilities of complexes containing orthophosphate ligands as compared with those formed by the co-ordination of chelate, condensed, phosphate groups. This may also account for the tendency of the tervalent metal ions to form the most symmetrical complexes possible for the octahedral configuration, the tris-chelate structures, in order to achieve an adequate degree of stability. Only those tervalent ions forming the most stable phosphato complexes, that is, ferric, and presumably titanium ions, show any great tendency to form complexes containing smaller numbers of chelate phosphate ligands.

Complexing of the vanadyl ion by orthophosphate species has not previously been studied. In fact, the interactions between vanadyl ion and the majority of inorganic species have previously received little attention. Before attempting such a study, therefore, the co-ordination number of the quadripole vanadium ion and the configurations of its complexes will be considered from the data which has accumulated from those systems which have previously been investigated.

In non-aqueous media, quadripole vanadium forms compounds in which it exhibits co-ordination numbers of four and six. The former group is exemplified by the compounds vanadium tetrachloride, tetrabromide, and numerous addition and substitution products of the tetrachloride (24-29). Orgel has shown that vanadium tetrachloride has a tetrahedral configuration from the peak in its absorption spectrum which occurs at a frequency of 9000 cm⁻¹ (30). Wilkinson and Birmingham have prepared the compounds dicyclo-
pentadienyl vanadium dichloride and dibromide, and these also may later be shown to have a similar configuration \((31)\). Complex species have been demonstrated in which the vanadium ion is coordinated by six cyanide, fluoride, or chloride ions, and the two halide complexes have been shown to have octahedral configurations from the characteristics of their respective absorption spectra \((32-34)\). In order to explain data from conductivity studies, Gutmann has also found it necessary to postulate complex species in which the vanadium ion is co-ordinated to five, seven, and eight chloride ions \((35)\).

In the presence of water, quadrivalent vanadium compounds are hydrolysed readily to form the vanadyl ion. Neglecting co-ordinated water molecules, the positive charge of two units and the formula, \(\text{VO}^{++}\), has been established for this ion by several workers \((e.g. 36, 37)\). Furthermore, the vanadyl ion, as would be expected, has been shown to contain a single unpaired electron from the measurements of the magnetic susceptibility of vanadyl sulphate and vanadyl chloride carried out by Bose, Blar, Wedekind, and Horst \((38, 39)\).

Hydrolysis of the vanadyl ion has been studied by many workers \((40-45)\). After introduction of the oxide ion of the vanadyl group, the vanadyl ion has been shown to undergo further hydrolysis to only a very small extent in solutions in which the concentration of free hydrogen ion is 0.02 moles per litre or more. However, under less acid conditions, solutions of vanadyl ion have been shown to contain the hydroxy species, \(\text{VOOH}^+\), and the more detailed work of Rossotti and Rossotti has also revealed the binuclear species, \((\text{VOOH})^+\) \((40)\). In solutions of pH 4, the vanadyl ion is
hydrolysed extensively, and grey gelatinous vanadyl hydroxide is precipitated. Infra-red absorption spectra, and other experimental data have shown that this material is not merely hydrated vanadium dioxide, but that it is polymeric in nature (40,41,44-49).

Since vanadium dioxide is amphoteric in nature, vanadyl hydroxide is found to dissolve in both acid and strong alkali solutions. Several workers have assigned the formula, $\text{M}^+\text{V}^4\text{O}_9$, to the brown, sparingly-soluble vanadites (IV) which have been isolated from alkaline solutions, and have found that these compounds are readily oxidised by atmospheric oxygen, particularly when in solution, to give compounds containing vanadium in the quinquevalent state (37,47,49-51). The preparation of several compounds of the type, $\text{M}^{II}\text{V}_2\text{O}_5$, has been described by Rudorff and co-workers. These involved the heating of an intimate mixture of vanadium dioxide and the oxide of a divalent metal, in vacuo (52).

The vanadyl ion is stable to oxidation in aqueous acid solutions at normal temperatures. However, it is oxidised in boiling, concentrated solutions of sulphuric acid, and equilibrium is established when vanadium is present in quadri- and quinquevalent states in an equimolar ratio. A variety of other oxidising agents will oxidise the vanadyl ion slowly in cold acidic solutions, to produce species containing vanadium in the quinquevalent state. Nitrate ion is included among these reagents. Thus, the variation in optical density, which has been observed in acidic solutions of vanadyl ion in the presence of nitrate, may be attributed to oxidation of the vanadyl ion (53,54). As mentioned previously, quadrivalent vanadium in alkaline solution is slowly oxidised by atmospheric oxygen at room temperatures (49,55-58).
The number of co-ordinated ligands, and the configuration, of the hydrated vanadyl ion have been difficult to resolve. X-ray investigations have shown that the quadripositive vanadium ion is surrounded by an octahedral arrangement of six oxygen atoms in crystals of vanadyl sulphate pentahydrate and vanadium dioxide (59, 60). This, therefore, would favour an octahedral configuration for the hydrated vanadyl ion in solution. However, as discussed by Jørgensen (61), an insufficient number of absorption bands are observed in the visible absorption spectrum of the vanadyl ion in aqueous acid solution to enable a distinction to be made between the several possible configurations for the hydrated ion on the basis of its absorption spectrum alone. Nevertheless, since this problem is discussed in detail in section E, it will be sufficient to mention here that the hydrated vanadyl ion is now considered to have a tetragonally distorted octahedral configuration.

The majority of the complexes of the vanadyl ion that have been studied have involved the co-ordination of chelate ligands, and these have shown that a maximum of two bidentate ligands may be accommodated by the vanadyl ion in aqueous solutions. The species, \( \text{VO(C}_2\text{O}_4\text{)} \) and \( \text{VO(C}_2\text{O}_4\text{)}_2^- \), have been demonstrated in solutions containing oxalate ion, and, under certain conditions of pH, complexes which contain acid-oxalate ligands have been detected (41,50,55,62-66). Vanadyl complexes are also formed with other chelate organic ligands, and these involve the displacement of up to four co-ordinated water molecules from the hydrated vanadyl ion. Vanadyl systems containing the following ligands have been studied: citrate (62,66-70), tartrate (55,61,62,70-73), malonate (74,75), salicylate and derivatives (55,76-79), acetylacetone and other \( \beta \)-diketones (80-82), succinate (62), catechol (83), and ethylenediaminotetraacetate (61, 84,85). Polynuclear complex species have been demonstrated in some of these systems.
Complexes of the vanadyl ion, involving the co-ordination of inorganic ligands, have generally not been studied in such detail. The absorption spectrum of the vanadyl ion has been found to be affected to a negligible extent by the presence of perchlorate ion, except in solutions with very high concentrations of the anion (61, 86). However, certain highly polarisable anions have been shown to replace up to four aquo groups of the hydrated vanadyl ion on complexing. Thus, Rivenq has demonstrated the formation of the ion, VO(CN)$_4$$^-$$^-$, but the neutral vanadyl cyanide, which he claimed to be precipitated from the solutions, has been disputed by Ducret, for he considered this to be a precipitate of vanadyl hydroxide (48,87). Complex thiocyanato species, of the type, M$_2$VO(CNS)$_4$$^+$, have been isolated by several workers (50,88-90). More recently, Furman and Garner have studied the thiocyanato complexes in solution by spectrophotometric and other methods (91,92). Largely as a result of investigations, in which they used Job's method of continuous variations (93), they claim to have demonstrated the formation of the complex, VO(CNS)$_2$$^+$, and while not overruling the possibility of complexes containing greater numbers of thiocyanato ligands, have stated that higher complexes of this kind are formed only in small concentrations in the solutions. A polarographic study has also been made of the thiocyanate system (94), and the considerable increase in the optical density of solutions containing vanadyl ion, caused by the addition of thiocyanate, has been utilised in the spectrophotometric estimation of vanadyl ion concentration (95).

Interactions between vanadyl ion and inorganic anions of low polarisability have been found to be very weak. Among the halide ions, fluoride ion forms the most stable complex species. Ahrland and Noren have given evidence for the ion, VOF$_2$$^+$, (96), and Walter has found that the vanadyl ion may be sorbed to a small extent
onto an anion-exchange resin in the presence of fluoride ion (66). The complex, $\text{VOCl}^+$, is formed with chloride ion (96), and again, vanadyl ion may be sorbed onto an anion-exchange resin from solutions containing high concentrations of chloride ion (97). Furman and Garner have reported that high concentrations of chloride ion produce only minor changes in the visible absorption spectrum of the vanadyl ion (86), but failed to report the nature of the changes produced. Other workers have described a spectrophotometric method for the estimation of vanadyl ion utilising the absorption bands of the visible absorption spectrum of the vanadyl ion, and have reported that the method was affected to a negligible extent by the presence of chloride ion (53). The bromide and iodide complexes of the vanadyl ion have not previously been investigated, in fact, vanadyl iodide has only recently been isolated from aqueous solution (98,99).

Interactions between vanadyl and sulphate ions in solution appear to be slight, since spectrophotometric methods of estimating vanadyl ion have been reported to be unaffected by wide variations in pH and concentration of sulphate ion in the solutions (53,100). Britton has shown that vanadyl hydroxide is precipitated from vanadyl/sulphate solutions of pH 4 (49). Other workers have prepared crystalline double sulphates which involve vanadyl sulphate (50,101), and also, a compound containing quadri- and quinquevalent vanadium in an equimolar ratio has been reported in solutions containing sulphate ion (102).

Walter has detected anionic, carbonato complexes of the vanadyl ion in ion-exchange studies (66), and the solvent-extraction studies performed by Zeigler have shown that vanadyl ion is complexed by thiosulphate ions in aqueous solution (103). Amide and imide derivatives of the vanadyl ion have also been investigated (51), and
the precipitate, which is formed by the addition of ferrocyanide ion to vanadyl-containing solutions, has been found to be of uncertain composition (104, 105).

References to systems involving vanadyl ion and orthophosphate species are few in number. Zolotavin and Kuznetsova claim to have established the formula, \((\text{VO})_2(\text{PO}_4)_2\), for vanadyl phosphate in the solid state, and have evaluated the solubility product of this material in aqueous solution (106). Furthermore, it has been shown that vanadyl ion may be separated quantitatively from phosphate in solution by sorbing the vanadyl ion onto a cation-exchange resin and washing the resin with water (107, 108). Orthophosphate complexes of the vanadyl ion have not previously been reported in the literature. However, species of this kind may be expected in vanadyl/phosphate solutions since Santini and co-workers, in reporting a spectrophotometric method for the estimation of vanadyl ion, have mentioned that the optical densities of vanadyl-containing solutions are unstable in the presence of phosphate (53).

II. Purpose of the investigations.

The work, described in the following pages, was undertaken in an attempt to extend the knowledge of the complex-forming reactions of various anions, particularly inorganic anions, with the vanadyl ion in aqueous solution. This was considered to be of interest, not only as a study of the complexes of the vanadyl ion in its own right, but also to observe the effect of the oxide ion on the complexing tendencies of the formally quadripotential metal ion of the vanadyl group. The oxide ion would be expected
to influence the tendency to complex formation by reducing the effective charge located on the vanadium ion, and by restricting the space around the metal ion, which would be required by complexing agents in order to compete effectively for co-ordination sites with co-ordinated water molecules, and to form bonds with the central metal ion.

The work was concentrated mainly on the vanadyl/phosphate system since this system appeared to suffer most from obscurity. Conclusions from previous studies, concerning the nature of thiocyanato vanadyl complexes in aqueous solution, appear, to some extent, to be contradictory. For this reason, it was decided to repeat and extend certain of the spectrophotometric investigations, which have been reported by Furman and Garner, and to supplement them by ion-exchange experiments, in an attempt to enable more satisfactory conclusions to be drawn concerning the nature of the thiocyanato vanadyl complexes formed in solution. The experiments, in which the effects of other anions on the properties of the vanadyl ion were studied, were less extensive since they were envisaged as fulfilling a predominantly supporting role.

The experiments discussed in the following pages involved the study of ion-exchange, pH-titration, spectrophotometric, and, in one instance, magnetic phenomena. The data obtained in this way have been used in an attempt to establish the composition of the complexes formed in the solutions studied. Attempts were not made to estimate the stability constants of these complexes with great precision since it was generally found that a number of such species co-existed in the solutions. The problems which would be associated with studies of this kind have been discussed in detail in paragraph D.I.
SECTION B.

PREPARATIVE AND ANALYTICAL METHODS.
Standard preparative and analytical procedures were carried out as described by Kolthoff and Sandell (109) and unless specifically stated to the contrary, analytical grade reagents were used in all experimental work. Other experimental procedures which were employed are described in the following paragraphs.

I. Preparation of solutions and materials.

(a) Ammonium molybdate reagent. The reagent was prepared by dissolving hydrated ammonium molybdate in water, and adding nitric acid to produce a solution which was 15% in the acid. The solutions were filtered immediately before use to remove small quantities of molybdenum trioxide which precipitated from the solutions on standing for long periods of time.

(b) Potassium perchlorate. An equivalent quantity of perchloric acid solution (3M) was added to a solution of potassium hydroxide (3M). After cooling, the solid precipitated was filtered off, washed with water, and dried to constant weight at 110°C. This material was not hygroscopic, and was used as a primary standard.

(c) Vanadyl/sulphate solution. A solution was prepared either,
   (i) by dissolving hydrated vanadyl sulphate, $\text{VOSO}_4\cdot\text{xH}_2\text{O}$, in water and adding sufficient sulphuric acid to prevent hydrolysis,
   or (ii) by suspending vanadium (V) pentoxide in water, adding sulphuric acid solution (2N), heating the mixture to 80°C., and passing sulphur dioxide until the solid had almost completely dissolved. The residue was then filtered off, and the solution evaporated to half volume to remove sulphur dioxide. Sulphuric acid was added as required during the evaporation to prevent precipitation.
The vanadium (V) pentoxide and hydrated vanadyl sulphate were not of analytical grade, but were found to be sufficiently free from impurity for immediate use.

(d) Vanadyl/perchlorate, phosphate, and thiocyanate solutions. Vanadyl/perchlorate solution was prepared by passing vanadyl/sulphate solution through a column of hydrogen-form, Zeo-karb 225 resin to convert the resin to the green-coloured, vanadyl form. The resin was then washed with water until the effluent was free from sulphate ion. Vanadyl/perchlorate solution was finally obtained as effluent from the column on eluting with a solution of perchloric acid of the required concentration.

Vanadyl/phosphate and vanadyl/thiocyanate solutions were prepared in a similar manner by eluting vanadyl-form resin with phosphoric acid, and ammonium thiocyanate solutions respectively.

(e) Water. Water, which had been distilled from glass apparatus and stored in contact with the atmosphere, was used in all experimental work, unless it was necessary to use de-ionised water. De-ionised water was prepared by passing the former distilled water through a column containing a mixed bed of hydrogen and hydroxyl forms of ion-exchange resins. Water treated in this way was transferred through a system completely closed to the atmosphere to the vessel in which it was ultimately used.

(f) The preliminary treatment of ion-exchange resins. Resins were stirred with portions of water until a clear liquid was obtained on decanting from the resin. This was repeated with acetone, and then again with water. The resin was then transferred in a slurry with water to an ion-exchange column before backwashing and resettling repeatedly with water to form a resin bed through which a solution
flowed in an even, non-channelling stream.

In the case of anion-exchange resin, De-acidite FF, the column was then eluted with hydrochloric acid (2N) to convert the resin to the chloride-form before washing with de-ionised water until the effluent was free from chloride ion. Finally, the resin was removed from the column, filtered, and air-dried. The dry resin was screened before use to give resin batches of uniform bead size.

With cation-exchange resin, Zeo-karb 225, the column was eluted with concentrated hydrochloric acid to convert the resin to the hydrogen-form and remove other cations, particularly ferric ion, originally sorbed onto the resin. Elution was then continued with dilute hydrochloric acid, and finally with water until the effluent was free from chloride ion. Finally, the resin was removed from the column and treated as described above for the anion-exchange resin.

All batches of resin used were of 40 - 80 mesh, except in the separation procedure described in paragraph III.

(g) The preparation of ion-exchange resins in various ion forms. The preparation of hydrogen-form, Zeo-karb 225 resin has been described in paragraph I(f). This resin was converted to the vanadyl form by eluting with vanadyl/sulphate solution until the hydrogen ion had been completely replaced by vanadyl ion. The resin was then washed with water until the effluent was free from electrolyte, removed from the column, filtered, and air-dried. Other forms of the resin were prepared in a similar manner.

The preparation of chloride-form, De-acidite FF resin has also been described in paragraph I(f), and this material was
converted to other forms by procedures similar to that described for the cation-exchange resin. However, de-ionised water was used to wash the anion-exchange resins.

II. Methods of estimation.

(a) Chloride ion. The Volhard method of estimation was used, and this was found to be unaffected by the presence of phosphate. Vanadyl ion, when present, was removed from solution as described in paragraph III before estimating chloride.

(b) Perchlorate and sulphate ions. An estimation of the concentration of these ions was not required in solutions which also contained other anions. Thus, the estimation was carried out by replacing metal ions in solution by an equivalent quantity of hydrogen ion, as described in paragraph III, and titrating with standard sodium hydroxide solution using phenol phthalein as indicator.

(c) Phosphate ion.

(i) By titration with sodium hydroxide solution. When present in solution as phosphoric acid alone, phosphate was estimated by pH-titration against a standard solution of sodium hydroxide. The volume of alkali used to reach the point of inflexion in the titration curve was found to be exactly reproducible.

(ii) By precipitation as ammonium phosphomolybdate. This method was used when ions additional to those of phosphoric acid were present in solution. A four times excess of ammonium molybdate reagent was used to effect a quantitative precipitation of the phosphate from solutions 2% in ammonium nitrate at 50°C.
The solutions were allowed to stand for 12 hours before filtering off the precipitate, washing with nitric acid (1%), and drying to constant weight at 110°C. It was found essential to allow a constant time of 20 minutes for the precipitates to cool after drying, for sufficient water was absorbed over longer periods, as a result of competition with the dessicant, to give rise to inaccurate weights for the precipitates. The precipitates treated in this way were considered to have the following composition:

\[(\text{NH}_4)_3\text{PO}_4\cdot 12\text{MoO}_3\cdot 2\text{HNO}_3\cdot \text{H}_2\text{O}\]

(see ref. 109, pages 378 - 380).

Vanadyl ion was found to interfere in the estimation of phosphate since it caused precipitation in method (i), and was co-precipitated as vanado (V) molybdate after being oxidised by nitrate ion in method (ii). It was necessary, therefore, to remove vanadyl ion from all solutions before estimating phosphate, and this was performed as described in paragraph III.

(d) Vanadyl ion. Vanadyl ion was estimated by acidifying aliquots of solution with sulphuric acid, heating to boiling, and titrating with a standard solution of potassium permanganate (0.05 N) to a straw-coloured end point. The reaction may be represented by the following equation:

\[2\text{VO}^{++} + \text{H}_2\text{O} + (\text{O}) = 2\text{VO}_2^+ + 2\text{H}^+\]

The end point obtained in this way was found to be reproducible to within two drops of the permanganate solution in a titration of 20 ml.

It was found that perchlorate, phosphate, and acetate ions did not interfere with this method of estimating vanadyl ion. However, nitrate, chloride, and thiocyanate ions did interfere, so that it was necessary to remove these ions before estimating vanadyl.
ion as described in paragraph III. Nitrate was found to interfere in the titration by oxidising the vanadyl ion, rapidly when hot (53,54). Chloride and thiocyanate ions also interfere for they are oxidised with the vanadyl ion by potassium permanganate in acid solutions (109,110).

(e) Determination of the capacity, and vanadyl-ion content of Zeokerb 225 resin. Weighed samples of the resin in the vanadyl form were transferred to ion-exchange columns and eluted with sulphuric acid (6N) to remove the vanadyl ion. The eluate was collected and the vanadyl ion content estimated by titrating with a standard solution of potassium permanganate. The resin was then washed with water until the effluent was free from electrolyte before eluting with sodium chloride solution (0.5 M) over a period of three hours. The hydrogen ion displaced from the resin in this way was estimated by titrating the latter effluent with a standard solution of sodium hydroxide (0.1 N). The vanadyl ion content of a resin was expressed in m.moles/g. of air-dried (vanadyl-form) resin.

The capacity of a resin was expressed in m.equivs./g. of air-dried (vanadyl-form) resin.

(f) Determination of the capacity and phosphate content of De-acidite FF resin. Weighed samples of phosphate-form resin were eluted with sodium nitrate solution (2M) over a period of 12 hours to displace the phosphate ion. The phosphate in the effluent was then estimated gravimetrically by precipitation as ammonium phosphomolybdate.

The capacity of the resin was estimated by converting the same samples of resin to the chloride form by eluting with sodium chloride solution and subsequently washing with de-ionised water until the effluent was free from electrolyte. The chloride ion
was then displaced by eluting with sodium nitrate solution (2M) and estimated by the Volhard method on samples of the eluate.

The phosphate content and capacity of the resin were expressed in similar ways to those described above for the cation-exchange resin.

III. Separation of cations, including vanadyl ion, from anions in solution.

Columns containing hydrogen-form, Zeo-karb 225 resin were employed. The resin used was of small bead size, greater than 100 mesh, to permit a rapid exchange of ions between the resin and solution phases (14), and was initially washed free from electrolyte with water. The cation-containing solution was then passed through the column and the effluent collected before washing the column again with water (3 x 10ml., followed by 1 x 200 ml.). The effluent and washings were combined and used in the estimation of the anion content of the original solution. The exchange reaction effected a replacement of the cations in the original solution by an equivalent quantity of hydrogen ion as follows:

\[
V_{0}^{++} + 2H^{+}R \rightarrow 2H^{+} + V_{0}^{++}R_{2}.
\]

R represents one exchange site of the resin.

Cationic complex species that may have initially been sorbed onto the resin were completely dissociated on washing since a quantitative recovery of the anion in the original solution was achieved in this way. In removing vanadyl ion from solution, it was important to ensure that the green band due to absorbed vanadyl ion, did not reach the bottom of the column during the separation
process. Vanadyl ion was not easily sorbed from solutions of high acidity. This was overcome by diluting the solutions ten times so that the divalent vanadyl ion could be sorbed more readily from the diluted solutions which were then of lower acidity (111,112).

Cations were recovered quantitatively after sorption onto the resin by eluting with a solution of sulphuric acid (6N). This process simultaneously reconverted the resin to the hydrogen form, and thus, after removing electrolyte from the resin by washing with water, the column was ready for use in further separation procedures.

IV. Measurement of pH.

A Cambridge pH-meter was used in conjunction with a glass electrode and a calomel reference electrode. When not in use, the glass electrode was immersed in dilute hydrochloric acid, and the calomel electrode in a saturated solution of potassium chloride. Both electrodes were thoroughly washed with water and the instrument calibrated against a standard buffer solution of pH 4 before use. The calibration of the instrument was checked in the same manner after use. Further checks were made during long series of observations to ensure that the instrument was recording pH consistently.

It was found that the instrument gave unsteady readings for solutions containing perchlorate ion if both electrodes were immersed directly into the solution for which the pH was being measured. This was overcome by dipping the calomel electrode into a saturated solution of potassium chloride, and linking this to the solution under observation through a salt bridge. The glass electrode was immersed directly into the solution under test in the
usual manner. When a salt bridge was used, the instrument was calibrated with the bridge in position, although this was observed to have no appreciable effect on the calibration. The electrolyte used in the bridge was saturated in potassium chloride, and was prepared by dissolving agar-agar and potassium chloride in warm water.

V. Measurement of optical density.

The solutions under observation were placed in quartz cells which gave a path length of 1 cm. through the solution as presented to the incident beam. Each cell was washed with water, and then four times with the solution to be examined before finally introducing solution for observation. The optical densities were measured with Unicam SP 500 and SP 600 spectrophotometers with light of wavelengths over the range 1000 to 250 μm.
SECTION C.

THE APPLICATION OF ION-EXCHANGE METHODS
TO THE STUDY OF SYSTEMS
CONTAINING COMPLEXES OF THE VANADYL ION.
I. Ion-exchange resins.

Although the sorption and release of ions has been studied in soils and similar natural materials from an early date, it was not until the nineteenth century that Thompson and Way recognised that the phenomenon could be attributed to an ion-exchange process. Subsequent investigations have demonstrated that a great variety of minerals contain certain ions which can be exchanged for those present in a surrounding solution. The ease of the exchange reaction depends to a considerable extent upon the structure of the minerals. The zeolites and ultramarines have open silicate structures which permit an easy diffusion of ions throughout each of the mineral fragments. Thus, cations, such as calcium and sodium, in these minerals may be readily and completely replaced by cations from solutions with which they are in contact. The mica and feldspar structures are more dense and do not permit a facile diffusion of ions. With these minerals, therefore, it is only possible for the ions near the surface of each fragment to be replaced, so that to effect an extensive exchange of ions, the minerals must be in a very fine state of subdivision.

Exploitation of the ion-exchange properties of minerals for industrial and analytical purposes, even those minerals permitting a facile exchange of ions, was only possible on a limited scale since the minerals were generally unable to withstand great extremes of acidity and alkalinity. Moreover, the mineral fragments were not resistant to mechanical stress, and varied sufficiently in crystal structure to result in inconsistent properties. This prevented extensive quantitative studies of the ion-exchange process using mineral exchangers. These limitations have since been overcome by the development of synthetic ion-exchange resins.
A variety of synthetic ion-exchange materials has been developed and most of these have a similar structure. This consists of an extensive hydrocarbon skeleton to which polar functional groups are bonded to give the resins ion-exchange properties. The investigations, described in the following pages, involved the use of resins with a cross-linked polystyrene structure, for although other types of hydrocarbon skeleton have been developed, the polystyrene resins have proved to be the most useful. The cross-linking of the polystyrene chains is achieved by mixing divinyl-benzene with styrene before carrying out the polymerisation reaction during synthesis. This cross-linked type of structure gives the resins great resistance to physical and chemical stresses. Moreover, since the resin beads are essentially molecules of very high molecular weight, they are virtually insoluble in aqueous solutions.

The cation-exchange resins have been developed and investigated most extensively, and functional groups of various types have been incorporated in their structure. These include sulphonic, phosphonic, and phenolic groups in the polystyrene resins, and methylenesulphonic and carboxylic groups in resins of the phenol-formaldehyde type. Cation-exchange resins have also been developed which contain more than one type of functional group. Anion-exchange resins may be divided into two main types, the weakly-basic exchangers in which the active sites are provided by amine groups, and the strongly-basic exchangers with quaternary ammonium groups. The experiments described in the following work involved the use of Zeokarb 225 resin, a strongly-acidic, cation exchanger with sulphonic functional groups, and De-acidite FF resin, a strongly-basic, anion-exchange resin with quaternary methylammonium groups.
The presence of fixed ionic groups on the hydrocarbon skeleton renders ion-exchange resins very hydrophilic. Various factors affect the extent to which water is taken up by a resin. The hydration of the fixed and counter ions of the functional groups accounts for a considerable uptake of water, depending on the density of distribution of the groups throughout the resin. An electrolyte solution may be considered to be formed within the resin beads in this way. This, due to its osmotic pressure, causes a further uptake of water from the surrounding aqueous phase. The factors opposing the uptake of water include the osmotic pressure of the aqueous phase surrounding the resin beads, and the pressure developed within each bead of resin. The latter factor arises because the mass of water accommodated within each bead causes the hydrocarbon network to approach its swelling limit. The resins cease to take up water as these opposing groups of forces balance each other in a state of equilibrium. The porosity of the resin, and the type and distribution density of its functional groups are the primary structural factors affecting the ability of a resin to take up water. An estimate of the combined effects may be expressed in the 'water-regain' value. This may be defined as the mass of water taken up per gram of dry resin, and must be measured under carefully controlled conditions.

The uptake of water is effected by the migration of water molecules through spaces in the hydrocarbon skeleton of the beads of resin. As the resin swells, the spaces become enlarged to a limit depending on the water-regain value. Exchanging ions also diffuse through these spaces from an external solution to the exchange sites situated within the resin, and the displaced counter-ions migrate out in a similar manner as they are exchanged. This mechanism for the exchange process is substantiated since large condensed ions are
virtually excluded from resins of low water-regain for the spaces available to them through which to diffuse to the exchange sites are too small (113). Although ion-exchange resins are non-crystalline materials, therefore, the exchange of the counter-ions of the functional groups may be considered to proceed in a manner analogous to that in which ions are replaced from the crystal-lattice of zeolitic minerals. Electrolytes, other than the exchanging ions also diffuse through the surface of the resin beads. However, the presence of the fixed electrolyte of the functional groups generally causes the concentration of such electrolytes to be lower within the resins than in the surrounding solution phase.

While providing a useful physical model on which to base an understanding of the ion-exchange process, the crystal-lattice theory does not readily lend itself to a quantitative description of the ion-exchange phenomena. The electrical double-layer theory of ion-exchange, in drawing an analogy with electrochemical theory, postulates the formation of a fixed layer of ions, that is those parts of the functional groups linked to the hydrocarbon skeleton, and a diffuse layer of counter-ions. This theory provides a treatment which is potentially quantitative, but while accounting for an exchange of ions during which electrical neutrality of the resin is maintained, it is unable to support the observed constancy of the exchange capacity of the resins when the pH and concentration of the electrolyte in the surrounding solution are varied. The Donnan theory, however, has been successfully applied to give a quantitative description of ion-exchange phenomena in systems involving dilute aqueous solutions and synthetic ion-exchange resins with strongly-acidic, sulphonic, functional groups (111,112).
In applying the Donnan theory, ion-exchange systems are considered as heterogeneous systems. The resin phase is treated as a highly-ionised salt solution in which the ionic groups attached to the resin are restricted to one side of the membrane, and the resin-solution interface as a membrane through which electrolyte may diffuse. The following system may now be considered in which an exchange reaction takes place between hydrogen and sodium ions on a cation-exchange resin,

\[
\begin{align*}
R^- & \quad Cl^- \\
H^+ & \quad H^+ \\
Na^+_{r} & \quad Na^+_{s} \\
Cl^-_{r} & \quad Cl^-_{s}
\end{align*}
\]

Resin phase. Solution phase.

When the activity of the species is represented by the symbol 'a', the Donnan theory shows that,

\[
\begin{align*}
a_{Na}^{+} \cdot a_{Cl}^{-} &= a_{Na}^{+} \cdot a_{Cl}^{-} \\
\text{and,} \\
a_{H}^{+} \cdot a_{Cl}^{-} &= a_{H}^{+} \cdot a_{Cl}^{-}
\end{align*}
\]

at equilibrium.

Then, on dividing these equations,

\[
\frac{a_{Na^{+}}}{a_{Na^{+}}} = \frac{a_{H^{+}}}{a_{H^{+}}}
\]

\[
\frac{a_{Na^{+}}}{a_{Na^{+}}} = \frac{a_{H^{+}}}{a_{H^{+}}}
\]

Thus, equilibrium is established in the system when the ratio of the activities of hydrogen and sodium ions in the resin and solution phases are equal.
Now, this exchange reaction may be represented in the following way:

\[ \text{Na}^+_s + \text{H}^+_r = \text{H}^+_s + \text{Na}^+_r \]

Then, on applying the Law of Chemical Equilibrium,

\[ K = \frac{a_{\text{Na}^+_r} a_{\text{H}^+_s}}{a_{\text{Na}^+_s} a_{\text{H}^+_r}} \]

Now the activity coefficients of species in solution tend to unity when the solutions are very dilute. Thus, when the molar concentrations, and activity coefficients of species are represented by the symbols 'C', and 'f' respectively, the exchange reaction may be represented in the following way for a system which involves dilute solutions:

\[ K^1 = \frac{C_{\text{Na}^+_r} C_{\text{H}^+_s}}{C_{\text{Na}^+_s} C_{\text{H}^+_r}} \times \frac{f_{\text{Na}^+_r}}{f_{\text{H}^+_r}} \]

That is, \[ K^1 \times \frac{f_{\text{H}^+_r}}{f_{\text{Na}^+_r}} x \frac{C_{\text{H}^+_r}}{C_{\text{Na}^+_r}} = \frac{C_{\text{Na}^+_r}}{C_{\text{Na}^+_s}} \]

Thus, the distribution of sodium ion between resin and solution phases in a system involving a dilute solution will depend both upon the concentration of the competing ion in the system, and upon the ratio of the activity coefficients of the two ions in the resin phase.

The equilibrium in a system involving an exchange between hydrogen and bivalent metal cations may be represented in the following way:

\[ \text{M}^{2+}_s + 2\text{H}^+_r = 2\text{H}^+_s + \text{M}^{2+}_r \]
Then, by an exactly analogous procedure to that described above, it may be shown that:

\[ K^{11} \times \frac{f_H^2}{f_{H^+}} x \frac{C_H^2}{C_{H^+}} = \frac{C_{M^+}^2}{C_{M^2}^2} \]

Strongly-acidic, cation-exchange resins are generally found to have a higher affinity for divalent ions than monovalent ions in systems involving dilute solutions. This phenomenon may be explained by the Donnan treatment if the divalent ions have the lower activity coefficient in the resin phase. This may reasonably be expected by analogy with the activity coefficients of ions observed in aqueous solutions.

By considering general cases, it may be shown, therefore, that the Donnan theory provides an explanation for the ion-exchange phenomena observed in systems involving dilute solutions. Quantitative description of the observed phenomena becomes more complex, however, for systems in which the solutions cannot be considered dilute, for then, the activity coefficients of ions in the solution phase differ appreciably from unity and may not be estimated individually. Moreover, the extent to which solution is taken up by a resin depends upon the ionic strength of the solution phase, and this may not be considered to be a constant factor in systems in which resins are brought to equilibrium with solutions which are not dilute. This, in turn, may be expected to affect the activity coefficients of the ions in the resin phase. Furthermore, the activity of the electrolyte in the solution occluded by the resin will vary, and will then assume an unknown significance. The theoretical treatments are further complicated when applied to systems involving more than two exchanging ions. Finally, the possibility of physical
adsorption of electrolyte onto the hydrocarbon skeleton must also be considered.

Baumann, Eichhorn, Gregor, and other workers have studied the Donnan theory in relation to cation-exchange systems (111, 112), and it may be presumed that the foregoing considerations apply equally to systems involving anion-exchange resins. The solutions used in the experiments described in the following pages were not dilute. For this reason, it was necessary to make allowance for the effects described above in some of the experiments carried out. This was achieved by analysing control solutions in which conditions were identical to those of the experimental solutions containing vanadyl ion, except for the replacement of the vanadyl ion by an equivalent amount of hydrogen ion. In the experiments which involved weak multibasic acids, the analysis of control solutions also made allowance for a change during equilibration in the ratio of uncomplexed anions containing different amounts of proton which were sorbed onto the resin.

The vanadyl systems studied were found to be of a labile nature. Thus, the resins could not be washed free from solution with which they had been equilibrated without disturbing the state of the species sorbed to a significant extent. For this reason, the solution phase was the only phase analysed in the systems studied.
II. Theories underlying methods used, experimental procedures, observations, and conclusions.

(a) The removal of vanadyl ion from vanadyl-form, cation-exchange resin.

(i) Theoretical and experimental principles. The experiments were performed to detect complex-forming reactions involving vanadyl ions and anions derived from the acids used. Where R represents one exchange site of a strongly-acidic, cation-exchange resin, the distribution of hydrogen and vanadyl ions between resin and solution phases is governed by the following equilibrium:

\[
\text{VO}^{2+} + 2R + 2\text{H}^+ \rightleftharpoons 2\text{H}^+ + \text{R} + \text{VO}^{2+}
\]

Now, the Donnan theory, discussed in paragraph C.I for a system containing divalent cations, shows that the hydrogen ion concentration in the systems will affect the distribution of vanadyl ion between resin and solution phases. This may be studied by bringing constant masses of vanadyl-form resin to equilibrium with constant volumes of solutions of an acid in which the pH is varied over a suitable range. To carry out a study of this kind, it would be necessary to use an acid which gave an anion on dissociation which does not react in any way with the vanadyl ion. Perchloric acid was used in the following experiments since it has generally been found to have negligible complexing power with metal ions of low charge, and only a very slight tendency to form complexes with tervalent cations.

Aqueous solutions of acids at the same pH can be considered, as a first approximation, to have identical concentrations of hydrogen ion. This would be independent of the strength of the acid.
Now, the simple exchange equilibrium between vanadyl and hydrogen ions, shown above, would be displaced if an acid solution effected a removal of vanadyl ion from vanadyl-form resin differing from that produced by a solution of perchloric acid of the same pH. This would be explained by the vanadyl ion taking part in complex-forming reactions, and thus establishing equilibria involving vanadyl ion in the system, other than the simple exchange equilibrium.

Vanadyl ion may be expected to react more readily with an oppositely charged anion to form complex species than with a neutral acid molecule. If the acids studied are monobasic, or effectively monobasic as for example phosphoric acid, solutions of the same pH may be considered to contain equivalent concentrations of anion derived from the acid. Thus, a qualitative estimate of the extent of complex formation may be obtained in acid solutions containing vanadyl ion by comparing the extent of removal of the vanadyl ion effected by the acids from vanadyl-form resin with that produced by perchloric acid at the same pH.

Since vanadyl ion is replaced by hydrogen ion in the exchange equilibrium shown above, it is apparent that the concentration of vanadyl ion in the resin phase must initially be the same in all experiments for which results are to be compared. This was achieved by preparing the vanadyl-form resin required for the complete series of experiments in one batch.
(ii) **Experimental procedure, observations, and conclusions.**

Constant masses of air-dried, vanadyl-form, Zeo-karb 225 resin, containing 1.73 m.moles of vanadyl ion per gram, were added to constant volumes of acid solutions of known pH. The systems prepared in this way were shaken and allowed to stand for 7 days to attain equilibrium before estimating the vanadyl ion removed from the resin using measured samples of the solution phase. This was performed with solutions of hydrochloric, perchloric, phosphoric, sulphuric, and acetic acids, each at 7 different pH values over the range 0.00 to 1.50.

The extent of removal of vanadyl ion effected by the acid solutions from vanadyl-form resin are shown in table C1, and figure 1. The figures given below are average values obtained from the analysis of a series of three identical systems at equilibrium.

**TABLE C1.**

<table>
<thead>
<tr>
<th>Original pH of solution</th>
<th>Percentage vanadyl ion removed from resin.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>with HClO₄</td>
</tr>
<tr>
<td>0.00</td>
<td>83.3</td>
</tr>
<tr>
<td>0.25</td>
<td>70.2</td>
</tr>
<tr>
<td>0.50</td>
<td>55.8</td>
</tr>
<tr>
<td>0.75</td>
<td>46.3</td>
</tr>
<tr>
<td>1.00</td>
<td>35.9</td>
</tr>
<tr>
<td>1.25</td>
<td>25.6</td>
</tr>
<tr>
<td>1.50</td>
<td>17.6</td>
</tr>
</tbody>
</table>
Removal of vanadyl ion from vanadyl-form resin by acid solutions of varying pH.

Fig. 1.

- ▲ phosphoric acid.
- ▼ sulphuric acid.
- ◇ hydrochloric acid.
- ○ perchloric acid.
- □ acetic acid.

Percentage removal of vanadyl ion.

pH

0.00 0.25 0.50 0.75 1.00 1.25 1.50
Under comparable conditions of pH, the observations show that the removal of vanadyl ion from vanadyl-form resin is effected by the acids studied in the following order of efficiency:

\[ \text{CH}_3\text{CO}_2\text{H} < \text{HClO}_4 < \text{HCl} < \text{H}_2\text{SO}_4 < \text{H}_3\text{PO}_4 \]

The removal curve for perchloric acid, shown in figure 1, exhibits the characteristics expected of a system in which the metal ion is involved only in a simple exchange equilibrium (cf. 5,16). In this case, vanadyl and hydrogen ions are involved in the equilibrium. The removal curves for the other acids, however, are displaced from that for perchloric acid in such a way as to indicate that the vanadyl ion is complexed in these systems by species derived from the acid. Thus, the vanadyl ion may be seen to have a slight tendency to form complex species with chloride ion, which is most pronounced at high concentrations of the anion. The removal curves indicate that similar phenomena characterise the vanadyl/sulphate system. However, the acid in this case is a strong dibasic acid. Under comparable conditions of pH, therefore, the total concentration of anion in the sulphate solutions is lower than that of a solution of perchloric acid. Then, the tendency in the vanadyl ion to form sulphato complexes, while remaining small, is shown to be greater than the tendency to form chloro complexes.

The greatest removal of vanadyl ion, and therefore, the greatest tendency to complex formation, was observed with the solutions of phosphoric acid. Vanadyl ion was removed to an extent intermediate between that observed in phosphate systems involving other divalent ions, and those involving tervalent ions. This can be shown to greater advantage by comparing the ratios of the percentages of metal ions removed by phosphoric and perchloric acids under the same conditions of pH, shown in table C2. The figures
given for ions other than vanadyl ion were calculated from data reported by Genge and Salmon (16). The ratios of the amounts of the different cations removed by the two acids are not affected by different metal ion contents of the resins, or by differing ratios of resin mass to solution volume which were employed in the experiments since these factors were presumably maintained constant during the studies with each ion considered.

TABLE C.2.

<table>
<thead>
<tr>
<th>Solution pH</th>
<th>Ratios of the amount of cation removed by $\text{H}_2\text{PO}_4^-$ : the amount of cation removed by $\text{HClO}_4^-$ with $\text{Fe}^{+++}$</th>
<th>with $\text{Al}^{+++}$</th>
<th>with $\text{VO}^{++}$</th>
<th>with $\text{Mn}^{++}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>2.00</td>
<td>1.74</td>
<td>1.41</td>
<td>slightly</td>
</tr>
<tr>
<td>0.50</td>
<td>2.59</td>
<td>2.00</td>
<td>1.62</td>
<td>greater</td>
</tr>
<tr>
<td>0.75</td>
<td>3.36</td>
<td>2.25</td>
<td>1.79</td>
<td>than</td>
</tr>
<tr>
<td>1.00</td>
<td>3.15</td>
<td>2.25</td>
<td>1.83</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The extent of the removal of vanadyl ion effected by solutions of acetic acid was found to be highest with the more dilute solutions, and was low as compared with the extent of the removal effected by other acids. This may be explained by the formation of cationic complex species in the system which are sorbed fairly strongly onto the cation-exchange resin. The positive slope of the removal curve for acetic acid (fig. 1.) shows that the formation of such complexes is favoured by high concentrations of acetic acid.
(b) Determination of the sign of the charge of complex vanadyl ions.

(i) Theoretical and experimental principles. Where 'R' represents one exchange site of a strongly-acidic, cation-exchange resin, a cationic complex vanadyl ion, $V_{c}^{X^+}$, formed in a system would be expected to be distributed between resin and solution phases in a manner governed by the equilibrium:

$$V_{c}^{X^+}R_{x} + xH^+ \rightleftharpoons V_{c}^{X^+} + xH^+R$$

Thus, in a system in which the vanadyl ion forms cationic complex species containing neutral or anionic ligand groups, the ligand would be sorbed onto a cation-exchange resin together with vanadyl ion. Cationic complex vanadyl species may be demonstrated, therefore, by detecting a reduction in the total ligand concentration of a solution on bringing it to equilibrium with hydrogen-form, cation-exchange resin. Similarly, a reduction in the total concentration of vanadyl ion in a solution, after bringing it to equilibrium with an anion-exchange resin, would show the formation of anionic complexes of the vanadyl ion in the system.

The detection of complexes of either charge type depends upon the estimation of a reduction in the total concentration of an ion. This reduction may be small. Now, as described in paragraph C.I, air-dried resins take up water and electrolyte on coming into contact with an aqueous solution. This, therefore, may produce an increase in the concentration of the ions present in the solution remaining outside the resin. Thus, the reduction in concentration of an ion in the solution due to sorption of complex species may be offset by the uptake of solution by the resin. This was overcome in the attempts to detect cationic complex species by the use of control solutions, as described in paragraph C.I, and by comparing
the concentrations of the anion in the control and experimental, vanadyl-containing solutions at equilibrium. Control solutions were not used in detecting anionic vanadyl complexes as a reduction in the total concentration of vanadyl ion was observed, in spite of opposing effects of solution uptake by the resin.

(ii) Experimental procedure, observations, and conclusions. Anionic, complex, vanadyl species were detected in the phosphate system by adding measured volumes of an analysed vanadyl/phosphate solution to weighed samples of phosphate-form, De-acidite FF resin, and estimating the vanadyl content of the solution after standing for 7 days when the system had attained equilibrium. Similar procedures were used in detecting anionic thiocyanato and sulphato complexes of the vanadyl ion.

Attempts were made to detect cationic complex–vanadyl species in phosphate, sulphate, and thiocyanate containing solutions by estimating the concentration of the anion in experimental, vanadyl-containing solutions, and in control solutions. In these experiments, analysed solutions were brought to equilibrium with hydrogen-form, Zeo-karb 225 resin. Data obtained in these studies are presented in tables C.3 to 8.

**TABLE C.3.**
(detecting anionic phosphato complexes)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial total vanadyl concentration.</td>
<td>0.1998 M.</td>
</tr>
<tr>
<td>Final total vanadyl ion concentration.</td>
<td>0.1980 M.</td>
</tr>
<tr>
<td>Percentage uptake of vanadyl ion.</td>
<td>0.9</td>
</tr>
<tr>
<td>Initial colour of resin.</td>
<td>pale-orange</td>
</tr>
<tr>
<td>Final colour of resin.</td>
<td>pale-green</td>
</tr>
<tr>
<td>pH of solutions at equilibrium.</td>
<td>0.40 - 0.45</td>
</tr>
</tbody>
</table>
### TABLE C.4.
(detecting anionic sulphato complexes)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial total vanadyl concn.</td>
<td>0.0555 M.</td>
</tr>
<tr>
<td>Final total vanadyl concn.</td>
<td>0.0521 M.</td>
</tr>
<tr>
<td>Percentage uptake of vanadyl ion</td>
<td>6.1</td>
</tr>
<tr>
<td>Initial colour of resin.</td>
<td>pale-orange</td>
</tr>
<tr>
<td>Final colour of resin.</td>
<td>pale-green</td>
</tr>
<tr>
<td>pH of solutions at equilibrium.</td>
<td>2.11 - 2.16</td>
</tr>
</tbody>
</table>

### TABLE C.5.
(detecting anionic thiocyanato complexes)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial total vanadyl concn.</td>
<td>0.0475 M.</td>
</tr>
<tr>
<td>Final total vanadyl concn.</td>
<td>0.0172 M.</td>
</tr>
<tr>
<td>Percentage uptake of vanadyl ion</td>
<td>63.8</td>
</tr>
<tr>
<td>Initial colour of resin.</td>
<td>pale-orange</td>
</tr>
<tr>
<td>Final colour of resin.</td>
<td>deep-green</td>
</tr>
</tbody>
</table>

### TABLE C.6.
(detecting cationic phosphato complexes)

<table>
<thead>
<tr>
<th>Solution</th>
<th>exptl.</th>
<th>ctrl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial total phosphate concn.</td>
<td>0.3562 M.</td>
<td>0.3562 M.</td>
</tr>
<tr>
<td>Final total phosphate concn.</td>
<td>0.3669 M.</td>
<td>0.3683 M.</td>
</tr>
<tr>
<td>%age increase in phosphate concn.</td>
<td>3.0</td>
<td>3.4</td>
</tr>
<tr>
<td>Initial total vanadyl concn.</td>
<td>0.0295 M.</td>
<td>—</td>
</tr>
<tr>
<td>Final total vanadyl concn.</td>
<td>0.0068 M.</td>
<td>—</td>
</tr>
<tr>
<td>%age decrease in vanadyl concn.</td>
<td>77.0</td>
<td>—</td>
</tr>
<tr>
<td>Solution.</td>
<td>exptl.</td>
<td>ctrl.</td>
</tr>
<tr>
<td>----------------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>Initial total sulphate concn.</td>
<td>0.0700 M.</td>
<td>0.0700 M.</td>
</tr>
<tr>
<td>Final total sulphate concn.</td>
<td>0.0704 M.</td>
<td>0.0704 M.</td>
</tr>
<tr>
<td>%age increase in sulphate concn.</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Initial total vanadyl concn.</td>
<td>0.0555 M.</td>
<td>—</td>
</tr>
<tr>
<td>Final total vanadyl concn.</td>
<td>0.0191 M.</td>
<td>—</td>
</tr>
<tr>
<td>%age decrease in vanadyl concn.</td>
<td>65.7</td>
<td>—</td>
</tr>
<tr>
<td>pH of solns. at equilibrium.</td>
<td>1.30</td>
<td>1.16</td>
</tr>
</tbody>
</table>

**TABLE C.8.**
(detecting cationic thiocyanato complexes)

<table>
<thead>
<tr>
<th>Solution.</th>
<th>exptl.</th>
<th>ctrl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial total thiocyanate concn.</td>
<td>0.1031 M.</td>
<td>0.1031 M.</td>
</tr>
<tr>
<td>Final total thiocyanate concn.</td>
<td>0.1029 M.</td>
<td>0.1037 M.</td>
</tr>
<tr>
<td>%age change in thiocyanate concn.</td>
<td>-0.2</td>
<td>+0.6</td>
</tr>
<tr>
<td>Initial total vanadyl concn.</td>
<td>0.0475 M.</td>
<td>—</td>
</tr>
<tr>
<td>Final total vanadyl concn.</td>
<td>0.0171 M.</td>
<td>—</td>
</tr>
<tr>
<td>%age decrease in vanadyl concn.</td>
<td>64.0</td>
<td>—</td>
</tr>
</tbody>
</table>

The observations given in tables C.3, 4, 6, and 7 show that cationic complex vanadyl species were not detected in either the sulphate or phosphate systems, but anionic complexes were found in both. The uptake of vanadyl ion onto the anion-exchange resins was found to be small in both systems. This indicates that the anionic sulphato and phosphato vanadyl complexes are present in low concentration in the solutions, and carry a negative charge which is small in magnitude.
Referring now to tables C.5, and 8, cationic complex species were not detected with certainty in the vanadyl/thiocyanate system when allowance is made for experimental error. However, anion-exchange resin effected a 64% uptake of vanadyl ion from the solutions, and became deep-green in colour due to anionic complex vanadyl ions sorbed. The anionic complexes sorbed in this way must contain at least three thiocyanate ligand groups per vanadyl ion.

N.Bjerrum has shown that complexes are generally formed in a step-wise manner (121,122). However, as has been stated above, the cationic 1 : 1 complex ion, $\text{VO(CNS)}^+$, was not detected with certainty in these studies, in spite of spectrophotometric evidence for such a species reported by Furman and Garner (91,92). Therefore, this cationic species must be present in very low concentration in the solutions. Since higher complex species must be formed from a 1 : 1 complex, the large uptake of vanadyl ion onto an anion-exchange resin shows either that the higher complex detected has a stable symmetrical configuration enabling it to be formed in high concentration in the solutions, or that it is sorbed strongly by the resin due to a multiple negative charge (see paragraph C.I.). Both of these possibilities may be explained by the formation of the 1 : 4 complex ion, $\text{VO(CNS)}_4^-$. This would be consistent with the formula of the solid thiocyanato vanadyl compounds isolated by Koppel, Goldmann, and other workers (50,88-90), and with the maximum number of sites available for co-ordination in the vanadyl ion as has been discussed in section A.
(c) The determination of the number of ligand groups and hydrogen atoms, and the magnitude of the negative charge of the anionic phosphato vanadyl complexes formed in solutions of differing pH.

(i) Theoretical and experimental principles. Vanadyl/phosphate systems were found to be of a labile nature so that ion-exchange resins could not be washed and analysed satisfactorily after being brought to equilibrium with vanadyl/phosphate solutions. For this reason, the metal : ligand ratio of the phosphato vanadyl complex anions could not be established by the method described by Salmon (114). It was necessary, therefore, to utilise analytical data derived solely from the analysis of solutions after equilibration with ion-exchange resins in these studies. As has been shown in paragraph C.I, control experiments are necessary when data from the analysis of solutions are to be utilised to allow for the effects of solution uptake by the resins. This precaution was also necessary in the experiments described below to allow for the change during equilibration in average charge of the uncomplexed phosphate ions sorbed by the resin to that found by an initial estimation of the phosphate content and capacity of the resin.

In the following discussion,

- 'P' represents the total number of moles of phosphate lost from a vanadyl/phosphate solution during equilibration,
- 'V' represents the total number of moles of vanadyl ion lost from a vanadyl/phosphate solution during equilibration,
- 'P₀' represents the total number of moles of phosphate lost from a control solution during equilibration,
- 'C' represents the capacity of the resin, expressed in equivalents per gram.
Also, the phosphate ions with which the anion-exchange resin was initially saturated are considered to be of the type $H_xPO_4^{(3-x)}$.  

If the solutions are considered to contain a single phosphato vanadyl complex anion with the following formula: 

$$VOH_q(PO_4)_{n}(3n-q-2)^-$$

the number of equivalents of exchange sites occupied on the resin by the $V$ moles of vanadyl ion lost from solution $= (3n-q-2)V$.  

Also, the number of moles of phosphate sorbed by the resin in association with vanadyl ion $= nV$, 

and the number of moles of uncomplexed phosphate displaced from the resin by the complex anion $= \frac{(3n-q-2)V}{(3-x)}$.

Now, the exchange sites of the resin were initially occupied by a mixture of mono and dihydrogen phosphate ions, as represented by the average formula, $H_xPO_4^{(3-x)}$. The mole ratio of these ions changed during equilibration with the result that $P_0$ moles of phosphate were sorbed by the resin in the system. Since 3 grams of resin were used in each batch in the experiments, $P_0$ moles of phosphate were taken up by $3C$ equivalents of resin sites.

Now, the number of equivalents of exchange sites occupied at equilibrium by uncomplexed phosphate ions in the systems containing vanadyl ion $= 3C - (3n-q-2)V$. Therefore, the number of moles of phosphate sorbed from the solutions of the vanadyl containing systems due to the change in mole ratio of uncomplexed mono and dihydrogen phosphate ions occupying resin sites $= \frac{(3C - (3n-q-2)V)P_0}{3C}$.
Finally, the total number of moles of phosphate lost from solution in the vanadyl-containing systems,

\[ P = nV + \frac{(3C - (3n-q-2)V)P_o - (3n-q-2)V}{3C} \cdot \frac{3 - x}{3} \]

Then, on rearranging,

\[ \frac{P_o - P}{V} + n = (3n-q-2)\left(\frac{P_o}{3C} + \frac{1}{3 - x}\right). \]

Now, \( P, P_o, \) and \( V \) may be evaluated from estimations of the total vanadyl ion and phosphate contents of vanadyl/phosphate, and phosphoric acid solutions before and after equilibration with phosphate-form, anion-exchange resin. Also, \( C \) and \( x \) may be evaluated from an initial estimation of the phosphate content and exchange capacity of the anion-exchange resin. This data may then be substituted into the equation derived above so that the magnitude of the negative charge, \( (3n-q-2) \), and the number of hydrogen atoms, \( q \), of the complex anion may be evaluated in conjunction with the most probable value for the number of phosphate ligands, \( n \). It would be necessary to inspect the values obtained by substituting all feasible values of \( \cdot n' \) into the foregoing equation.

(ii) Experimental procedure, observations, and conclusions. Resin samples for the estimation of all experimentally determined quantities were weighed at the same time, and from the same batch of resin in order to obtain consistent series of experimental data. Errors arising from the preparation of separate batches of resin, and the varying moisture content of the air-dried resin were avoided in this way.
Measured volumes (75.0 ml.) of an analysed vanadyl/phosphate solution were added to samples of air-dried, phosphate-form, De-acidite FF resin (3.00 g. exactly) of known capacity and phosphate content. The vanadyl ion and phosphate contents of the solutions were estimated after the systems had attained equilibrium over a period of 7 days. Control experiments, in which the vanadyl ion was replaced by an equivalent amount of hydrogen ion, were performed in a similar manner.

Experimental data for solutions 0.02 M. in vanadyl ion are presented in tables C.9, 10, and 11. In these experiments, the capacity of the resin used = 2.793 m.eq./g. of air-dried (phosphate-form) resin.

Therefore, \( 3.C = 8.38 \times 10^{-3} \).

Also, the initial phosphate content of the resin = 2.321 m.moles/g. of air-dried (phosphate-form) resin.

Therefore, \( 1/(3-x) = 0.831 \).

**TABLE C.9.**

<table>
<thead>
<tr>
<th>Solution</th>
<th>exptl. a.</th>
<th>ctrol. a.</th>
<th>exptl. b.</th>
<th>ctrol. b.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial total ((P0_4^{3-}))</td>
<td>0.3000 M.</td>
<td>0.3000 M.</td>
<td>0.2415 M.</td>
<td>0.2415 M.</td>
</tr>
<tr>
<td>Final total ((P0_4^{3-}))</td>
<td>0.2369 M.</td>
<td>0.2399 M.</td>
<td>0.1823 M.</td>
<td>0.1859 M.</td>
</tr>
<tr>
<td>(P \times 10^{-3})</td>
<td>4.73</td>
<td>—</td>
<td>4.44</td>
<td>—</td>
</tr>
<tr>
<td>(P_0 \times 10^{-3})</td>
<td>—</td>
<td>4.51</td>
<td>—</td>
<td>4.17</td>
</tr>
<tr>
<td>Initial total ((VO^{++}))</td>
<td>0.0200 M.</td>
<td>0.0000 M.</td>
<td>0.0200 M.</td>
<td>0.0000 M.</td>
</tr>
<tr>
<td>Final total ((VO^{++}))</td>
<td>0.0149 M.</td>
<td>—</td>
<td>0.0142 M.</td>
<td>—</td>
</tr>
<tr>
<td>(V \times 10^{-4})</td>
<td>3.80</td>
<td>—</td>
<td>4.32</td>
<td>—</td>
</tr>
<tr>
<td>pH of solns. at equil.</td>
<td>1.40</td>
<td>1.40</td>
<td>1.44</td>
<td>1.42</td>
</tr>
</tbody>
</table>
para. C.II.

TABLE C.10.
(for experiments with solutions a)

\[ \frac{P_0}{3C} + \frac{1}{(3-x)} = 1.369 \]

This is used to evaluate the data tabulated below in conjunction with equation I, derived in paragraph C.II(c)(i).

<table>
<thead>
<tr>
<th>No. of phosphate ligands in cplx anion, 'n'</th>
<th>( \frac{P_0-P}{V} + n )</th>
<th>negative charge units of cplx. anion (3n-q-2)</th>
<th>no. of hydrogen atoms in cplx. anion, 'q'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.421</td>
<td>0.31</td>
<td>0.69</td>
</tr>
<tr>
<td>2</td>
<td>1.421</td>
<td>1.04</td>
<td>2.96</td>
</tr>
<tr>
<td>3</td>
<td>2.421</td>
<td>1.77</td>
<td>5.23</td>
</tr>
<tr>
<td>4</td>
<td>3.421</td>
<td>2.50</td>
<td>7.50</td>
</tr>
<tr>
<td>5</td>
<td>4.421</td>
<td>3.23</td>
<td>9.77</td>
</tr>
</tbody>
</table>

TABLE C.11.
(for experiments with solutions b)

\[ \frac{P_0}{3C} + \frac{1}{(3-x)} = 1.329 \]

This is used to evaluate the data tabulated below in conjunction with equation I, derived in paragraph C.II(c)(i).

<table>
<thead>
<tr>
<th>No. of phosphate ligands in cplx anion, 'n'</th>
<th>( \frac{P_0-P}{V} + n )</th>
<th>negative charge units of cplx. anion (3n-q-2)</th>
<th>No. of hydrogen atoms in cplx. anion, 'q'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.375</td>
<td>0.28</td>
<td>0.72</td>
</tr>
<tr>
<td>2</td>
<td>1.375</td>
<td>1.04</td>
<td>2.96</td>
</tr>
<tr>
<td>3</td>
<td>2.375</td>
<td>1.79</td>
<td>5.21</td>
</tr>
<tr>
<td>4</td>
<td>3.375</td>
<td>2.54</td>
<td>7.46</td>
</tr>
<tr>
<td>5</td>
<td>4.375</td>
<td>3.29</td>
<td>9.71</td>
</tr>
</tbody>
</table>
Experiments were also performed with solutions 0.040 M. in vanadyl ion. The pH of the experimental and control solutions of this series was varied by the introduction of varying quantities of sodium hydroxide. The capacity of the resin used in these experiments = 2.640 m.equivs./g. of air-dried (phosphate-form) resin.

Therefore, \(3C = 7.92 \times 10^{-3}\).

The initial phosphate content of the resin = 2.365 m.moles/g. of air-dried (phosphate-form) resin.

Therefore, \(1/(3-x) = 0.896\).

The weights of the precipitates of ammonium phosphomolybdate obtained by analysing the control solutions for these series of experiments are presented in table C.12, and figure 2, and are equivalent to 1/60 th of the total phosphate content of the control solutions. The curves of figure 2 were then used to estimate the weights of precipitates which were expected from control solutions under conditions of pH corresponding to those prevailing in the vanadyl-containing solutions at equilibrium.

**TABLE C.12.**

<table>
<thead>
<tr>
<th>Series of solutions</th>
<th>Av. pH of solutions at equilibrium</th>
<th>Av. wt. of ppts. of ammonium phosphomolybdate (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.91</td>
<td>0.5042</td>
</tr>
<tr>
<td>initially 0.2629 M. in phosphate</td>
<td>2.65</td>
<td>0.5525</td>
</tr>
<tr>
<td></td>
<td>4.58</td>
<td>0.6076</td>
</tr>
<tr>
<td>D</td>
<td>1.97</td>
<td>0.6552</td>
</tr>
<tr>
<td>initially 0.3310 M. in phosphate</td>
<td>2.66</td>
<td>0.7020</td>
</tr>
<tr>
<td></td>
<td>3.33</td>
<td>0.7431</td>
</tr>
</tbody>
</table>
The weights of precipitates of ammonium phospho-
molybdate obtained in the analysis of control
solutions of varying pH.

Fig. 2.

- Solution D, 0.3310 M in phosphate.
- Solution C, 0.2629 M in phosphate.
Experimental data for the vanadyl-containing solutions of series C are presented in table C.13, and the data derived in conjunction with equation I of paragraph C.II(c)(i) in table C.14.

**TABLE C.13.**

<table>
<thead>
<tr>
<th></th>
<th>1.73</th>
<th>2.29</th>
<th>3.26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Av. pH of solns. at equil.</td>
<td>1.73</td>
<td>2.29</td>
<td>3.26</td>
</tr>
<tr>
<td>Initial total (PO$_4^{3-}$)</td>
<td>0.2629 M.</td>
<td>0.2629 M.</td>
<td>0.2629 M.</td>
</tr>
<tr>
<td>Final total (PO$_4^{3-}$)</td>
<td>0.2040 M.</td>
<td>0.2077 M.</td>
<td>0.2231 M.</td>
</tr>
<tr>
<td>$P$ (x 10$^{-4}$)</td>
<td>44.18</td>
<td>41.37</td>
<td>29.83</td>
</tr>
<tr>
<td>Expected wt. of ctrol.ppts.</td>
<td>0.4850 g.</td>
<td>0.5320 g.</td>
<td>0.5760 g.</td>
</tr>
<tr>
<td>$P_0$ (x 10$^{-4}$)</td>
<td>42.16</td>
<td>27.14</td>
<td>13.08</td>
</tr>
<tr>
<td>Initial total (VO$^{2+}$)</td>
<td>0.0400 M.</td>
<td>0.0400 M.</td>
<td>0.0400 M.</td>
</tr>
<tr>
<td>Final total (VO$^{2+}$)</td>
<td>0.0285 M.</td>
<td>0.0178 M.</td>
<td>0.0043 M.</td>
</tr>
<tr>
<td>$V$ (x 10$^{-4}$)</td>
<td>8.66</td>
<td>16.62</td>
<td>26.78</td>
</tr>
<tr>
<td>$(P_0 - P)/V$</td>
<td>-0.2333</td>
<td>-0.8562</td>
<td>-0.6255</td>
</tr>
<tr>
<td>$P_0/3C + 1/(3-x)$</td>
<td>1.428</td>
<td>1.239</td>
<td>1.061</td>
</tr>
</tbody>
</table>
TABLE C.14.

<table>
<thead>
<tr>
<th>Av. pH of solution at equil.</th>
<th>No. phosphate ligands in cplx. 'n'.</th>
<th>$\frac{P_0 - P}{V} + n$</th>
<th>Negative charge units of complex anion, $(3n-q-2)$</th>
<th>No. H atoms in complex, 'q'.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.73</td>
<td>1</td>
<td>0.767</td>
<td>0.54</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.767</td>
<td>1.24</td>
<td>2.76</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.767</td>
<td>1.94</td>
<td>5.06</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3.767</td>
<td>2.64</td>
<td>7.36</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.767</td>
<td>3.34</td>
<td>9.66</td>
</tr>
<tr>
<td>2.29</td>
<td>1</td>
<td>0.144</td>
<td>0.12</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.144</td>
<td>1.16</td>
<td>2.84</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.144</td>
<td>1.73</td>
<td>5.27</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3.144</td>
<td>2.54</td>
<td>7.46</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.144</td>
<td>3.35</td>
<td>9.65</td>
</tr>
<tr>
<td>3.26</td>
<td>1</td>
<td>0.375</td>
<td>0.35</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.375</td>
<td>1.30</td>
<td>2.71</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.375</td>
<td>2.24</td>
<td>4.76</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3.375</td>
<td>3.18</td>
<td>6.82</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.375</td>
<td>4.12</td>
<td>8.88</td>
</tr>
</tbody>
</table>
Experimental data for the vanadyl-containing solutions of series D are presented in table C.15 and the data derived in conjunction with equation I of paragraph C.II(c)(i) in table C.16.

<table>
<thead>
<tr>
<th>TABLE C.15.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Av. pH of solns. at equil.</td>
</tr>
<tr>
<td>Initial total (PO$_4^{3-}$).</td>
</tr>
<tr>
<td>Final total (PO$_4^{3-}$).</td>
</tr>
<tr>
<td>P (x 10$^{-4}$)</td>
</tr>
<tr>
<td>Expected wt. of control ppts.</td>
</tr>
<tr>
<td>P$_o$ (x 10$^{-4}$)</td>
</tr>
<tr>
<td>Initial total (VO$^{2+}$).</td>
</tr>
<tr>
<td>Final total (VO$^{2+}$).</td>
</tr>
<tr>
<td>V (x 10$^{-4}$)</td>
</tr>
<tr>
<td>(P$_o$ - P)/V</td>
</tr>
<tr>
<td>P$_o$/3C + 1/(3-x)</td>
</tr>
</tbody>
</table>
Referring to tables C.9, 10, and 11, if only one complex species is sorbed onto the resin, the experimental data for solutions 0.020 M. in vanadyl ion of pH 1.40 show that the anionic phosphato vanadyl species contain two phosphato ligands, and carry a negative charge of one unit, for a value of 'q' which is very close to an integer is obtained in this way. The formula of this ion may, therefore, be written thus:- $\text{VO}_2^+(\text{PO}_4)_2^-$.
The observations from solutions more concentrated in vanadyl ion over the pH range 1.5 to 3.2, which have been presented in tables C.13 to 16, show that the anion-exchange resin sorbed vanadyl ion to a greater extent from solutions of low hydrogen ion concentration. The formation of the anionic complex species is, therefore, favoured by conditions of high pH. This may be attributed either to a removal of hydrogen ion from the system which is liberated in the complex-forming reactions, or to an increase in the concentration of reactant phosphate ions. If both of these factors contribute to the increased formation of the complexes, the formation of the complex anion, mentioned above, may be represented by the following equilibria:—

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$$, and other dissociation equilibria, and

$$2H_2PO_4^- + VO^{2+} \leftrightarrow VOH_2(PO_4)_2^- + H^+$$.

The observations from the solutions 0.040 M. in vanadyl ion suggest that the anionic complexes contain either two or three phosphate ligands, but do not permit a further differentiation between these possibilities. This may be expected since the term, $$(P_0 - P)/V$$, which features in the equation derived in paragraph C.II(c)(i), is subject to a considerable accumulation of experimental error. This term involves both a difference and a quotient of experimentally determined quantities, and moreover, each of these quantities are obtained by difference from experimental data. In any case, the sorption of both bis- and tris-phosphato complexes cannot be ruled out on the basis of this evidence alone.
(d) Determination of the average number of ligand groups in the phosphato vanadyl complex species, and the investigation of an equilibrium constant describing the overall formation of complexes in the system.

(i) Theoretical and experimental principles. Omitting charges for the sake of clarity, the overall dissociation constant, $k_c$, for the complex species, $ML_n$, may be represented as follows:

$$k_c = \frac{(M)(L)^n}{(ML_n)^{1}}.$$  

Then, when

$$K_d = \frac{\% M \text{ on resin}}{\% M \text{ in soln.}} \times \frac{\text{vol. of soln.}}{\text{mass of resin}},$$

and $K_d^0$ is the value of $K_d$ when $(L)$ is zero, Schubert and co-workers (115) have shown that:

$$\frac{1}{\frac{1}{K_d}} = \frac{1}{K_d^0} + \frac{(L)^n}{K_d^0k_c}.$$  

Now, in the vanadyl/phosphate system, hydrogen ions have been shown to be liberated during the formation of complexes (see for example paragraph C.II(c)(ii)). Therefore, where 'L' represents phosphato ligand groups, and 'n' the average number of such groups co-ordinated to the vanadyl ions in the complexes, complex formation in the vanadyl/phosphate system may be represented by the equilibrium:

$$M + n\frac{H}{X/n}L \Rightarrow ML_n + xH \quad \text{.....1}$$

Then, using a similar method to that described by Schubert (115), it may be shown that:

$$\frac{1}{\frac{1}{K_d}} = \frac{1}{K_d^0} + \frac{(H/X/nL)^n}{K_d^0k_c(H)^x}, \quad \text{.....2}$$
when 'k_c' is now defined thus:

$$k_c = \frac{(M)(H_x/L)^n}{(ML_n^*)(H)^X}$$

On rearranging equation 2 and taking logarithms, it may be shown that:

$$\log_{10}(1/K_d - 1/K_d^0) = n \log_{10}(H_x/L) - \log_{10}K_d^0 \cdot k_c \cdot (H)^X \ldots 3$$

Now, in solutions in which the pH and ionic strength are constant, the term $(H)^X$ is also constant, for 'x', although unknown, is a function of $(H)$. Then, it may be seen from equation 3 that the plot of $\log_{10}(1/K_d - 1/K_d^0)$ against $\log_{10}(H_x/L)$ would be linear, and the average number of phosphate ligand groups in the vanadyl complexes, 'n', may be evaluated from the slope of this graph. Equation 2 shows that such a value of 'n' would give rise to a linear plot of $1/K_d$ against $(H_x/L)^n$. The slope of this graph would represent the term:

$$1/(K_d^0 \cdot k_c \cdot (H)^X)$$

Now, 'K_d^0' may be estimated experimentally, and the value obtained in this way may be checked from the intercept of the graph at the $1/K_d$ axis. Such a value may then be used in conjunction with the slope of the graph to evaluate the product $k_c \cdot (H)^X$. This product would apply to an equilibrium represented by equation 1 in which an average number of phosphate ligands were considered to be co-ordinated to vanadyl ions in the complexes.

For reasons discussed by Schubert (115), this method is strictly applicable only when very dilute solutions of constant ionic strength are employed. Very low concentrations of vanadyl
ion were not used in the experiments described below since suitable radio-isotopes of vanadium were not obtainable. The conclusions drawn from the experiments are, therefore, subject to limitations, but nevertheless, are of value since the ionic strength was maintained approximately constant in the solutions by the addition of perchloric acid. The ionic strengths were raised in this way to that of the solution containing the highest concentration of phosphate.

In the experiments described below, the solution with the highest phosphate content was first prepared. The pH of this solution was then measured. Since this was low at 0.88, only the dissociation of the first hydrogen ion of the phosphoric acid was considered in calculating the ionic strength of this solution. The value $7.85 \times 10^{-3}$ was used for the first dissociation constant of phosphoric acid at 20°C, and was obtained from data reported by Nims (116). Perchlorate ion was considered to be completely dissociated in the system. The ionic strength of each of the remaining solutions to be prepared was then calculated assuming the pH of these solutions to be 0.88. Finally, the quantity of perchloric acid required to raise the ionic strength in these solutions to that of the solution with the highest phosphate content was calculated. Such quantities of perchloric acid were introduced into these solutions during their subsequent preparation. The pH of each solution prepared was ultimately found to fall within the range 0.88 to 0.90.
(ii) Experimental procedure, observations, and conclusions.
Measured volumes of solution (75.0 ml.), initially 0.0200 M. in vanadyl ion, were added to samples of air-dried, hydrogen-form, Zeo-karb 225 resin (1.00 g. exactly). The vanadyl content of the solution phase was then estimated after the system had been allowed to attain equilibrium over a period of 7 days. The initial total phosphate concentration of the solutions was varied from 0.000 to 0.300 M. by the introduction of phosphoric acid. Although phosphate ion is not sorbed from vanadyl/phosphate solutions by cation-exchange resin, as shown in paragraph C.II(b)(ii), the phosphate content was checked at equilibrium in some of the solutions from the series. Perchlorate ion was also present in the solutions since vanadyl/perchlorate solution was used in their preparation, and perchloric acid was added to most solutions to maintain constant ionic strength throughout the series. The ionic strength of the solutions was maintained approximately constant at 0.18, and the pH of all solutions was found to be within the range 0.88 to 0.90.

Referring to paragraph C.II(d)(i), the reactant phosphate species, H\(_{x/L}\), were considered to be dihydrogen phosphate ions. Under the conditions of experiment, the molar concentration of these ions, \((H_2PO_4^-)\) = 0.0569 x the total phosphate concentration. Further experimental data are presented in tables C.17 and 18. In these tables, 

\[
K_d = \frac{\% \text{ vanadyl ion on resin}}{\% \text{ vanadyl ion in solution}} \times \frac{\text{vol. of soln.}}{\text{mass of resin}}
\]

and \(K_d^0\) is the value of \(K_d\) found in the solution with zero concentration of phosphate.
### TABLE C.17.

<table>
<thead>
<tr>
<th>Initial total phosphate concentration</th>
<th>Final total phosphate concn.</th>
<th>Perchlorate ion concn.</th>
<th>$K_d$</th>
<th>$1/K_d$ (x $10^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.299 M.</td>
<td>0.300 M.</td>
<td>0.136 M.</td>
<td>65.62</td>
<td>1.524</td>
</tr>
<tr>
<td>0.270</td>
<td>0.272</td>
<td>0.139</td>
<td>68.67</td>
<td>1.456</td>
</tr>
<tr>
<td>0.232</td>
<td>-</td>
<td>0.141</td>
<td>72.84</td>
<td>1.373</td>
</tr>
<tr>
<td>0.189</td>
<td>-</td>
<td>0.146</td>
<td>73.83</td>
<td>1.354</td>
</tr>
<tr>
<td>0.140</td>
<td>0.143</td>
<td>0.150</td>
<td>81.57</td>
<td>1.226</td>
</tr>
<tr>
<td>0.110</td>
<td>-</td>
<td>0.152</td>
<td>92.25</td>
<td>1.084</td>
</tr>
<tr>
<td>0.100</td>
<td>-</td>
<td>0.153</td>
<td>95.70</td>
<td>1.045</td>
</tr>
<tr>
<td>0.087</td>
<td>-</td>
<td>0.155</td>
<td>99.75</td>
<td>1.003</td>
</tr>
<tr>
<td>0.075</td>
<td>-</td>
<td>0.156</td>
<td>106.0</td>
<td>0.944</td>
</tr>
<tr>
<td>0.061</td>
<td>-</td>
<td>0.157</td>
<td>104.5</td>
<td>0.957</td>
</tr>
<tr>
<td>0.043</td>
<td>0.044</td>
<td>0.158</td>
<td>113.2</td>
<td>0.884</td>
</tr>
<tr>
<td>0.000</td>
<td>0.000</td>
<td>0.162</td>
<td>127.5</td>
<td>0.784</td>
</tr>
</tbody>
</table>
TABLE C.18.

<table>
<thead>
<tr>
<th>$1/K_d$ (x $10^{-2}$)</th>
<th>$-\log_{10}\left(\frac{1}{K_d} - \frac{1}{K'_d}\right)$</th>
<th>$(H_2PO_4^-)$ (x $10^{-3}$)</th>
<th>$(H_2PO_4^-)^{1.2}$ (x $10^{-3}$)</th>
<th>$-\log_{10}(H_2PO_4^-)$ (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.524</td>
<td>2.131</td>
<td>17.0</td>
<td>7.54</td>
<td>1.769</td>
</tr>
<tr>
<td>1.456</td>
<td>2.173</td>
<td>15.4</td>
<td>6.67</td>
<td>1.813</td>
</tr>
<tr>
<td>1.373</td>
<td>2.230</td>
<td>13.6</td>
<td>5.76</td>
<td>1.866</td>
</tr>
<tr>
<td>1.354</td>
<td>2.244</td>
<td>10.8</td>
<td>4.35</td>
<td>1.968</td>
</tr>
<tr>
<td>1.226</td>
<td>2.355</td>
<td>7.97</td>
<td>3.03</td>
<td>2.099</td>
</tr>
<tr>
<td>1.084</td>
<td>2.523</td>
<td>6.26</td>
<td>2.27</td>
<td>2.203</td>
</tr>
<tr>
<td>1.045</td>
<td>2.584</td>
<td>5.69</td>
<td>2.03</td>
<td>2.245</td>
</tr>
<tr>
<td>1.003</td>
<td>2.660</td>
<td>4.95</td>
<td>1.71</td>
<td>2.305</td>
</tr>
<tr>
<td>0.944</td>
<td>2.797</td>
<td>4.27</td>
<td>1.43</td>
<td>2.370</td>
</tr>
<tr>
<td>0.957</td>
<td>2.762</td>
<td>3.47</td>
<td>1.12</td>
<td>2.459</td>
</tr>
<tr>
<td>0.884</td>
<td>3.002</td>
<td>2.45</td>
<td>0.736</td>
<td>2.611</td>
</tr>
<tr>
<td>0.784</td>
<td>inf.</td>
<td>0.00</td>
<td>0.000</td>
<td>inf.</td>
</tr>
</tbody>
</table>

Equation 1 of paragraph C.II(d)(i) may be rewritten here in the form:-

$$V_0^{++} + nH_2PO_4^- \rightarrow VOH_{(2n-x)}(PO_4)_n + xH^+ \quad \ldots \ldots \ldots 4$$

It has been shown in the foregoing pages that the slope of the plot of figure 3 (columns (*) of table C.18) represents the average number of phosphate ligand groups, 'n', which are co-ordinated to vanadyl ions in the complex vanadyl species formed in the solutions. Thus, it is found that the average number of phosphato ligands per vanadyl ion in the complexes is 1.2. Now, the experiments described in paragraph C.II(c) have shown that anionic complex species in the solutions contain two phosphate ligands. The experimental data of
Determination of the average number of phosphato ligand groups in the complexes of the vanadyl-phosphate system.

$-\log_{10}\left(\frac{1}{K_d} - \frac{1}{K_{d'}}\right)$

slope of the graph, $n = 1.20$. 

$-\log_{10}[H_2PO_4^-]$
this study, therefore, shows that a 1 : 1 complex is also formed. Since the experimental solutions were of low pH, and cationic complexes were not detected in the vanadyl/phosphate system in the studies described in paragraph C.II(b), the formula, VOHPO\textsubscript{4}\textsuperscript{0}, may be attributed to this 1 : 1 complex species.

Of the complex species formed in the vanadyl/phosphate solutions, the average number of phosphato ligands shows that the 1 : 1 complex is formed in greatest concentration in the system. This may be represented by the following equilibrium:-

\[
\text{VO}^{++} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{VOHPO}_4^- + \text{H}^+
\]

To obtain an indication of the order of magnitude of the equilibrium constant for the complex-forming reactions in the system, therefore, the quantity 'x' of equation 4 may be equated to unity. Now, figure 4 (columns (**) of table C.18) shows that the plot of \(1/K_d\) against \((\text{H}_2\text{PO}_4^-)^{1.2}\) is linear. This also indicates that the average number of phosphato ligands co-ordinated in the vanadyl complexes in the system is 1.2. However, as shown in paragraph C.II(d)(i), the slope of this plot and the intercept on the \(1/K_d\) axis may be combined to show that the product,

\[
k_c \cdot (\text{H})^x = 0.6
\]

Now, the experimental solutions were of pH 0.9. Assuming unit value for the activity coefficient for the hydrogen ion in the system, the hydrogen ion concentration,

\[
(\text{H}) = 10^{-0.9} \text{ g.ions/l.}
\]

Therefore, with unit value of 'x', the equilibrium constant for the reactions represented by equation 4,

\[
1/k_c = 0.2
\]
Determination of the average number of phosphato ligand groups in the complexes of the vanadyl-phosphate system.

Fig. 4:

\[ (2 - 0.1 \times) \frac{P}{M} \]
This figure may be considered to provide only an approximate order of magnitude for the equilibrium constant. However, it is apparent from this that the phosphato vanadyl complex species are of low stability.

(e) The investigation of the magnitude of the charge of the phosphato vanadyl complex anions, and its dependence upon solution pH.

(i) Theoretical and experimental principles. It has been shown in paragraph C.I that multivalent ions are sorbed more strongly by ion-exchange resins than ions of lower charge when the systems involve dilute solutions. Where the suffixes 's' and 'r' refer to ions in solution and resin phases respectively, the exchange equilibria in a system, in which chloride-form, anion-exchange resin is brought to equilibrium with a solution containing phosphate, may be represented as follows:

\[ \text{H}_2\text{PO}_4^- + \text{Cl}^- \rightleftharpoons \text{Cl}^- + \text{H}_2\text{PO}_4^- \]  \hspace{1cm} \text{(a)}

\[ \text{HPO}_4^{--} + 2\text{Cl}^- \rightleftharpoons 2\text{Cl}^- + \text{HPO}_4^{--} \]  \hspace{1cm} \text{(b)}

\[ \text{PO}_4^{3--} + 3\text{Cl}^- \rightleftharpoons 3\text{Cl}^- + \text{PO}_4^{3--} \]  \hspace{1cm} \text{(c)}

Equation 'c' may be neglected in further discussion here since the solutions used in the studies described below were of low pH. Thus, the release of chloride ion effected by acid phosphate solutions from chloride-form resin may be represented by the equilibria shown in equations 'a' and 'b'. Considering systems of the same phosphate content, the more extensive ionisation of phosphoric acid molecules under conditions of higher pH would give rise to a greater release of chloride ion from the resin phase. However, in solutions of
pH 4 or less, chloride ion would be displaced mainly by exchange with singly-charged, dihydrogen phosphate ions, as shown in equation 'a'.

Now, in systems containing vanadyl ion, the release of chloride ion would also be caused by the sorption of anionic phosphato vanadyl complexes onto the resin. If such complex anions were singly charged, the charge density around the ions would be lower than around the smaller dihydrogen phosphate ions. Thus, considering systems of the same phosphate content and pH, the solutions containing vanadyl ion would give rise to a slightly lower release of chloride ion than solutions in which vanadyl ion was absent. However, ion-exchange resins have a greater affinity for ions of higher charge. Thus, the release of chloride ion would be greatest in the vanadyl-containing system if the complex species carried a charge of two or more units. Furthermore, the anion-exchange resin would take up a large proportion of the vanadyl ion if the complex anions carried a multiple charge. This effect would be expected to be marked even if the concentration of such complexes in solution were low at equilibrium. Thus, by estimating the vanadyl ion taken up, and comparing the extents to which chloride ion is released from chloride-form resin by solutions constant in phosphate content, in the presence and absence of vanadyl ion, the charge of the phosphato vanadyl anions may be established under various conditions of pH.

(ii) Experimental procedure, observations, and conclusions. Constant volumes of solution, constant in phosphate concentration, and under various conditions of pH, were added to constant masses of air-dried, chloride-form, De-acidite FF resin. The chloride content
of these solutions was then estimated after being allowed to stand for 7 days to attain equilibrium. A similar procedure was carried out using solutions which contained constant total concentrations of vanadyl and phosphate ions. Both the chloride and vanadyl ion concentrations were estimated in these solutions at equilibrium. The pH of all solutions was measured immediately before analysis.

The initial total concentration of vanadyl ion in the vanadyl/phosphate solutions = 0.0500 M.

The initial total concentration of phosphate ion in all solutions = 0.414 M.

Further observations recorded in the studies are recorded in tables C.19 and 20, and in figure 5.

**TABLE C.19.**
(for control solutions)

<table>
<thead>
<tr>
<th>Solution pH at equilibrium</th>
<th>Chloride ion released from the resin (m.moles).</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.10</td>
<td>3.26</td>
</tr>
<tr>
<td>1.67</td>
<td>4.69</td>
</tr>
<tr>
<td>2.27</td>
<td>5.39</td>
</tr>
<tr>
<td>2.80</td>
<td>5.54</td>
</tr>
<tr>
<td>3.92</td>
<td>5.58</td>
</tr>
</tbody>
</table>
The effect of solution pH on the release of chloride ion, and uptake of vanadyl ion brought about by bringing chloride-form anion-exchange resin to equilibrium with vanadyl/phosphate, and control solutions of constant total phosphate concentration.

Fig. 5:

- Chloride ion released into control solutions.
- Chloride ion released into vanadyl solutions.
- Vanadyl ion sorbed from vanadyl solutions.
The observations presented in figure 5 show that a slightly lower release of chloride ion was brought about by the vanadyl-containing solution than by the control solution over the pH range 1.2 to 2.3. Furthermore, this was accompanied by a low uptake of vanadyl ion by the anion-exchange resin. Thus, for reasons discussed in paragraph C.II(e)(i), the anionic phosphato vanadyl complexes formed in solution under these conditions may be considered to be singly charged. However, the greatest release of chloride ion was brought about by the vanadyl-containing solution, and the uptake of vanadyl ion was doubled when the pH of the solution was increased from 2.3 to 2.8. This phenomenon may be attributed to the formation of significant concentrations of an anionic complex carrying two units of negative charge under these conditions of pH. These studies show, therefore, that the experimental data presented in tables C.13 to 16 may be considered to demonstrate the formation of a singly-charged complex anion containing two phosphato ligands. This is then in agreement with the conclusions drawn from the data presented in tables C.9 to 11.
The conclusions drawn from these studies may now be combined with those drawn from the ion-exchange studies discussed in previous paragraphs. In this way, the formation of complexes in the vanadyl/phosphate solutions of low pH may be summarised by the following equilibria:

\[ \text{VO}^{++} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{VOHPO}_4^- + \text{H}^+ \]
\[ \text{VOHPO}_4^- + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{HVO(HPO}_4)_2^- \]
\[ \text{HVO(HPO}_4)_2^- \rightleftharpoons \text{VO(HPO}_4)_2^- + \text{H}^+ \]

The data presented in figure 5 indicates that the reaction shown in equation 'f' proceeds to a significant extent in solutions of pH greater than 2.3. Experimental observations discussed in paragraphs C.II(d) and (e) indicate that the ligands of the phosphato vanadyl complexes are monohydrogen phosphate groups. As discussed in section A, similar ligand groups have been found by previous workers in the phosphato complexes of other transition metal ions in acid solutions. For this reason, the phosphato ligands are represented as such in the equilibria presented above.
SECTION D.

THE APPLICATION OF pH-TITRATION METHODS TO THE STUDY OF SYSTEMS CONTAINING COMPLEXES OF THE VANADYL ION.
I. Electrometric titrations in the study of complex systems.

One of the earliest reports of studies in which electrometric titrations were employed appeared late in the nineteenth century when Bottger used a hydrogen electrode to measure hydrogen ion activity during the titration of solutions of borax and aniline with hydrochloric acid (117). Although such methods were not used extensively at first, a similar experimental approach was later adopted to study the precipitation of the hydroxides of alkaline-earth and rare-earth metal cations (118,119). The development of the glass electrode, which is reversible to hydrogen ions, greatly facilitated the measurement of hydrogen ion activity in solution. This eventually led to an extensive use of titration methods in the investigation of complex formation in aqueous solution.

The overall stability of the complex species, which are formed in systems by the interaction of ligand groups and metal ions, was investigated at an early date by Abegg and Bodlander using a knowledge of the stoichiometric composition of the complex systems (120). N.Bjerrum later demonstrated that complex species are generally formed in a step-wise manner in aqueous solution. This may be represented as follows:

\[
\begin{align*}
M + L & \rightleftharpoons K_1^{1} ML, \\
ML + L & \rightleftharpoons K_2^{2} ML_2, \ldots, \\
ML_{i-1} + L & \rightleftharpoons K_i^{i} ML_i, \\
ML_{i-1} + L & \rightleftharpoons (ML_i) \\
where \quad K_i &= \frac{(ML_i)}{(ML_{i-1})(L)}
\end{align*}
\]

Since identical ligand groups are linked to the central metal ion by bonds of approximately the same strength, such complex systems are
characterised by a series of stability constants, \( K_1, K_2, \ldots, K_i \), each of the same order of magnitude. Thus, two or more complex species generally co-exist in systems in which the maximum value of 'i' is greater than unity (121,122).

Anions, which are derived from weak acid molecules by the dissociation of one or more protons, frequently complex with metal ions. To illustrate this, a system in which only one complex species is formed may be considered, as shown in the following equations:

\[
\begin{align*}
H_y A & \rightleftharpoons yH^+ + Ay^- \\
M^{m+} + Ay^- & \rightleftharpoons MA^{(m-y)+} \\
\end{align*}
\]

These equations may be condensed into the following form:

\[
M^{m+} + H_y A \rightleftharpoons MA^{(m-y)+} + yH^+ \\
\]

This system may then be represented by the Law of Chemical Equilibrium in the following way:

\[
K = \frac{(MA^{(m-y)+})(H^+)^y}{(M^{m+})(H_y A)}
\]

It is apparent therefore, that complex formation in such a system is dependent upon the concentration of hydrogen ion in the solutions. This pH dependence of such complexing systems forms the basis of the experimental methods which have been developed by Bjerrum, Leden, Fronaeus, Irving, and other workers to determine the stability constants of a series of complex species formed in solution (123-133). These methods involve the evaluation of the concentration of free ligand, and the average number of ligand groups co-ordinated to the metal ions, that is, the formation function 'n', at intermediate stages in the calculation of the stability constants of the complexes.
These methods have been successfully applied to systems in which the ligand was derived from a monobasic acid. However, more elaborate treatments are required to deal with systems in which the ligands are derived from a polybasic weak acid to allow for interactions between the free ligand ions and hydrogen ions (128,130). Furthermore, the foregoing methods have been applied to systems containing one or two complex species, but data from systems containing greater numbers of complexes becomes increasingly difficult to interpret due to the cumbersome nature of the calculations involved. Experimental data is particularly difficult to handle for systems in which the ligand is derived from a polybasic weak acid. In these systems, the dissociation constants of the acid and the association of protons with the complexes formed must be considered, in addition to the number of ligand groups co-ordinated to the metal ion. These quantitative treatments must also make allowance for hydrolysis of the metal ions, progressive dilution of the solutions during titration, and changes in activity coefficients of the species in solution. Bronsted has shown that the latter factor may be overcome by introducing a highly dissociated salt, which will not interact with the other species in solution, in sufficient quantity to render negligible the changes in ionic strength of the solutions during titration (134).

The inflexions in the pH-titration curves on titrating orthophosphate and condensed phosphate solutions with alkali have been interpreted where no complex interactions with metal ions take place (2). However, the foregoing discussion shows that the complexing of metal ions by orthophosphate species, and other anions derived from weak polybasic acids, would be difficult to study by the methods developed by Bjerrum and later workers. Nevertheless, pH-titration methods have enabled the formation of complex species to be detected.
in phosphate, arsenate, and silicate systems, particularly with multivalent transition metal ions (5, 10, 15, 135, 136). Salmon has detected complex phosphato species by comparing the titration curves obtained by titrating equimolar solutions of potassium ion and the metal ion under consideration with a solution of phosphoric acid. Addition of the acid causes a fall of pH in both solutions. This is due entirely to the ionisation of the acid in the solutions of potassium ion, that is:

\[ H_3PO_4 \rightarrow H^+ + H_2PO_4^- \]

and further dissociations.

However, since phosphate ions are taken up in the solutions in the formation of complexes, a greater drop in pH is observed in the solutions of the other metal ion, after comparable additions of acid, when complexing equilibria are established in the system (see equations 1 & 2 above). The lower pH is caused by the more extensive liberation of hydrogen ions required to establish the dissociation equilibria of the acid in the system.
II. Theories underlying methods used, experimental procedures, observations, and conclusions.

(a) The titration of potassium perchlorate and vanadyl/perchlorate solutions with phosphoric and sulphuric acids.

(i) Theoretical and experimental principles. In the following discussion, it is shown that the number of hydrogen ions which are replaced by a metal ion, M, from an acid, $H_2A$, in forming the first of a series of complex species may be estimated from the initial slope of the curve obtained by plotting $\frac{h}{t(M)}$ against $\frac{t(H_2A)}{t(M)}$.

In solutions in which the total concentration of metal ion, $t(M)$, is much greater than the total concentration of the complexing acid, $t(H_2A)$, the acid may be considered to react completely with the metal ions to form complex species. Furthermore, when the total concentration of the acid tends to zero, the first-formed complex of the series may be considered to be the only complex formed in significant concentration in the solution. Complex formation may be represented in the system under these conditions by the equilibrium:

$$H_2A + M \rightleftharpoons MH_{3-x}A + xH$$

Therefore, as discussed above, when $t(M)$ is much greater than $t(H_2A)$, and $t(H_2A)$ tends to zero,

$$t(H_2A) = (MH_{3-x}A)$$

Now, 'h' may be defined as the increase in concentration of hydrogen ion over that present in the solution when $t(H_2A) = 0$. Then, considering equation 3,

$$h = x.(MH_{3-x}A)$$

Hence, under the conditions specified above,

$$h = x.t(H_2A)$$
Finally, dividing by \( t(M) \),

\[
\frac{h}{t(M)} = x \cdot \frac{t(H_2A)}{t(M)}
\]

Thus, under conditions in which \( t(H_2A) \) tends to zero, the slope of the curve obtained by plotting \( \frac{h}{t(M)} \) against \( \frac{t(H_2A)}{t(M)} \) will be given by 'x', that is, the initial slope of the curve obtained in such a plot = x. The number of hydrogen ions, 'x', liberated from the acid, \( H_2A \), and the nature of the ligands, \( H_{3-x}A \), co-ordinated to metal ions in the complex species first formed in the system may, therefore, be deduced in this way.

Addition of the acid, \( H_2A \), to solutions in which complex-forming equilibria are not established gives rise to 'h' values due entirely to the liberation of hydrogen ion in the dissociation of the acid. When the acid, \( H_2A \), is phosphoric acid, complex species are not formed with potassium ions. Complex formation may be detected in a system, therefore, by titrating solutions of potassium ion and the metal ion under consideration with a solution of the acid, \( H_2A \). When complex formation takes place in one of the systems, different curves are obtained by using the experimental data to plot pH against \( \frac{t(H_2A)}{t(M)} \), and \( \frac{h}{t(M)} \) against \( \frac{t(H_2A)}{t(M)} \).

Systems involving weak dibasic acids may be treated in a similar manner. Such a treatment would be appropriate for titrations with sulphuric acid since the second hydrogen atom of the acid is incompletely dissociated in solutions of low pH.

(ii) Experimental procedure, observations, and conclusions. 25 ml. samples of potassium perchlorate solution (0.100 M) were titrated with a standard solution of phosphoric acid (1.3 M). The pH of the solutions was measured initially, and after successive
additions of the acid. This was repeated with vanadyl/perchlorate solution (0.100 M in vanadyl ion) in which the pH was initially raised to about 2.0 by the addition of a measured volume of potassium hydroxide solution. The experiments were also carried out while titrating with a standard solution of sulphuric acid. It was necessary to allow for the progressive dilution of the solutions in calculating the total concentrations of species present at each stage in the titrations.

The curve representing the titration of solutions of vanadyl ion with phosphoric acid, shown in figure 6, lies at lower pH values than that for the solutions of potassium ion. Therefore, as discussed in paragraph II(a)(i), this shows that the vanadyl ion takes part in complexing reactions with phosphoric acid in the solutions. This becomes more readily apparent on comparing the experimental data for the two systems as presented in the curves shown in figure 7. The initial slope of the curve for the system containing potassium ion is 0.8. This shows that the first hydrogen atom does not completely ionise from the phosphoric acid molecules initially introduced into these solutions. However, the initial slope of the curve for the vanadyl systems, that is 'x', is 2.0. Thus, as discussed in the foregoing theory, the formation of phosphato vanadyl complex species brings about the displacement of two hydrogen ions from the molecules of phosphoric acid first introduced into the system. This also shows that the complex species first formed in these solutions contain monohydrogen phosphate ligands since the ligand group, H_{3-x}A, becomes HPO_4^{2-} when 'x' is equal to 2. The formation of the first complex species of the vanadyl/phosphate system may, therefore, be represented as follows:-

\[ \text{VO}^{2+} + H_3PO_4 \rightarrow \text{VOHPO}_4 + 2H^+ \]
The titration of potassium perchlorate, and vanadyl/perchlorate solutions with phosphoric acid.

Fig. 6.

a — potassium perchlorate.

b — vanadyl/perchlorate.

\[ \left[ H_3PO_4 \right]/\left[ VO^{2+} \right] \text{ and } \left[ H_3PO_4 \right]/\left[ K^+ \right] \]
The titration of potassium perchlorate, and vanadyl/perchlorate solutions with phosphoric acid.

\[
\frac{h}{[\text{VO}^{2+}]} \quad \text{and} \quad \frac{h}{[\text{K}^+]} \]

- Figure 7:

\[
\frac{[\text{H}_3\text{PO}_4]}{[\text{VO}^{2+}]} \text{ and } \frac{[\text{H}_3\text{PO}_4]}{[\text{K}^+]} \]

- Graphs a and b:
  - a — potassium perchlorate.
  - b — vanadyl/perchlorate.
The titration of potassium perchlorate, and vanadyl/perchlorate solutions with sulphuric acid.

Fig. 8.

- $[\text{H}_2\text{SO}_4]/[\text{VO}^{2+}]$ and $[\text{H}_2\text{SO}_4]/[\text{K}^+]$
The titration of potassium perchlorate, and vanadyl/perchlorate solutions with sulphuric acid.

\[
\frac{h}{[\text{VO}^{2+}]} \quad \text{and} \quad \frac{h}{[\text{K}^+]}.
\]

\[
\frac{[\text{H}_2\text{SO}_4] / [\text{VO}^{2+}]}{[\text{H}_2\text{SO}_4] / [\text{K}^+]}
\]

Fig. 9.

- a - potassium perchlorate.
- b - vanadyl/perchlorate.
In a similar way, the observations presented in figures 8 and 9 show that complex sulphato vanadyl species are formed in the vanadyl/sulphate solutions. Now, both hydrogen atoms ionise to a considerable extent from the molecules of sulphuric acid in aqueous solution. Thus, the initial slope of 1.8 of the curve shown in figure 9, representing the titration of potassium perchlorate solution, may be explained by dissociation of the sulphuric acid. The initial slope of the curve obtained by titrating vanadyl/perchlorate solution is, however, unexpectedly large. Hydrolysis of the vanadyl ion would have been very limited under the conditions of the experiment. Furthermore, a drift of pH was not observed during the titrations as would have been expected if hydrogen ions were liberated as a result of the formation of hydroxy ligands. The titration characteristics of the vanadyl/sulphate system may, therefore, be attributed to interactions between the electrodes of the pH-meter and the species present in solution.

(b) The titration of perchloric, phosphoric, and sulphuric acids with sodium hydroxide solution in the presence and absence of vanadyl ion.

(i) Theoretical and experimental principles. The following investigations were designed to study the effect of complexing anions on the behaviour of vanadyl ions in aqueous solution when the acidic conditions, which initially prevailed in the solutions, were varied through neutral to alkaline by the addition of sodium hydroxide. As shown in section A, the hydrolysis and precipitation of the vanadyl ion, the polymeric nature of vanadyl hydroxide, and the formation of brown, sparingly-soluble vanadites in alkaline media have been studied by other workers. In fact, Britton has previously reported observations for the titration of vanadyl/sulphate solutions
with sodium hydroxide as described below (49). However, hydrolytic reactions are frequently characterised by slow rates of reaction. It was suspected, therefore, that more detailed observations could be drawn from this particular titration than those reported previously, and that these would be potentially useful when compared with observations from similar studies of the vanadyl/perchlorate and phosphate systems for which experimental data have not previously been reported.

(ii) Experimental procedure, observations, and conclusions.
25 ml. samples of perchloric acid and vanadyl/perchlorate solution (0.050 M in vanadyl ion), each with the same total concentration of perchlorate ion, were titrated with a standard solution of sodium hydroxide (0.745 N). The pH of the solution and the appearance of the system was noted after each addition of the alkali. Similar procedures were used in studies with solutions containing phosphate and sulphate ions in place of the perchlorate ions.

The observations for the titration of the perchlorate systems are presented in figure 10, and in an abbreviated form in table D1, (overleaf). A rapid rise of pH was brought about by the addition of sodium hydroxide at stages in the titration corresponding to the first inflexions in the titration curves shown in figure 10. These inflexions occurred as expected when the free hydrogen ion present in the solutions, which was derived from the strong acid, perchloric acid, was neutralised by the sodium hydroxide introduced. However, the rapid increase in pH was arrested at 3.8 in the vanadyl solutions when precipitation ensued. Only a small rise of pH followed the onset of precipitation until a further quantity of sodium hydroxide, equivalent to the vanadyl ion present in the system, had been introduced. The inflexion, after which the
The titration of perchloric acid, and vanadyl/perchlorate solutions with sodium hydroxide.

Fig. 10.

- $a$—vanadyl/perchlorate. ($\text{VO}^{2+}$ ion, 0.050 M, $\text{ClO}_4^-$ ion, 0.215 M).
- $b$—perchloric acid (0.215 M).

1—neutralisation of free $H^+$ ion of "a".
2—neutralisation of $H^+$ ion of "b".

volume of NaOH soln. (0.745 N) added. (ml.)
TABLE D1.
(for the vanadyl/perchlorate system)

<table>
<thead>
<tr>
<th>Volume of NaOH soln. added (ml)</th>
<th>Average pH of soln.</th>
<th>Appearance of system, and further observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.97</td>
<td>Royal-blue solution.</td>
</tr>
<tr>
<td>3.90</td>
<td>3.06</td>
<td>Royal-blue solution.</td>
</tr>
<tr>
<td>4.00</td>
<td>3.50</td>
<td>Grey-blue solution.</td>
</tr>
<tr>
<td>4.10</td>
<td>3.65</td>
<td>Grey-blue solution.</td>
</tr>
<tr>
<td>4.20</td>
<td>3.76</td>
<td>Steel-blue solution.</td>
</tr>
<tr>
<td>4.30</td>
<td>3.80</td>
<td>Steel-blue soln. + grey ppt.</td>
</tr>
<tr>
<td>4.40</td>
<td>3.81</td>
<td>Grey soln. + grey ppt.</td>
</tr>
<tr>
<td>6.60</td>
<td>4.11</td>
<td>Grey soln. + grey ppt.</td>
</tr>
<tr>
<td>6.80</td>
<td>4.22</td>
<td>Brown-grey soln. + ppt.</td>
</tr>
<tr>
<td>7.20</td>
<td>5.13</td>
<td>Brown-grey soln. + ppt.</td>
</tr>
<tr>
<td>7.40</td>
<td>6.86</td>
<td>Brown soln. + ppt., fast pH drift to higher values.</td>
</tr>
<tr>
<td>7.60</td>
<td>9.20</td>
<td>Brown soln. + ppt., pH steady.</td>
</tr>
<tr>
<td>7.70</td>
<td>10.00</td>
<td>Brown soln. + ppt., slow pH drift to lower values.</td>
</tr>
<tr>
<td>10.00</td>
<td>11.16</td>
<td>Brown soln. + ppt., slow pH drift to lower values.</td>
</tr>
<tr>
<td>approx. 20</td>
<td>11.36</td>
<td>Ppt. slowly dissolved to give brown solution.</td>
</tr>
</tbody>
</table>

solutions became alkaline, occurred in each solution after the same total quantity of sodium hydroxide had been introduced. These phenomena may be explained by the complete precipitation of the vanadyl ion as vanadyl hydroxide, $\text{VO(OH)}_2^-$, since the total concentration of perchlorate ion was the same in each solution. This is in accordance with the properties of the hydrated vanadyl ion
discussed in section A. The slow formation of a brown, sparingly-soluble material was observed in the system containing vanadium under alkaline conditions. This may be attributed to the formation of vanadite (IV) species. Previous investigators have assigned the formula, $V_4O_{10}^{2-}$, to the anion of these compounds.

**TABLE D2**
(for the vanadyl/sulphate system)

<table>
<thead>
<tr>
<th>Volume of NaOH soln. added (ml)</th>
<th>Average pH of soln.</th>
<th>Appearance of system, and further observations.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.66</td>
<td>Royal-blue solution.</td>
</tr>
<tr>
<td>1.30</td>
<td>2.92</td>
<td>Royal-blue solution.</td>
</tr>
<tr>
<td>1.40</td>
<td>3.24</td>
<td>Greenish-blue solution.</td>
</tr>
<tr>
<td>1.60</td>
<td>3.77</td>
<td>Blue-green solution.</td>
</tr>
<tr>
<td>1.70</td>
<td>3.89</td>
<td>Blue-grey solution.</td>
</tr>
<tr>
<td>1.90</td>
<td>4.00</td>
<td>Blue-grey solution, + grey ppt.</td>
</tr>
<tr>
<td>2.00</td>
<td>4.02</td>
<td>Deep greenish-grey solution, + ppt.</td>
</tr>
<tr>
<td>2.20</td>
<td>4.06</td>
<td>Deep grey soln. + grey ppt.</td>
</tr>
<tr>
<td>4.70</td>
<td>5.13</td>
<td>Brownish-grey soln. + ppt.</td>
</tr>
<tr>
<td>5.20</td>
<td>10.00</td>
<td>Brown soln. + ppt., fast pH drift to lower values.</td>
</tr>
<tr>
<td>7.00</td>
<td>11.56</td>
<td>Brown soln. and ppt., pH drift to lower values.</td>
</tr>
</tbody>
</table>

The observations for the sulphate systems are presented in figure 11, and are summarised above in table D2. These show that a similar behaviour is exhibited by vanadyl ion in vanadyl/sulphate solutions to that discussed above for the vanadyl/perchlorate system. The hydrated vanadyl ion appears to be completely converted to
The titration of sulphuric acid, and vanadyl/sulphate solutions with sodium hydroxide.

Fig. 11.

a—vanadyl/sulphate.
\( \text{VO}^{2+} \text{ion, } 0.050 \text{ M} \)
\( \text{SO}_4^{2-} \text{ion, } 0.070 \text{ M} \)

b—sulphuric acid
\( (0.070 \text{ M}) \)

1—neutralisation of free \( \text{H}^+ \) ion of "a".

2—neutralisation of \( \text{H}^+ \) ion of "b".

volume of sodium hydroxide solution
\( (0.745 \text{ N}) \) added. (ml.)
vanadyl hydroxide in both systems. However, the slightly higher pH of 4.0 which is required to initiate the precipitation of vanadyl hydroxide in the solutions containing sulphate ion is indicative of reactions involving vanadyl and sulphate ions which are not paralleled in vanadyl/perchlorate solutions. Whereas low concentrations of hydrogen ion caused blue vanadyl/perchlorate solutions to become grey in colour before the onset of precipitation, similar pH conditions in the vanadyl/sulphate systems were found to give rise to the appearance of green colourations. Hydrolysis of vanadyl-containing species may account for the observed phenomena in both systems. However, conclusive deductions may not be drawn for either system on the basis of this evidence alone.

Observations for the phosphate systems are presented in figure 12, and summarised for the solutions containing vanadyl ion in table D3 (overleaf). In contrast to the perchlorate and sulphate systems, the same quantity of sodium hydroxide was required by both solutions containing phosphate to reach the first point of inflexion in the titration curves shown in figure 12. These occurred at pH 4.6. In the solutions of phosphoric acid, this inflexion corresponds to the neutralisation of the first hydrogen atom of the acid. However, the solutions containing vanadyl ion were initially of the same total concentration of phosphate as the solution of phosphoric acid. Thus, complex-forming reactions between vanadyl and phosphate ions were shown to cause the liberation of hydrogen ion from the second or third ionising hydrogen atoms of the phosphate species at pH 4.6. Furthermore, the quantity of hydrogen ion which was liberated in this way was found to be equivalent to the vanadyl ion present in the solutions. Now, the experiments described in paragraph II(a) have shown that the phospho vanadyl species, which are first formed in the vanadyl/phosphate solutions, contain
The titration of phosphoric acid, and vanadyl/phosphate solutions with sodium hydroxide.

**Fig. 12.**

- **a**—vanadyl/phosphate. ($\text{VO}^{2+}$ ion, 0.050 M; $\text{PO}_4^{3-}$ ion, 0.848 M)
- **b**—phosphoric acid (0.848 M).

1—neutralisation of 1st $\text{H}^+$ ion of "b".
2—neutralisation of 2nd $\text{H}^+$ ion of "b".

**Volume of NaOH soln. (0.745 N) added. (ml.)**
TABLE D3
(for the vanadyl/phosphate system)

<table>
<thead>
<tr>
<th>Volume of NaOH soln. added (ml)</th>
<th>Average pH of soln.</th>
<th>Appearance of system, and further observations.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.92</td>
<td>Royal-blue solution.</td>
</tr>
<tr>
<td>24.00</td>
<td>3.03</td>
<td>Royal-blue solution.</td>
</tr>
<tr>
<td>24.50</td>
<td>3.16</td>
<td>Royal-blue soln. + slight ppt.</td>
</tr>
<tr>
<td>26.00</td>
<td>3.54</td>
<td>Royal-blue soln. + pale-green ppt.</td>
</tr>
<tr>
<td>27.50</td>
<td>4.02</td>
<td>Less intense blue soln. + pale-green ppt.</td>
</tr>
<tr>
<td>30.00</td>
<td>5.35</td>
<td>Ditto, slow pH drift to lower values.</td>
</tr>
<tr>
<td>33.00</td>
<td>5.86</td>
<td>Turquoise soln., pale-green ppt., slow pH drift to lower values.</td>
</tr>
<tr>
<td>56.00</td>
<td>8.48</td>
<td>Ditto.</td>
</tr>
<tr>
<td>57.00</td>
<td>9.28</td>
<td>Brown-green soln., green ppt., pH drifting.</td>
</tr>
<tr>
<td>58.00</td>
<td>9.80</td>
<td>Deep green soln., less green ppt., pH drifting.</td>
</tr>
<tr>
<td>59.00</td>
<td>10.03</td>
<td>Green soln., slight green ppt., pH drifting.</td>
</tr>
<tr>
<td>59.50</td>
<td>10.13</td>
<td>Green soln., no ppt., pH steady.</td>
</tr>
<tr>
<td>63.00</td>
<td>10.56</td>
<td>Green soln., no ppt., pH steady.</td>
</tr>
</tbody>
</table>

monohydrogen phosphate ligand groups. Furthermore, as shown in section A, other workers have found that orthophosphate complexes of tervalent metal ions contain chelate monohydrogen phosphate ligands in acid solutions. Therefore, the hydrogen ion liberated at pH 4.6 in the vanadyl/phosphate solutions may be accounted for
by a virtually quantitative complexing of the vanadyl ion in species of formula, VO(\text{HPO}_4)_2^{3-}. Since dihydrogen phosphate ions predominate in orthophosphate solutions of pH 4.6, the formation of these complex species may be represented by the following equation:

\[
\text{VO}^{++} + 2\text{H}_2\text{PO}_4^- \rightleftharpoons \text{VO(HPO}_4)_2^{3-} + 2\text{H}^+ .
\]

The precipitate which formed in the vanadyl/phosphate solutions of pH greater than 3.0 was not accompanied by a levelling of the titration curve as was found to occur during the precipitation of vanadyl hydroxide from vanadyl/perchlorate solutions (figs. 10 & 12). Moreover, the precipitate in the vanadyl/phosphate system was green rather than grey in colour. Therefore, the precipitate could not have been one of vanadyl hydroxide. This shows that the complexing of vanadyl ions by phosphate proceeds to such an extent in solutions of pH 3 to 4 that the concentration of hydrated and hydrolysed vanadyl ions is sufficiently reduced to prevent the formation of a precipitate of vanadyl hydroxide. For this reason, the green solid was considered likely to contain both vanadyl and phosphate ions and was studied in greater detail as described in section F.

Referring again to tables D1 and D3, it may be seen that alkaline conditions gave rise to green colourations in vanadyl/phosphate solutions, whereas brown colourations were observed under similar conditions in the vanadyl/perchlorate systems. Furthermore, the green species formed in the phosphate system were of greater solubility than the brown species formed in the perchlorate media. Now, the addition of disodium hydrogen phosphate solution to the brown alkaline solutions of the vanadyl/perchlorate system was found to cause the solutions to turn green rapidly. It is clear, therefore, that the species containing quadrivalent vanadium in alkaline...
phosphate solutions are of a different nature to those formed in perchlorate media. The pH was found to be unsteady during the titration of vanadyl/phosphate solutions in the alkaline region. The uptake of atmospheric carbon dioxide would have caused the pH of the solutions to drift to some extent, but this phenomenon may also have been caused by the slow formation of polymeric species in the system.
SECTION E.

THE APPLICATION OF SPECTROPHOTOMETRIC METHODS TO THE STUDY OF SYSTEMS CONTAINING COMPLEXES OF THE VANADYL ION.
I. The visible and ultraviolet absorption spectra of complexes of the vanadyl ion.

Comprehensive general accounts of the application of the crystal-field and ligand-field theories to the explanation of the absorption spectra of inorganic complex species have been presented by several workers (137-139). Certain aspects of these theories, which are of importance in explaining the absorption spectra of complexes of the vanadyl ion, are summarised below.

Transition metal ions, if completely isolated from the field forces of co-ordinated ligands, would be characterised by a completely degenerate set of five d-orbitals. However, a symmetrical octahedral arrangement of ligands produces an electrostatic field of cubic symmetry, and this has the effect of separating these orbitals in energy such that the \( d_{xy}, d_{yz}, \) and \( d_{xz} \) orbitals are stabilised, and the \( d_{x^2-y^2}, d_z^2 \) orbitals are destabilised. This is shown in the following diagram:

The separation of the energies of the two groups of orbitals, \( 10D_q, \)
brought about in this way depends upon the magnitude of the pertur­
bing field forces.

Considering an ion characterised by a single d-electron
under the influence of field forces of cubic symmetry, the electron
will occupy one of the orbitals of lowest energy when the ion is in
the ground state. On absorbing a suitable quantum of energy, in
the form of electromagnetic radiation, the electron is excited and
moves to one of the orbitals of higher energy. Such a transition
of the electron gives rise to an absorption peak in the absorption
spectrum of the ion. Absorption peaks due to transitions of this
nature are generally found at wavelengths in the vicinity of 1000 µm
for divalent cations and 500 µm for tervalent cations.

The splitting of the energy levels described above takes
place only in systems characterised by field forces of cubic sym­
metry. In such systems, if the central metal ion is considered
to be situated at the origin of co-ordinates, the sums of the dipole
moments along each of the axes x, y, and z, are equal. That is,

\[ \mu_x = \mu_y = \mu_z. \]

Systems with a distorted form of octahedral symmetry are character­
ised by different modes of splitting of the energy levels of the
d-orbitals. These may be grouped into two classes,

(i) the tetragonal systems, in which

\[ \mu_x = \mu_y \neq \mu_z, \]

and, (ii) the rhombic systems, where

\[ \mu_x \neq \mu_y \neq \mu_z. \]
Non-cubic fields may originate from several causes. The Jahn-Teller theorem states that totally symmetric configurations are unstable with respect to other less symmetrical forms, which retain the same centre of symmetry as the totally symmetric structure. Effects of this type, therefore, give rise to distortions which occur in all complex species except those with a linear structure. Inequivalent ligands in a complex also produce unequal sums of the dipole moments. Furthermore, it is possible for species outside the co-ordination sphere of the central metal ion to affect the symmetry of a complex, although this effect is usually negligible with complexes of metal ions of the first transition series.

Now, the spin and translatory movements of the orbital electrons give rise to magnetic field forces. These forces interact in a quantised manner to produce spin-orbit coupling effects which cause a further resolution of the energy levels of the d-orbitals. However, spin-orbit splitting is small in comparison with that produced by strong electrostatic fields in an octahedral system and is still less important in systems in which the effects of a distorted configuration also contribute to the resolution of the orbital energies.

Each of the factors described above contributes to the splitting of the orbital energy levels. The overall resolution of the energy levels of the d-orbitals, which is produced in tetragonally distorted octahedral systems containing a single d-electron, is shown in the following diagram:
(a) Degenerate energy levels in a field-free system.
(b) System with strong, totally-symmetric, octahedral field.
(c) Octahedral system with medium, tetragonal distortion.
(d) System (c) with additional weak, spin-orbit coupling.
(e) System (c) with additional medium spin-orbit coupling.

It may be seen from the diagram, and has been discussed by Sutton (140), that an ion containing a single d-electron may show up to four distinct absorption bands if it is subject to tetragonal field forces which are sufficiently strong to completely separate the energies of the d-orbitals. The shoulder in the absorption band of the hexaquo titanium (III) ion, although weak, is considered to be due to a tetragonally distorted configuration arising from Jahn-Teller effects. Systems with very weak field forces, however, may merely exhibit a broad absorption peak due to a small splitting of the orbital energy levels.
From the properties of a cube, four negative groups arranged tetrahedrally around an ion would produce the same type of splitting of energy levels as an octahedral arrangement of six positive groups. Thus, the energy levels of an ion surrounded tetrahedrally by four ligand groups may be represented diagrammatically by inverting the schemes presented above for the octahedral systems. Therefore, complexes with a distorted tetrahedral configuration may also exhibit up to four absorption bands. It can also be shown that rhombic distortions of the octahedral configuration would give rise to two further energy levels and, in consequence, exhibit a maximum of six absorption bands. A trigonal-bipyramidal arrangement of ligands would be expected to give rise to a maximum of two absorption bands.

The absorption spectrum and configuration of the vanadyl complexes will now be considered in relation to the theory discussed above. As may be expected, the vanadyl ion has been shown to have a single d-electron (38,39) and, in aqueous perchlorate media of low pH, exhibits an absorption peak at 760 μ, and an unresolved peak at 620 μ (40,86). Similar, although more distinct absorption characteristics have been demonstrated in solutions containing vanadyl ion in the presence of thiocyanate, oxalate, and a variety of other organic anions. Distorted tetrahedral or octahedral, or even trigonal-bipyramidal configurations of the vanadyl complexes in these solutions may equally account for the two absorption peaks observed in their visible absorption spectra. Thus, no indication of the configuration of the hydrated vanadyl ion, or the complex vanadyl species containing the other ligands mentioned, may be obtained from their absorption spectra alone.

The ethylenediaminetetraacetate and tartrate complexes of the vanadyl ion are species with strong field forces and exhibit three
and four peaks respectively in their visible and ultraviolet absorption spectra. These complexes cannot, therefore, have the configuration of a trigonal bipyramid. Only distorted tetrahedral or octahedral configurations are consistent with the observed number of absorption bands of these species. Since the configuration of the hydrated vanadyl ion is unlikely to be modified fundamentally on complexing with these quadridentate ligands, the hydrated vanadyl ion, and the vanadyl complexes involving simpler ligands, may also be assumed to have distorted tetrahedral or octahedral configurations. The appearance of only two absorption maxima with the latter species may be attributed either to a small splitting of the energy levels, or to the occlusion of certain of the absorption peaks by the strong ultraviolet absorption band. Several workers have shown that charge-transfer phenomena involving electrons of the vanadium-oxygen double bond may account for the strong absorption band of the complexes in the ultraviolet region (61,137,141).

Carpenter, Ducret, and other workers have demonstrated that the hydrated vanadyl ion carries a positive charge of two units (36, 55,58). This may now be used to distinguish between the possible tetrahedral or octahedral configurations of this species. If the hydrated vanadyl ion were of tetrahedral configuration, it would be formed by the dissociation of two protons from the ion, $V(H_2O)^{4+}$. Now, hydrolysis of the hydrated vanadyl ion does not take place easily, but causes the slow formation of polymeric hydroxy species or vanadites (IV) (40-49). Thus, the tetrahedral configuration of the hydrated vanadyl ion may be eliminated since an irregular gradation in the tendency of successive protons to dissociate from the species, $V(H_2O)^{4+}$, is not to be expected.
Now, Palma-Vittorelli and co-workers have used paramagnetic resonance studies to demonstrate that one oxygen atom of the hydrated vanadyl ion is linked by a double bond to the central vanadium ion (142). Furthermore, Jones has prepared the diacetylacetone complex of the vanadyl ion in an anhydrous state and, by studying the absorption spectrum of the compound, has shown that the vanadium-oxygen bond is not modified to two hydroxyl groups on coming into contact with water (80). The hydrated vanadyl ion may, therefore, be considered to have an octahedral configuration with one co-ordination site occupied by an oxide ion. In this way, the positive charge of the quadrivalent vanadium ion would be reduced to two units. The absorption characteristics may then be explained since the inequivalence of the ligands in the complex would give rise to a tetragonally distorted configuration. Furthermore, this is consistent with the octahedral configurations demonstrated by Hoppe and Gutman for the complex ions, $\text{VCl}_6^{2-}$ and $\text{VF}_6^{2-}$, which also contain quadrivalent vanadium (33,34). The vanadyl complexes containing simple ligands which are characterised by similar absorption spectra to the hydrated vanadyl ion may also be considered to have tetragonally distorted octahedral configurations. Ethylenediaminetetraacetate and tartrate ligands are able to occupy four co-ordination sites more readily in an octahedral than in a tetrahedral structure. The absorption spectra of the vanadyl complexes with these ligands may be attributed, therefore, to strong field forces in these species.

Jones has pointed out that ligand groups appear to be able to occupy a maximum of four co-ordination sites in vanadyl complexes in aqueous media (143). Thus, in addition to a tetragonally distorted octahedral structure, it is also possible for vanadyl complexes to have a five-co-ordinate configuration in the form of a
The crystal-field theory provides a qualitative explanation of the absorption characteristics of the vanadyl complexes, but is unable to account exactly for the frequencies at which the absorption bands occur. Furlani has shown that the ligand-field theory has similar limitations in explaining the absorption spectra of vanadyl species (141). Now, the separation of the energy levels of the d-orbitals depends upon the magnitude of the disturbing field-forces produced by the ligand groups. Thus, as indicated by Smithson, Williams, and other workers, the formation of complex species may be detected, and the magnitude of the disturbing fields of the ligand groups be studied qualitatively from the shifts of the absorption bands of the hydrated metal ion on introducing the complexing agent to the system (144,145). These workers have also indicated that weak interactions between the metal ion and other species may result in an appreciable shift of the strong ultraviolet absorption band alone, since this is due to the transition of electrons which, unlike d-electrons, are not localised to the immediate vicinity of the central metal ion. In the case of the hydrated vanadyl ion, Furlani has indicated that the strong ultraviolet absorption band may be due to the transition of electrons of the bond between the vanadium and oxide ions (141).

Quantitative spectrophotometric methods, such as those described by Job, Frank and Oswalt, and other workers (93,146), may be applied to systems in which species react to form a single product. These methods enable the ratio of the constituent species, and the stability constant of the complex to be estimated. Other workers, including Vosburgh and Cooper (147), and Trujillo and Torres (148),
have formulated extensions to these treatments for the study of systems in which the constituent species react to form more than one product. However, the application of these extensions is frequently restricted by the nature of the absorption spectra of the systems and the accuracy of experimental measurements.

II. Theories underlying methods used, experimental procedures, observations, and conclusions.

(a) The study of the absorption spectra of solutions of constant total concentration of vanadyl ion, but differing in total concentration of complexing agent.

(i) Theoretical and experimental principles. In order to simplify the discussion, a system is considered in which a metal ion, 'M', reacts with an acid, 'H_A', to form a single complex species in the manner indicated in the following equation:-

\[ nM + H_yA \to MH_{y-x}A + xH \]

Such a system may be represented by the Law of Chemical Equilibrium as follows:-

\[ K = \frac{(NH_{y-A})(H)^x}{(M)(H_yA)} \]

Thus, the extent to which the metal ion is complexed will depend upon the concentration of the complexing agent, 'H_yA', in the system. Now, as discussed in paragraph E.I, the absorption spectrum of a hydrated metal ion is modified as the ligand water molecules are replaced by other ligands. When complex formation takes place, therefore, the absorption spectra of solutions constant in total
concentration of metal ion, will be progressively modified as the concentration of complexing agent is increased. Now, complexing of the metal ion will tend to completion when excesses of the complexing agent are present. Thus, considering observations at one particular wavelength, the optical density of the solutions may be expected to approach a limiting value as the concentration of complexing agent is increased. The rate at which the limiting optical density is approached will depend upon the stability of the complexes formed. The observations for studies of this kind have been presented in the experiments described below by plotting $D_{\text{inc}}$ against the total concentration of complexing agent. $D_{\text{inc}}$ represents the increase in optical density of the solution, at the wavelength specified, over that of a solution containing zero concentration of the complexing agent. It is shown above that complex formation depends upon the concentration of hydrogen ion in systems in which the ligand groups are derived from a weak acid. However, useful experimental data may be expected on varying the total concentration of complexing agent in solutions of constant metal ion concentration without maintaining strictly constant conditions of pH.

The absorption spectrum of the vanadyl ion in aqueous solution has been found by other workers to be unaffected by the concentration of perchlorate ion, except under extreme conditions (61, 86). It was considered unnecessary, therefore, to control the concentration of this ion in the experiments described below.

(ii) Experimental procedure, observations, and conclusions. Vanadyl/perchlorate solution was used to prepare solutions with a constant total concentration of vanadyl ion. The complexing anions
were introduced into these solutions in measured quantities as the acid or sodium salt. The solutions were allowed to stand for 7 days before measuring the pH and the optical density over the wavelength range 1000 to 280 \( \mu \text{m} \). The optical densities of the solutions of the acid or sodium salt of each anion were also measured over the same range of wavelengths and were found to be negligible in each case.

Observations for the vanadyl/phosphate system are presented in figures 13 and 14. For reasons discussed in paragraphs E.I and E.II(a)(i), these show that the vanadyl ion forms complex species containing phosphato ligands. The progressive increase in phosphate concentration in the systems caused parallel increases in the extent of complex formation in spite of opposing decreases in pH. The pH of the solutions varied from 0.98 at zero phosphate concentration to 0.06 in the solutions 3.0 molar in phosphate. However, the phosphato complexes, formed in the system, were found to be of low stability since addition of phosphate caused the optical density of the solutions to vary, even after a large excess of phosphate had previously been introduced into the system. Now, the observations show that the absorption bands of the hydrated vanadyl ion occur at wavelengths of 625 and 765 \( \mu \text{m} \). The formation of phosphato complexes, however, causes both of these bands to shift to longer wavelengths and, in so doing, to become more distinct and separate in wavelength. Thus, considering the theory of visible absorption spectra discussed in paragraph E.I, this shows that phosphato ligands produce stronger ligand-field forces than aquo ligands in complexes of the vanadyl ion.

Figures 15, 16, and 17 show the observations for the vanadyl/thiocyanate system. These indicate that complex formation takes
Absorption spectra of solutions 0.050 M in vanadyl ion in which the total phosphate concentration was varied.

**Fig. 17**

<table>
<thead>
<tr>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
</tr>
<tr>
<td>1.0</td>
</tr>
<tr>
<td>0.9</td>
</tr>
<tr>
<td>0.8</td>
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<td>0.7</td>
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<td>0.6</td>
</tr>
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<td>0.5</td>
</tr>
<tr>
<td>0.4</td>
</tr>
<tr>
<td>0.3</td>
</tr>
<tr>
<td>0.2</td>
</tr>
<tr>
<td>0.1</td>
</tr>
<tr>
<td>0.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wavelength (m(\mu))</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
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<tr>
<td>900</td>
</tr>
<tr>
<td>950</td>
</tr>
<tr>
<td>1000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total [PO(_4)^3-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(~ 10)</td>
</tr>
<tr>
<td>3.000</td>
</tr>
<tr>
<td>1.000</td>
</tr>
<tr>
<td>0.300</td>
</tr>
<tr>
<td>0.100</td>
</tr>
<tr>
<td>0.020</td>
</tr>
<tr>
<td>0.010</td>
</tr>
<tr>
<td>0.000</td>
</tr>
</tbody>
</table>
The effect of total phosphate concentration on the optical density of solutions 0.050 M in vanadyl ion.

**Fig. 14:**

- **at 850 mµ.**
- **at 925 mµ.**
Absorption spectra of solutions 0.015 M in vanadyl ion in which the total thiocyanate concentration was varied.  

**Fig. 15.**

<table>
<thead>
<tr>
<th>total [CNS⁻]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3000</td>
</tr>
<tr>
<td>0.1500</td>
</tr>
<tr>
<td>0.0600</td>
</tr>
<tr>
<td>0.0450</td>
</tr>
<tr>
<td>0.0300</td>
</tr>
<tr>
<td>0.0225</td>
</tr>
<tr>
<td>0.0150</td>
</tr>
<tr>
<td>0.0075</td>
</tr>
<tr>
<td>0.0000</td>
</tr>
</tbody>
</table>

Optical density

wavelength (μ)
Absorption spectra of solutions 0.015 M in vanadyl ion in which the total thiocyanate concentration was varied.

Fig. 16.

<table>
<thead>
<tr>
<th>Curve</th>
<th>Total [CNS⁻]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.0000</td>
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<tr>
<td>b</td>
<td>0.0075</td>
</tr>
<tr>
<td>c</td>
<td>0.0150</td>
</tr>
<tr>
<td>d</td>
<td>0.0300</td>
</tr>
<tr>
<td>e</td>
<td>0.1500</td>
</tr>
<tr>
<td>f</td>
<td>0.3000</td>
</tr>
</tbody>
</table>
The effect of total thiocyanate concentration on the optical density of solutions 0.015 M in vanadyl ion.

**Fig. 17:**

- At 750 m\(\mu\).
- At 800 m\(\mu\).
- At 600 m\(\mu\).
place between vanadyl and thiocyanate ions. However, for reasons discussed above for the phosphato complexes, the curves of figure 17 show that the thiocyanato complexes are characterised by low stability. Furthermore, a comparison of the curves of figures 14 and 17 shows that the order of stability of the thiocyanato complexes is similar to that of the phosphato vanadyl species.

Referring now to figures 15 and 16, the peak and shoulder characters of the visible absorption band of the hydrated vanadyl ion shift only to a small extent on complexing with thiocyanate ion and no additional absorption bands appear in the near ultraviolet region. The thiocyanato ligands, therefore, give rise to ligand-field forces similar in magnitude to those produced by aquo ligands in the vanadyl complexes. Thus, considering the spectrochemical series discussed by Dunn (139), the thiocyanate ligands may be considered to be linked through the nitrogen atoms to the vanadyl ion. Bonding through the sulphur atoms would be expected to give rise to smaller ligand-field forces, and therefore, a smaller separation of the energy levels of the d-orbitals.

As discussed in paragraph E.I, the strong ultraviolet absorption band is considered to be associated with the electrons of the vanadium-oxygen bond. The marked displacement of this band towards longer wavelengths, which was found to occur in the presence of thiocyanate ion, shows, therefore, a fairly strong interaction between the bonding orbitals of the vanadium-oxygen group and the thiocyanato ligands. This may be expected, since pi-bonds feature in the constitution of each of these groups, and the bonding orbitals involved are not localised along the axes of the bonds.
The marked increase in optical density of vanadyl solutions caused by the addition of thiocyanate ion is difficult to explain. A possible explanation may lie in the larger size of the thiocyanato complex as compared with that of the hydrated vanadyl ion. In this way, the thiocyanato complex would present the larger target area over which to capture incident photons of suitable energy in the excitation of the d-electron of the vanadium ion.

The observations shown in figures 18, 19, and 20 show that oxalate and vanadyl ions react to form complexes in solution and confirm the conclusions of other workers who employed experimental methods of a different nature to study the system (section A). For reasons similar to those discussed above for the phosphate system, the observations demonstrate that the replacement of aquo ligands by oxalate ions in the co-ordination sphere of the vanadyl ion gives rise to stronger ligand-field perturbing forces. However, in this case, the absorption band of the hydrated vanadyl ion at 625 nm was found to shift towards the shorter wavelengths. Furthermore, as with the thiocyanato complex species, the shifts of the ultraviolet absorption band indicate that there are strong interactions between the bonding orbitals of the vanadium-oxygen group and the oxalato ligands in the oxalato complexes. The curves shown in figure 20 indicate that the optical densities of the solutions approached limiting values when oxalate and vanadyl ions were present in a mole ratio of 4 : 1. Thus, the oxalato vanadyl complexes have a considerably higher stability than the thiocyanato and phosphato complexes (cf. figs. 14, 17).

Figures 18 and 19 also show that complex formation takes place between vanadyl and chloride ions, but apparently only to a
Absorption spectra of solutions 0.0475 M in vanadyl ion in which the total oxalate, or total chloride concentration was varied.

![Graph showing absorption spectra with wavelength (mμ) on the x-axis and optical density on the y-axis.](Image)

**Fig. 18.**

- **Curve** -----
- total \([C_2O_4^{2-}]\) = 0.02
- \(pH = 0.34\)
- \(pH = 1.07\)
- \(0.195\)
- \(0.193\)
- \(0.039\)
- \(0.000\)

**Table:**

<table>
<thead>
<tr>
<th>total ([C_2O_4^{2-}])</th>
<th>(pH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.195</td>
<td>1.07</td>
</tr>
<tr>
<td>0.193</td>
<td>0.72</td>
</tr>
<tr>
<td>0.039</td>
<td>0.63</td>
</tr>
<tr>
<td>0.000</td>
<td>0.70</td>
</tr>
</tbody>
</table>
Absorption spectra of solutions 0.0475 M in vanadyl ion in which the total oxalate, or total chloride concentration was varied.

![Graph showing absorption spectra with wavelengths and optical density values.]

**Fig. 19.**

<table>
<thead>
<tr>
<th>Curve</th>
<th>Total $[C_2O_4^{2-}]$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.000</td>
<td>0.70</td>
</tr>
<tr>
<td>b</td>
<td>0.039</td>
<td>0.63</td>
</tr>
<tr>
<td>c</td>
<td>0.113</td>
<td>0.72</td>
</tr>
<tr>
<td>d</td>
<td>0.195</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Curve -----  

Total $[Cl^-] = 3.02$  
P$\text{H} = 0.34$
The effect of total oxalate concentration on the optical density of solutions 0.0475 M in vanadyl ion.

Fig. 20.

at 800 mμ.

at 575 mμ.
Absorption spectra of solutions 0.0475 M in vanadyl ion in which the total sulphate, or total bromide concentration was varied.

\[
\begin{array}{cc}
\text{total } [\text{SO}_4^{2-}] & \text{pH} \\
0.858 & 1.32 \\
0.506 & 1.15 \\
0.000 & 0.70 \\
\end{array}
\]

\[
\text{total } [\text{Br}^-] = 2.00
\]

para. E.II.
Absorption spectra of solutions 0.0475 M in vanadyl ion in which the total sulphate, or total bromide concentration was varied.

Fig. 22.

<table>
<thead>
<tr>
<th>Curve</th>
<th>Total $[SO_4^{2-}]$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.000</td>
<td>0.70</td>
</tr>
<tr>
<td>b</td>
<td>0.858</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>0.506</td>
<td>1.15</td>
</tr>
</tbody>
</table>

curve ______

total $[Br^-] = 3.00$
very small extent. This is in agreement with the conclusions of Ahrland, Noren, Kraus and other workers, who used different experimental methods to study this system (96,97).

The formation of sulphato vanadyl complexes is demonstrated by the observations presented in figures 21 and 22. These complexes appear to be formed in very low concentrations, however, since the absorption spectrum of the hydrated vanadyl ion was modified to only a small extent by the introduction of large excess concentrations of sulphate in both the visible and ultraviolet regions. The absorption curves of figures 21 and 22 also show that weak complexes are formed between vanadyl and bromide ions. However, on comparing these absorption curves with those of figures 18 and 19, it may be seen that introduction of bromide ion was found to modify the vanadyl ion absorption spectrum to a smaller extent than the introduction of the same concentration of chloride ion.

(b) The study of the absorption spectra of solutions constant in total concentration of vanadyl ion and anion, but differing in pH.

(i) Theoretical and experimental principles. As in paragraph E.II(a)(i), in order to simplify the discussion, a system is considered in which only one complex species is formed by the reaction of a metal ion, 'M', with a weak acid, 'H_yA'. This may be represented by the following equation:

\[ M + H_yA \rightarrow MH_{y-x}A + xH \]
This may, then, be described by the Law of Chemical Equilibrium as follows:

\[ K = \frac{(M \cdot H^y \cdot A)^{(H)^x}}{(M)(H^y \cdot A)} \]

Thus, the extent to which the metal ion is taken up in complex formation will depend upon the concentration of hydrogen ion in the system and will be greatest in solutions of higher pH. Now, it has been shown in paragraph E.I that the absorption spectrum of a hydrated metal ion is modified as the aquo ligands are replaced by other ligand groups. This may be studied, therefore, together with the nature of the complex species formed, by investigating the way in which the absorption spectra of solutions, constant in total concentrations of metal ion and complexing agent, are modified by varying the conditions of pH in the systems.

A system in which a metal ion, 'M', reacts with the anion of a strong acid, 'S', to form a single complex species may be represented by the following equation:

\[ M + S \rightarrow MS \]

It may be seen, therefore, that the extent of complex formation in such a system will be independent of the conditions of pH, provided hydrolysis of the metal ion may be neglected.

Now, hydrolysis of the vanadyl ion has been studied by several workers (40-49), and, as pointed out by Jones and Ray (42), is negligible in solutions of pH less than 2. Some of these workers have shown that the species, VO\textsubscript{OH}\textsuperscript{+}, is formed in solutions of low hydrogen ion concentration before precipitation of polymeric vanadyl hydroxide ensues at pH 4. Rossotti and Rossotti have shown that
the dimeric species, (VOOH)\textsuperscript{2+}, is also formed in solutions of low hydrogen ion concentration (40). Thus, the first co-ordination sphere of the hydrated vanadyl ion is modified by hydrolysis under such conditions. The effect of this on the absorption spectrum of the vanadyl ion was studied in the experiments described below by varying the pH of solutions in which constant total concentrations of vanadyl and perchlorate ions were maintained.

(ii) Experimental procedure, observations, and conclusions. Solutions were prepared which contained constant total concentrations of vanadyl ion and complexing anion. The pH was varied in these solutions by the introduction of suitable quantities of sodium hydroxide. After preparation, the solutions were allowed to stand for 7 days before measuring the pH and optical densities over the wavelength range 1000 to 280 nm, and then were stored in stoppered flasks for a period of 3 months. Precipitation had not taken place in any of the solutions when their absorption spectra were recorded.

Observations for the vanadyl/perchlorate system are presented in figures 23 and 24. As discussed in paragraph E.I, the solutions of pH 2 or less, which are blue in colour, exhibit absorption characters which may be attributed to a tetragonally distorted hydrated vanadyl ion. However, the solutions became green in colour and the absorption spectra continuous, over the range of wavelengths studied, under conditions of higher pH. The visible absorption bands of the hydrated vanadyl ion were modified by a slight reduction in optical density, while the ultraviolet absorption band shifted considerably towards longer wavelengths. Furthermore, a new, weak, unresolved, absorption peak appeared at a wave-
Absorption spectra of solutions 0.050 M in vanadyl ion, with differing pH.

Fig. 29:

<table>
<thead>
<tr>
<th>Curve</th>
<th>pH</th>
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<tbody>
<tr>
<td>a</td>
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</tr>
<tr>
<td>b</td>
<td>2.02</td>
</tr>
<tr>
<td>c</td>
<td>2.26</td>
</tr>
<tr>
<td>d</td>
<td>2.44</td>
</tr>
<tr>
<td>e</td>
<td>2.60</td>
</tr>
<tr>
<td>f</td>
<td>2.81</td>
</tr>
</tbody>
</table>

- Optical density
- Wavelength (μm)

-128- para. E.II.
Absorption spectra of solutions 0.050 M in vanadyl ion, and constant in concentration of perchlorate ion, with differing pH.

Fig. 24.

<table>
<thead>
<tr>
<th>curve</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.65</td>
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<tr>
<td>b</td>
<td>2.02</td>
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<tr>
<td>c</td>
<td>2.26</td>
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<tr>
<td>d</td>
<td>2.44</td>
</tr>
<tr>
<td>e</td>
<td>2.81</td>
</tr>
</tbody>
</table>
length of 340 mp. Thus, the dissociation of protons from the hydrated vanadyl ion, which has been established by other workers under these conditions, gives rise to a fundamental change in the absorption characters of the vanadyl ion. The appearance of the new absorption band indicates that the hydroxyl ligand groups give rise to weaker ligand-field forces than co-ordinated water molecules. This is in agreement with the spectrochemical series of ligands discussed by Dunn (139). Now, each of the solutions of pH greater than 2 were green in colour and deposited a green gelatinous material on standing for several weeks. Polynuclear hydroxy species are known to be characterised by slow formation reactions. Furthermore, as discussed in paragraph E.II(b)(i), Rossotti and Rossotti, and other workers have demonstrated the formation of polynuclear, hydroxy, vanadyl species both in solution, and in the solid state. Thus, the precipitated material may be considered to be polymeric in nature, and to be preceded by the formation of polymeric hydroxy species in solution. Such species may, therefore, be considered to contribute to the absorption phenomena observed in the vanadyl/perchlorate solutions of higher pH.

Figures 25, 26, 29, and 30 show that a more extensive formation of complex species takes place in the phosphate and oxalate systems under conditions of low hydrogen ion concentration, and generally substantiate the conclusions concerning the nature of the complexes formed which were drawn from the studies described in paragraph E.II(a).

Observations from the studies of the vanadyl/arsenate system are presented in figures 27 and 28. The visible absorption characters are modified in the solutions of lower pH in a manner similar
Absorption spectra of solutions 0.050 M in vanadyl ion, and 1.00 M in phosphate, with differing pH.

Fig. 25.

<table>
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</thead>
<tbody>
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<td>a</td>
<td>-ve</td>
</tr>
<tr>
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<tr>
<td>c</td>
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<td>d</td>
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</table>
Absorption spectra of solutions 0.050 M in vanadyl ion, and 1.00 M in phosphate, of differing pH.

**Fig. 26.**

<table>
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<tr>
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<td>d</td>
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<td>2.77</td>
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</table>
Absorption spectra of solutions 0.0475 M in vanadyl ion, and

0.24 M in arsenate, of differing pH.

Fig. 27:

<table>
<thead>
<tr>
<th>Curve</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.75</td>
</tr>
<tr>
<td>b</td>
<td>2.04</td>
</tr>
<tr>
<td>c</td>
<td>2.63</td>
</tr>
</tbody>
</table>

Optical density.

Wavelength (μm)
Absorption spectra of solutions 0.0475 M in vanadyl ion, and 0.24 M in arsenate, of differing pH.

**Fig. 28.**

<table>
<thead>
<tr>
<th>curve</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.75</td>
</tr>
<tr>
<td>b</td>
<td>2.04</td>
</tr>
<tr>
<td>c</td>
<td>2.63</td>
</tr>
</tbody>
</table>

![Graph showing absorption spectra with optical density on the y-axis and wavelength (µm) on the x-axis.](image-url)
Absorption spectra of solutions 0.0475 M in vanadyl ion, and 0.12 M in oxalate, of differing pH.

Fig. 29.

<table>
<thead>
<tr>
<th>Curve</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.34</td>
</tr>
<tr>
<td>b</td>
<td>0.96</td>
</tr>
<tr>
<td>c</td>
<td>3.95</td>
</tr>
</tbody>
</table>
Absorption spectra of solutions 0.0475 M in vanadyl ion, and 0.12 M in oxalate, of differing pH.

**Fig. 30.**

<table>
<thead>
<tr>
<th>Curve</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.34</td>
</tr>
<tr>
<td>b</td>
<td>0.96</td>
</tr>
<tr>
<td>c</td>
<td>3.95</td>
</tr>
</tbody>
</table>
to that found in the phosphate systems. The formation of arsenato vanadyl complex species is, therefore, indicated in such solutions. However, the absorption spectrum of the solution of higher pH was continuous throughout the range of wavelengths studied and exhibited a new absorption peak at a wavelength of 505 μ. Furthermore, the visible absorption band at 800 μ was reduced in intensity under these conditions. These phenomena are similar to those observed in the vanadyl/perchlorate solutions of higher pH, and may, therefore, be considered to indicate the formation of polynuclear hydroxy vanadyl species. The shifts in the visible absorption bands show that arsenate ligands give rise to stronger ligand-field forces than aquo ligands, and appear to indicate that the co-ordinated arsenate groups are retained during the formation of polynuclear species.

Figures 31 and 32 show that the formation of sulphato complex species is almost unaffected by the conditions of pH, except in solutions of very low hydrogen ion concentration. This may be expected since sulphate ion is derived from a strong acid. However, the solution of pH 3.38 slowly changed from blue to bright-green in colour on standing. Then, after 7 days, light absorption was found to be continuous throughout the range of wavelengths studied. Furthermore, the ultraviolet absorption band was found to have shifted considerably towards the longer wavelengths. Thus, as in the perchlorate systems (figs. 23, 24), these phenomena may be attributed to the formation of vanadyl species containing hydroxy ligands. However, precipitation did not take place in the vanadyl/sulphate solutions on standing for 3 months. Thus, sulphate ion may be considered to react with these species in a manner which prevents the formation of polynuclear species containing many vanadyl ions. This is in marked contrast to solutions of the vanadyl/perchlorate
Absorption spectra of solutions 0.050 M in vanadyl ion, and 0.60 M in sulphate, of differing pH.

Fig. 31.

<table>
<thead>
<tr>
<th>Curve</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.25</td>
</tr>
<tr>
<td>a</td>
<td>1.78</td>
</tr>
<tr>
<td>c</td>
<td>3.38</td>
</tr>
</tbody>
</table>
Absorption spectra of solutions 0.050 M in vanadyl ion, and 0.60 M in sulphate, of differing pH.

Fig. 32.

<table>
<thead>
<tr>
<th>curve</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.25</td>
</tr>
<tr>
<td>b</td>
<td>1.78</td>
</tr>
<tr>
<td>c</td>
<td>3.38</td>
</tr>
</tbody>
</table>
system for a green gelatinous material precipitated from these on standing, even in the presence of greater concentrations of hydrogen ion. For reasons similar to those discussed for the thiocyanato complexes (paragraph E.II(a)(ii), and figs. 15, 16), the increase in intensity of the visible absorption bands of the vanadyl/sulphate solutions at pH 3.38 may be attributed to an increase in target area per vanadyl ion in the species containing vanadyl ion over which to capture incident photons.

Variations of pH over the range 0.16 to 2.26 was not found to affect the optical properties of solutions constant in total concentrations of vanadyl and thiocyanate ions. As shown in paragraph E.II(b)(i), this may be expected since the thiocyanate ion is derived from a strong acid. The absorption spectra of solutions within this range of pH are, therefore, represented by the curves of figures 15 and 16.

(c) The study of the optical density of solutions constant in total concentration of perchlorate, phosphate, or thiocyanate ion in which the total concentration of vanadyl ion was varied.

(i) Theoretical and experimental principles. The following experiments were designed to investigate the validity of the Lambert-Beer Law for systems containing vanadyl ion in the presence and absence of complexing agents. This was required to assess the possibilities of further studies of these systems by Job's method of continuous variations, as described in paragraph E.II(d).

If the Lambert-Beer Law applies to a solution containing a single absorbing species, then the optical density of the solution,
'D', with respect to monochromatic light, is proportional to the molar concentration of the species, 'c'. Thus, when 'e' represents the molar extinction coefficient of the species,

\[ D = ec. \]

Now, at the wavelengths used in the studies described below, the only absorbing species were those containing metal ion. Thus, in the perchlorate systems, in which the metal ion, 'M', is present entirely as the aquo complex,

\[ D = e_M c_M. \]

The curve obtained by plotting the optical density of the solutions, 'D', against the concentration of metal ion, 'c_M', will, therefore, be linear with a slope of 'e_M'.

A system may now be considered which contains a constant total concentration of complexing agent. If the total concentration of the complexing agent were much greater than that of the metal ion, then the metal ion may be considered to be entirely in the form of the complex containing the highest number of ligand groups derived from the complexing agent. Thus, when the suffix, 'cp' refers to this complex species, the total concentration of metal ion, \( c_M^o = c_{cp} \), and \( c_M = 0 \). Then, if the solution containing this complex species obeys the Lambert-Beer Law,

\[ D = e_{cp} c_{cp}. \]

That is, \( D = e_{cp} c_{cp}^o \).

Therefore, under the conditions specified, the curve obtained by plotting the optical density of the solutions, 'D', against the total concentration of metal ion, 'c_M^o', will be linear with a slope of 'e_{cp}'. 
Experimental procedure, observations, and conclusions. Vanadyl/perchlorate and perchloric acid solutions were used to prepare solutions 1.500 molar in perchlorate ion in which the total concentration of vanadyl ion was varied from zero to 0.080 M. The solutions were allowed to stand for 7 days before measuring the pH and optical density at selected wavelengths. Similar procedures were carried out with solutions in which the total concentrations of phosphate and thiocyanate ions were maintained constant at 1.500 M.

Observations for these studies are presented in tables E.1, 2, 3, and figures 33, 34, and 35.

**TABLE E.1.**

<table>
<thead>
<tr>
<th>Total concn. of vanadyl ion</th>
<th>Optical density of solutions 1.500 M. in perchlorate ion.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 800 mp.</td>
<td>at 765 mp.</td>
</tr>
<tr>
<td>0.001 M.</td>
<td>0.020</td>
<td>0.021</td>
</tr>
<tr>
<td>0.003</td>
<td>0.049</td>
<td>0.055</td>
</tr>
<tr>
<td>0.005</td>
<td>0.080</td>
<td>0.091</td>
</tr>
<tr>
<td>0.007</td>
<td>0.112</td>
<td>0.125</td>
</tr>
<tr>
<td>0.010</td>
<td>0.153</td>
<td>0.173</td>
</tr>
<tr>
<td>0.020</td>
<td>0.308</td>
<td>0.348</td>
</tr>
<tr>
<td>0.040</td>
<td>0.606</td>
<td>0.693</td>
</tr>
<tr>
<td>0.060</td>
<td>0.908</td>
<td>1.040</td>
</tr>
<tr>
<td>0.080</td>
<td>1.235</td>
<td>1.400</td>
</tr>
</tbody>
</table>
Optical density of solutions 1.50 M in perchlorate ion, of differing total concentration of vanadyl ion.

Fig. 33.

- at 765 μμ.
- at 800 μμ.
- at 700 μμ.
- at 630 μμ.

Total concentration of vanadyl ion (moles).
### TABLE E.2.

| Total concn. of vanadyl ion. | Optical density of solutions 1.500 M. in phosphate ion. | pH  
|------------------------------|--------------------------------------------------------|-----  
|                              | at 800 μm. | at 700 μm. | at 630 μm. |  
| 0.001 M.                    | 0.027      | 0.017      | 0.012      | 0.67  
| 0.003                        | 0.065      | 0.042      | 0.029      | 0.58  
| 0.005                        | 0.105      | 0.067      | 0.047      | 0.55  
| 0.007                        | 0.147      | 0.092      | 0.063      | 0.52  
| 0.010                        | 0.205      | 0.130      | 0.089      | 0.47  
| 0.020                        | 0.396      | 0.247      | 0.170      | 0.40  
| 0.040                        | 0.785      | 0.485      | 0.332      | 0.29  
| 0.060                        | 1.170      | 0.739      | 0.495      | 0.24  
| 0.080                        | 1.600      | 0.990      | 0.663      | 0.21  

### TABLE E.3.

| Total concn. of vanadyl ion. | Optical density of solutions 1.500 M. in thiocyanate ion. | pH  
|------------------------------|----------------------------------------------------------|-----  
|                              | at 800 μm. | at 765 μm. | at 700 μm. | at 630 μm. |  
| 0.001 M.                    | 0.064      | 0.070      | 0.052      | 0.030      | 2.46  
| 0.003                        | 0.168      | 0.192      | 0.142      | 0.079      | 1.89  
| 0.005                        | 0.277      | 0.318      | 0.235      | 0.133      | 1.66  
| 0.007                        | 0.384      | 0.440      | 0.323      | 0.180      | 1.57  
| 0.010                        | 0.547      | 0.620      | 0.453      | 0.255      | 1.37  
| 0.020                        | 1.100      | 1.240      | 0.910      | 0.501      | 1.01  
| 0.040                        | >2.0       | >2.0       | 1.820      | 1.025      | 0.78  

Optical density of solutions 1.50 M in phosphate, of differing total concentration of vanadyl ion.

Fig. 34:

- △ at 800 mμ.
- □ at 700 mμ.
- ▽ at 630 mμ.

Total concentration of vanadyl ion (moles).
Optical density of solutions 1.50 M in thiocyanate ion, of differing total concentration of vanadyl ion.

**Fig. 35:**

- △ at 765 mμ.
- □ at 800 mμ.
- ○ at 700 mμ.
- ▽ at 690 mμ.

**Total concentration of vanadyl ion (moles).**
The observations presented in figures 33 to 35 show that the optical densities of each of these series of solutions are proportional to the total concentration of vanadyl ion. Thus, the vanadyl ion may be considered to be complexed by the maximum number of phosphate or thiocyanate ligands in the phosphate and thiocyanate solutions respectively. Furthermore, the observations show that solutions containing either of these complex species or the hydrated vanadyl ion obey the Lambert-Beer Law. As shown in paragraph E.II(c)(i), the molar extinction coefficients for each of these species may be obtained from the slopes of the linear plots of figures 33 to 35. These values are presented below in table E.4.

<table>
<thead>
<tr>
<th>Complex vanadyl species</th>
<th>Molar extinction coefficient in aqueous solution.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 800 μm.</td>
</tr>
<tr>
<td>aquo</td>
<td>15.3</td>
</tr>
<tr>
<td>phosphato</td>
<td>19.5</td>
</tr>
<tr>
<td>thiocyanato</td>
<td>55.0</td>
</tr>
</tbody>
</table>

It may be seen from this data that the molar extinction coefficients of the aquo and phosphato vanadyl complexes are too similar to enable reliable studies of the vanadyl/phosphate system to be carried out if these depend upon the estimation of a difference in optical density of solutions containing vanadyl ion in the presence and absence of phosphate. These observations show that this limitation would not apply to the thiocyanate systems. For this reason, the thiocyanato complexes were studied by Job's method of continuous variations as described in paragraph E.II(d).
(d) The study of complexes of the vanadyl/thiocyanate system by the method of continuous variations.

(i) Theoretical and experimental principles. Considering a system in which a metal ion, 'M', reacts with a complexing agent, 'L', to form a single complex species as follows,

\[ M + nL \rightarrow ML_n \]

Job has shown that the metal : ligand ratio of the complex may be estimated from observations with solutions containing a variety of metal : ligand ratios (93).

When the experimental procedure involves the mixing of a volume, 'V_M', of metal ion solution with a volume, 'V_L', of ligand solution, the two solutions being of the same molar concentration, 'm', the term 'x' may be defined as follows:

\[ x = \frac{V_L}{V_L + V_M} \]

Also, 'D' may be defined as the optical density of a solution in which the reactant species are mixed in known proportions to give a particular value of 'x', and 'D_o' as the optical density that may have been expected for this solution if complex formation did not take place between the reactant species. Furthermore, 'e_M' and 'e_L' represent the molar extinction coefficients of the metal ion and ligand in solution respectively. Then, if the solutions obey the Lambert-Beer Law,

\[ D_o = (1-x)\cdot m\cdot e_M + e_L\cdot x\cdot m \]

and

\[ \Delta D = D - D_o \]

Then, as has been shown by Job, the curve obtained by plotting \( \Delta D \) against 'x' would exhibit a single maximum or minimum value of \( \Delta D \) when,

\[ x = \frac{n}{n+1} \]
Experimental data may be obtained for a study of this kind by using monochromatic light to measure the optical density of solutions with 'x' values ranging from 0.0 to 1.0. These may be prepared by mixing equimolar metal perchlorate and ligand solutions in various proportions. Hence, the number of ligand groups, 'n', may be estimated if the species, 'ML_n', is the only complex formed in the system. If this condition is satisfied, the values of 'x' at which \( \Delta D \) reaches an extreme are independent of the wavelength of the light used. In systems in which more than one complex species is formed, the different extinction coefficients of the complexes would cause the position of the maximum in the curve, obtained by plotting \( \Delta D \) against 'x', to vary with the wavelength of the light employed. Furthermore, the values of 'n' arising from such curves would not necessarily be integral. Systems containing a series of complex species may give rise to more than one extreme in the \( \Delta D \) against 'x' curve if the complexes are characterised by suitable extinction coefficients.

The values of \( \Delta D \) depend upon the estimation of a difference in the optical density of solutions and are, therefore, affected to a considerable extent by experimental errors. For this reason, reliable experimental data may be obtained only for those systems in which complex formation gives rise to large changes in optical density. As shown in paragraph E.II(c), this condition is satisfied in vanadyl/thiocyanate, but not vanadyl/phosphate solutions. The former system has, therefore, been studied in the experiments described below.
(ii) Experimental procedure, observations, and conclusions. Vanadyl/perchlorate solution (0.036 M. in vanadyl ion) and an equimolar solution of ammonium thiocyanate were mixed in varying proportions to give solutions in which the 'x' ratios (defined in paragraph E.II(d)(i)) were known, and varied over the range 0.0 to 1.0. After standing for 7 days, the optical density of each of these solutions was measured at the wavelengths specified below. The optical properties of vanadyl/thiocyanate solutions have been found to be independent of hydrogen ion concentration in solutions of pH 2.26 or less (see paragraph E.II(b)). For this reason, the pH of the solutions was not controlled or recorded since the solutions were low in pH due to the presence of perchloric acid.

It has been shown in the previous paragraph that:

$$D_0 = (1-x) \cdot m \cdot e_M + e_L \cdot x \cdot m$$

Now, the experimental data presented in table E.5 show that the solutions in which x = 1.00 exhibited an optical density of zero at each of the wavelengths studied. Thus, the molar extinction coefficients of the thiocyanate ions, 'e_L', are zero in each case.

Therefore, $$D_0 = (1-x) \cdot m \cdot e_M$$

That is, $$D_0 = m \cdot e_M - x \cdot m \cdot e_M$$

D_o, therefore, varied linearly with 'x' in these experiments and may be evaluated graphically by linear proportionation of the optical density of the solution for which x = 0.00.

Now, $$\Delta D = D - D_0$$

\(\Delta D\) values have, therefore, been estimated and plotted directly from the vertical separation of the curves obtained by plotting D and D_o against 'x'. Experimental observations obtained in these studies are presented in table E.5, and figures 36 to 39.
TABLE E.5.

<table>
<thead>
<tr>
<th>x (V_L/(V_M + V_L))</th>
<th>Optical density, D, of solutions.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 800 m(\mu)</td>
</tr>
<tr>
<td>0.00</td>
<td>0.543</td>
</tr>
<tr>
<td>0.20</td>
<td>0.463</td>
</tr>
<tr>
<td>0.30</td>
<td>0.419</td>
</tr>
<tr>
<td>0.40</td>
<td>0.375</td>
</tr>
<tr>
<td>0.46</td>
<td>0.349</td>
</tr>
<tr>
<td>0.50</td>
<td>0.326</td>
</tr>
<tr>
<td>0.54</td>
<td>0.306</td>
</tr>
<tr>
<td>0.56</td>
<td>0.293</td>
</tr>
<tr>
<td>0.60</td>
<td>0.270</td>
</tr>
<tr>
<td>0.64</td>
<td>0.247</td>
</tr>
<tr>
<td>0.68</td>
<td>0.226</td>
</tr>
<tr>
<td>0.72</td>
<td>0.203</td>
</tr>
<tr>
<td>0.76</td>
<td>0.176</td>
</tr>
<tr>
<td>0.80</td>
<td>0.147</td>
</tr>
<tr>
<td>0.90</td>
<td>0.080</td>
</tr>
<tr>
<td>1.00</td>
<td>0.000</td>
</tr>
</tbody>
</table>

The curves of \(\Delta D\) against 'x' presented in figures 36 to 39 each show a single peak at values of 'x' ranging from 0.55 to 0.64 depending upon the wavelength of the light employed. Thus, these observations show that more than one thiocyanato vanadyl complex is formed in the solutions. Therefore, for reasons discussed in paragraph E.II(d)(i), further quantitative deductions, concerning the nature of the complexes formed, may not be drawn from the observations of a study of this kind. The data presented in these pages contrasts
Continuous variation curves for the vanadyl/thiocyanate system.

Observations with light of wavelength 800 μm.

Fig. 36.

a—curve for D values.
b—curve for D_0 values.
c—curve for ΔD values.

ΔD = D - D_0.

Optical densities D, D_0, and ΔD (x5).

mole fraction of thiocyanate ion, "x".
Continuous variation curves for the vanadyl/thiocyanate system.

Observations with light of wavelength 755 mu.

Fig. 37:

a—curve for D values.
b—curve for D₀ values.
c—curve for ΔD values.

ΔD = D - D₀.

Optical densities D, D₀, and ΔD(x5).

Mole fraction of thiocyanate ion, "x".
Continuous variation curves for the vanadyl/thiocyanate system.

Observations with light of wavelength 620 μm.

Fig. 38.

a—curve for D values.
b—curve for D₀ values.
c—curve for ∆D values.

\[ ∆D = D - D₀. \]

Optical densities D, D₀, and ∆D (x5).

Mole fraction of thiocyanate ion, "x".
Continuous variation curves for the vanadyl thiocyanate system.

Observations with light of wavelength 350 μμ.

Fig. 39.

a—curve for
D values.

b—curve for
D₀ values.

c—curve for
ΔD values.

ΔD = D - D₀.

Optical densities D, D₀, and ΔD.

mole fraction of thiocyanate ion, "x".
markedly with those reported by Furman and Garner (91), for these workers claim to have demonstrated the formation of the species, VOCNS⁺, from the single peak in the ΔD against 'x' curves, which they found at x = 0.50, on studying this system by the method of continuous variations.
SECTION F.

STUDIES OF THE GREEN SOLID
PRECIPITATED FROM VANADYL/PHOSPHATE SOLUTIONS
OF LOW HYDROGEN ION CONCENTRATION.
I. Inorganic polymers.

Whereas the majority of pure substances are precipitated from solution in well defined crystals, the hydroxides of certain metal ions of high valency, for example, aluminium and chromic ions, are deposited as flocculent, amorphous masses of material. These gelatinous hydroxides, once formed, have very low solubilities in neutral aqueous media, and have the ability to absorb large quantities of electrolyte from solution. Such properties do not characterise simple substances, but could be explained if the material were polymeric in nature, as will be shown below (149).

It is believed that the metal ions of such a polymeric material are linked by hydroxyl groups co-ordinated simultaneously to two metal ions, thereby acting as bridges. This phenomenon is known as olation. The process of forming these hydroxyl bridges is initiated by the loss of a proton from a hydrated metal ion as follows:

\[
\text{Cr(H}_2\text{O)}_6^{3+} \rightarrow \text{Cr(H}_2\text{O)}_5\text{OH}^{2+} + \text{H}^+ .
\]

This is then followed by the condensation of two such hydrolysed ions to form an olated dimer:

\[
(\text{H}_2\text{O})_4\text{Cr}^{2+} \text{OH}_2 \rightarrow (\text{H}_2\text{O})_4\text{Cr}^{2+}(\text{H}_2\text{O})_4 \rightarrow (\text{H}_2\text{O})_4\text{Cr}^{4+} \text{OH}_2\text{OH}_2 + 2\text{H}_2\text{O}.
\]

This bridge-forming process, when continued indefinitely, ultimately gives rise to an olated polymeric unit containing many metal ions, as follows:
Electrical neutrality in such polymeric materials is maintained by unco-ordinated ions, that is, counter ions, distributed throughout the polymer network. The low solubility of a polymer of this type in neutral aqueous media can therefore be attributed to its very high molecular weight.

As shown above, the formation of hydroxy ligands gives rise to an increase in hydrogen ion concentration in the solutions during precipitation. Pfeiffer has reported such a phenomenon from his studies of precipitation in the tervalent chromium systems (150). For this reason, the formation of olated polymers is favoured by low concentrations of hydrogen ion. Elevated temperatures are also found to favour the formation of polymers of this type since the rates of the formative hydrolytic and condensation processes are moderately high under these conditions. It has also been found that polymers are formed most readily from solutions of high concentration (149).

Other types of olated polymer are known, particularly in tervalent chromium and aluminium systems. These include polymers in which metal ions are linked by one or three hydroxyl bridges, ring polymers, and also cross-linked polymers in which olation serves additionally to link polymer chains sideways. Olation also features in polymers in which other types of ligands are co-ordinated to the metal ions (151). These include:

\[
\text{(en)}_2\text{Cr(OH)}_2\text{Cr(en)}_2^{4+}, \quad (\text{NH}_3)_4\text{Co(OH)}_2\text{Co(NH}_3)_4^{2+}
\]

'\text{en}' represents the ethylenediamine molecule, \(\text{H}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2\).
and the compounds characterised by very high powers of optical rotation which were isolated by Werner (152,153):

\[
\left[ \text{Co}(\text{OH})\left(\text{Co}(\text{NH}_3)_4\right)_4 \right]^{x-} \cdot
\]

Electrolytes are absorbed tenaciously by olated polymers, since ions are able to penetrate the polymer structures and replace water and hydroxyl groups co-ordinated to the metal ions. Anions are frequently absorbed in this way. In systems in which co-ordinated hydroxyl groups are displaced, the phenomenon is accompanied by an increase in pH of the solution phase from which electrolyte is absorbed (149,151). In some instances, ions are absorbed by the replacement of bridging hydroxyl groups, the \( \text{ol} \) groups. Thus, chloride ion has been found to replace \( \text{ol} \) groups in olated chromium (III) polymers. Ligands which are potentially bidentate in nature are particularly effective in replacing hydroxyl bridges without disrupting the polymer structure. This has been observed with anions derived from certain carboxylic acids.

In solutions of low hydrogen ion concentration, the \( \text{ol} \) groups of certain polymers are slowly modified by the dissociation of a proton to form an oxide bridge, without disrupting the link between metal ions, as follows:

\[
\text{M} - \text{OH} \rightarrow \text{M} - \text{O}^- \text{M} + \text{H}^+.
\]

Bridge structures of this type are referred to as oxo bridges and usually give the polymer an increased resistance to chemical attack, particularly by acids.
However, olated and oxolated polymers are all disrupted in solutions of low pH due to attack at the hydroxo and oxo bridges in the following manner:

\[
\text{H}_3\text{O}^+ + \text{M} \xrightarrow{\text{O}^-} \text{M} \xrightarrow{\text{OH}} \text{M} + \text{H}_2\text{O},
\]

then,

\[
\text{M} \xrightarrow{\text{OH}} \text{M} + \text{H}_3\text{O}^+ \xrightarrow{\text{OH}_2} \text{M}.
\]
II. Experimental procedures and observations.

(a) Preparation of the solid and the effect of precipitation on the solution pH. Solutions 0.050 M in vanadyl ion and 1.00 M in phosphate, to which varying quantities of sodium hydroxide had been introduced, were prepared and allowed to stand for 14 days after measuring the pH. The pH of each solution was measured again at the end of this time after precipitated material had been removed by filtration.

The observations recorded for each system are given in Table FI. The properties of the green solid precipitated from solution no. 7 were investigated in the following experiments after the material had been washed free from electrolyte with water and air-dried.

<table>
<thead>
<tr>
<th>Soln. no.</th>
<th>Appearance of system immediately after preparation.</th>
<th>Appearance of system after standing for 14 days.</th>
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<td>2.20</td>
<td>Blue soln. no ppt.</td>
</tr>
<tr>
<td>6</td>
<td>2.52</td>
<td>Blue soln. no ppt.</td>
</tr>
<tr>
<td>7</td>
<td>3.00</td>
<td>Blue soln. very small quant. green ppt</td>
</tr>
</tbody>
</table>
Since green solid material was precipitated only from the solutions of higher pH, that is, from those to which the greater quantities of sodium hydroxide had been added, it was first suspected that the precipitated material was a simple sodium salt. For this reason, solid sodium perchlorate was dissolved in a sample of solution no. 7, after removing the precipitated material, in an attempt to cause a further precipitation of the green solid by the common ion effect. However, no further precipitate developed after the solution had been allowed to stand for three weeks, although that part of solution no. 7, to which no sodium perchlorate was added, produced a further small quantity of green precipitate after this time.

(b) Estimation of the vanadyl ion and phosphate content of the solid. The estimations were performed on a sample of the green solid precipitated from solution no. 7 (paragraph II(a)), which, after being air-dried, had been dried further by heating for 90 minutes at 110°C. A weighed sample of this solid was dissolved in perchloric acid (2N), and the vanadyl ion content of the resulting solution estimated after separation of the phosphate as described in section B. The phosphate content was then estimated with a solution free from vanadyl ion by precipitation as ammonium phosphomolybdate.

The solid was found to contain:

- 58.51 % by weight of phosphate (calculated as HPO$_4^{2-}$ ions),
- and 24.80 % by weight of vanadyl ion.

Thus, the molar ratio of vanadyl to phosphate ions in the solid was 1 : 1.65.
(c) Measurement of the magnetic susceptibility of the green solid over a range of temperatures, and hence the effective magnetic moment of the vanadyl ion in the material.

A Gouy balance was used to measure the magnetic susceptibility, \( \chi_v \), of the air-dried, green solid, which was precipitated from solution no. 7 (paragraph II(a)), over the temperature range 80 to 300°K. (154,155). The temperature was controlled during the experiments with an automatic cryostat in which liquid nitrogen was used as the refrigerant. The observations are presented in table F2, and figure 40.

<table>
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<tr>
<th>Temperature (°K)</th>
<th>Magnetic susceptibility, ( \chi_v ) (x 10^-6)</th>
<th>( 1/\chi_v ) (x 10^2)</th>
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<td>295.1</td>
<td>440.2</td>
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<tr>
<td>81.0</td>
<td>1270</td>
<td>7.874</td>
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The magnetic susceptibility of a material is mainly determined by the number of unpaired electrons present in unit volume of the substance. However, this is effectively reduced by the opposing diamagnetic effects arising from the paired electrons present in the
The effect of temperature on the reciprocal of the magnetic susceptibility of the green polymer precipitated from vanadyl phosphate solutions.

Fig. 40.

Reciprocal of magnetic susceptibility, \( \frac{1}{X_n} \)

Temperature (°K)

-165-
system. It was necessary to allow for this effect, therefore, by evaluating the 'diamagnetic correction term' for the green solid and applying this to the values of the magnetic susceptibility measured experimentally. For reasons discussed in paragraph F.III, the following empirical formula for the green solid was used to evaluate the diamagnetic correction term:

\[(\text{Na}^+)_{1.65}(\text{VO}^{2+})(\text{HPO}_4^{-})_{1.65}\text{(OH}^{-})_{0.35}\cdot\]

Hence, it was found that the 'diamagnetic correction' was \(-1.04 \times 10^{-4}\). The effective magnetic moment, \(\mu\), of a material at \(T^0\)K. may be calculated from the formula:

\[\mu_T = 2.84\cdot \sqrt{T\lambda_v}\] Bohr magnetons (B.M.)

Thus, the observations show that the effective magnetic moment of the vanadyl ion in the green solid at \(300^0\)K. was 1.02 B.M., that is, \(\mu_{300} = 1.02\) B.M.

This is considerably lower than the value of 1.73 B.M. expected for ions containing single unpaired electrons, and demonstrated for the vanadyl ion by Bose and Blair (38), and Wedekind and Horst (39). The observations indicate, therefore, that the green solid has a structure which prevents the independent alignment of the magnetic dipoles of the constituent vanadyl ions with a magnetic field applied from an external source. Other workers have shown that an 'ideal' system, in which the magnetic dipoles of ions are completely free to align with an externally applied magnetic field, would give rise to a linear plot of \(1/\lambda_v\) against \(T\), passing through the origin of co-ordinates (139,156-160). Thus, the curve shown in figure 40, obtained by plotting the experimental data, indicates that the green solid deviates from this form of ideal behaviour, particularly at low temperatures, and may also be considered to demonstrate a restriction in the free and independent rotation of the vanadyl ions in the material.
(d) General properties of the solid.

The behaviour of the air-dried, green solid was investigated qualitatively with various reagents. Water was observed to have no appreciable effect, both in the cold, and on boiling, but dilute hydrochloric, perchloric, sulphuric, and phosphoric acids, were found to react readily with the solid in the cold to produce blue solutions, characteristic of aqueous solutions of the vanadyl ion. Dilute sodium hydroxide solution caused the solid to turn brown, and slowly dissolve to give brown solutions. The same observations were recorded on applying the tests to the solid which had been heated for 30 hours at 110°C., although the reactions which occurred proceeded with greater difficulty.

The air-dried solid was found to lose weight when heated at 110°C, presumably due to loss of water. A considerable period of time was required before the weight became constant, as shown in figure 41, and this occurred after the weight had been reduced by approximately 12%. Such properties would be expected of an amorphous rather than a crystalline material, and this was substantiated by microscopic examination of the green solid which showed that the material was amorphous in nature.

Sodium ion in the solid produced a brilliant yellow colouration of the Bunsen flame. This remained undisturbed when the material was eluted with water, but elution with a solution of potassium chloride caused a small quantity of the sodium ion to appear in the eluate. Thus, it appears that sodium ion can be displaced from the solid by an ion-exchange process, at least near the surface of the fragments of material.
The effect of time on the loss of weight of the air-dried green polymer when heated at 110°C.

**Fig. 41.**

<table>
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<th>Time (hours)</th>
<th>Percentage decrease in weight</th>
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<td>30</td>
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</table>
III. Conclusions drawn from the investigations of the green solid.

The foregoing series of investigations demonstrates that the precipitated green solid was not a sodium salt of a complex phosphato vanadyl anion which had crystallised from solution, because:

1. sodium perchlorate, when dissolved in the solution from which the precipitate had formed, failed to cause a further precipitation of the green solid which would otherwise have been expected due to the common ion effect,

2. precipitation of the green solid was slow, and continued over a long period of time, whereas complete precipitation would have been expected after about six hours for the crystallisation of a simple salt,

3. once formed, the solid was insoluble in both cold and hot water,

4. the precipitate was green, rather than blue like the solution phase in which phosphato vanadyl complex species have been shown to exist in the experiments described in preceding sections. Each of the foregoing observations would, however, have been expected if the solid were polymeric in nature. A structure of this kind would be further supported by the following observations:

   1. microscopic examination showed that the solid was amorphous and opaque,

   2. the solid continued to lose weight, probably due to loss of water, over a long period of time at 110°C. (fig. 41),

   3. the ratio of vanadyl to phosphate ions in the green solid was irregular at 1 : 1.65, and contrasts with the 1 : 1 and 1 : 2 ratios of the complex species for which evidence has been obtained in vanadyl/phosphate solutions of greater hydrogen ion concentration,
4. the vanadyl and phosphate analyses accounted for only 83.31% of the weight of the sample of solid analysed,

5. the effective magnetic moment of the vanadyl ion was lower in the green solid than previously observed for the vanadyl ion in vanadyl sulphate and chloride (38,39). Furthermore, the magnetic susceptibility showed deviations from ideality which may be attributed to a restriction of the free and independant orientation of the magnetic dipoles of the vanadyl ions under the influence of an applied magnetic field (fig. 40).

An extensive polymer structure would account for the observed properties of the green solid summarised above. Since the experiments described in the foregoing sections have demonstrated that the vanadyl ion can accommodate up to two monohydrogen phosphate ligands in complex species formed in solution, a structure, similar to that shown in the following illustration, may be postulated for the green solid in which four co-ordination sites of the vanadyl ion continue to be occupied by ligand groups:

```
\[
\begin{align*}
\text{VO}^{++} & \quad \text{HPO}_4^{-} \\
\text{OH}^{-} & \quad \text{HPO}_4^{-} \\
\text{VO}^{++} & \quad \text{HPO}_4^{-} \\
\text{OH}^{-} & \quad \text{HPO}_4^{-} \\
\text{VO}^{++} & \quad \text{HPO}_4^{-} \\
\text{OH}^{-} & \quad \text{HPO}_4^{-} \\
\end{align*}
\]
```

In a structure of this kind, both hydroxyl and monohydrogen phosphate ions would form bridges to link adjacent vanadyl ions in a polymer network of indefinite limits.

This isolated type of structure is not only compatible with the properties of the green solid already discussed, but would also
account for the liberation of hydrogen ion observed as a result of the precipitation process (table F.1), since the initial step in the formation of hydroxyl bridges involves the dissociation of protons from water molecules co-ordinated to the vanadyl species in solution (see paragraph F.1). Rossotti and Rossotti, and other workers have shown that the vanadyl ion is hydrolysed fairly extensively in this way in solutions of such low concentrations of hydrogen ion (40-45). Furthermore, the spectrophotometric studies discussed in section E have shown that aqueous solutions containing vanadyl ion slowly become green in colour under conditions of low hydrogen ion concentration in the perchlorate and sulphate systems. Thus, although the vanadyl/phosphate solutions from which the polymeric material precipitated remained blue in colour, the green colouration of the precipitated solid becomes strongly indicative of the co-ordination of hydroxyl groups to vanadyl ions in the material.

Finally, it was found that the green solid contained vanadyl and phosphate ions in the ratio 1 : 1.65. Thus, if a ratio of two bidentate ligands to one vanadyl ion is maintained in the polymer, as required by the structure postulated above, a ratio of 1 vanadyl ion to 0.35 hydroxyl groups would be required if all phosphate and hydroxyl ions occupied two co-ordination sites of vanadyl ions in the polymer. Under these conditions, the polymer network would carry a nett negative charge. However, the experiments described in paragraph F.II have shown that sodium ion in the green solid may be displaced readily by potassium ion, at least near the surface of the fragments. It appears, therefore, that the negative charge of the polymer network is neutralised by the distribution of sodium ions throughout the material. This would require a ratio of 1 vanadyl to 1.65 sodium ions.
Thus, the green solid may be considered to have the following empirical formula:

$$(\text{Na}^+)_{1.65}(\text{VO}^{++})(\text{HPO}_4^{--})_{1.65}(\text{OH}^-)_{0.35}$$

This formula may be used to calculate the percentage weight of the polymer due to sodium and hydroxyl ions from the value determined experimentally for the vanadyl ion. Thus, the composition of the green solid may be summarised as follows:

- vanadyl ion (VO$^{++}$) ...... 24.80% (determined experimentally)
- phosphate ion (HPO$_4^{--}$) ...... 58.51% (determined experimentally)
- sodium ion (Na$^+$) ...... 14.06% (calculated)
- hydroxyl ion (OH$^-$) ...... 2.21% (calculated)

Total ...... ...... 99.58%

When allowance is made for experimental error, 100% of the weight of the solid may be accounted for in this way. This, therefore, together with the other properties described, may be considered to provide substantial evidence to support the polymeric structure postulated above for the precipitated material.
SECTION G.

CONCLUSIONS DRAWN FROM THE STUDIES OF SYSTEMS CONTAINING VANADIUM IN THE QUADRIVALENT STATE.
Index to figures.

<table>
<thead>
<tr>
<th>Fig. No.</th>
<th>Page No.</th>
<th>Fig. No.</th>
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The conclusions presented in foregoing sections are accompanied by a discussion of the experimental data and methods employed. In this section, therefore, the discussion is limited to the co-ordination of observations and conclusions for each of the systems which have been studied.

Vanadyl/perchlorate solutions have been used to study the effects of hydrolysis on the absorption spectrum of the hydrated vanadyl ion. As shown in figures 23 and 24, the absorption characters of the hydrated vanadyl ion, particularly in the ultraviolet region, are modified in solutions of low hydrogen ion concentration on standing and a new weak absorption band appears at a wavelength of 340 mp. The replacement of water molecules by hydroxyl ions at the co-ordination sites of the quadrispositive vanadium ion, therefore, appears to give rise to weaker ligand-field forces. Phenomena of this type were not reported by Furman and Garner who also studied the absorption spectra of vanadyl/perchlorate solutions under various conditions of pH.(86). The solutions of higher pH are green in colour and appear to contain polymeric hydroxy species because a green gelatinous material precipitated from the solutions on standing for several weeks. These observations substantiate the conclusions of Rossotti and Rossotti who have shown that the species, \((\text{VOOH})^2++\), is formed in vanadyl solutions of low hydrogen ion concentration (40). The absorption spectra of the vanadyl/perchlorate solutions have been used to deduce the nature of vanadyl-containing species from the absorption spectra of other systems at low hydrogen ion concentration. Vanadyl/perchlorate solutions have been titrated with sodium hydroxide, and the data obtained in these studies have shown that the pH of the solutions remained almost constant at 4 during the precipitation of vanadyl hydroxide (table D.1, fig. 10).
The vanadyl/phosphate system has been studied most extensively. Complex formation was initially detected in these solutions by the higher percentage removal of vanadyl ion, effected from vanadyl-form, cation-exchange resin, by phosphoric acid solution than by a solution of perchloric acid at the same pH (table C.1, fig. 1). The observations presented in tables C.3 and 6 show that anionic, but not cationic, complexes were detected in these solutions. The anionic species have been studied in several further investigations. The formation of these species was found to be most extensive in solutions of low hydrogen ion concentration for a greater uptake of vanadyl ion onto an anion-exchange resin was achieved under these conditions (tables C.9, 13, 15, 20, and fig. 5). Moreover, the absorption spectra shown in figures 13, 15 and 26 indicate that the formation of phosphato vanadyl complexes is favoured by conditions of high pH and phosphate concentration. Furthermore, the observations presented in figure 5 indicate that such species carry unit negative charge in solutions of pH 2.3 or less, but in solutions of higher pH, appreciable concentrations of doubly charged complex anions are also formed. The observations from these experiments enabled the data obtained from studies described in paragraph C.11(c) to be fully interpreted. In this way, the single charge of the anionic complexes in solutions of low pH was confirmed and, in addition, they were shown to contain two phosphato ligand groups (tables C.10, 14, and 16). The observations from pH-titration studies, which are presented in table D.3 and figure 12, show that hydrogen ion, equivalent in quantity to the vanadyl ion present, is liberated from dihydrogen phosphate ions in solutions of pH 4.6. This may be explained by a virtually quantitative complexing of the vanadyl ion in the form of complexes containing two monohydrogen phosphate ligands per vanadyl ion. Thus, the data summarised above may be
explained by the formation of complex species, $HVO(HPO_4)_2^-$, and $VO(HPO_4)_2^{--}$, in the solutions.

As mentioned in paragraph D.I, Bjerrum has shown that complex species are formed in a step-wise manner (121,122). For this reason, a phosphato complex, containing a single phosphate ligand group, may be expected. Now, the observations presented in tables C.17, 18, and figures 3 and 4 show that the average number of phosphate groups, bonded to vanadyl ions in the complex species formed, is 1.2, under the conditions of the experiment described. This may be explained, therefore, by the co-existence of vanadyl complexes containing one and two phosphato ligands. Furthermore, the initial slope of the curve for vanadyl/perchlorate solutions in figure 7 shows that two hydrogen ions are liberated from molecules of phosphoric acid in the formation of the first phosphato vanadyl complexes. Since, as indicated above, cationic complexes were not detected in vanadyl/phosphate solutions, the 1:1 complex species may be considered to have the formula, $VOHPO_4^-$. Now, the uncomplexed phosphate species, which are present in greatest concentrations in solutions of low pH, are unionised molecules of phosphoric acid and dihydrogen phosphate ions. Hydrated vanadyl ions may be considered to react with both of these species in complex formation. However, the reactions involving ions of opposite charge are likely to proceed more readily. Thus the formation of phosphato vanadyl complexes, in solutions of low pH, may be summarised in the following equations:

\[
\begin{align*}
    VO^{++} + H_2PO_4^- & = VOHPO_4^- + H^+ , \\
    VOHPO_4^- + H_2PO_4^- & = HVO(HPO_4)_2^- , \\
    HVO(HPO_4)_2^- & = VO(HPO_4)_2^{--} + H^+ .
\end{align*}
\]

The observations presented in figure 5 indicate that the reaction
represented by equation 3 proceeds to an appreciable extent in solutions of pH greater than 2.3, while the data shown in figure 12 have been interpreted as indicating that vanadyl ion is largely present as the doubly charged bis-phosphato complex in solutions of pH 4.6. The phosphato vanadyl complex species, the formative reactions presented above, and the parallel reactions with phosphoric acid molecules have not previously been reported in the literature.

Genge and Salmon have shown that monohydrogen phosphate ligands may be considered to form chelate rings in the phosphato complexes of tervalent metal ions (16). Thus, the monohydrogen phosphate ligands, which have been detected in the phosphato vanadyl complexes, may also be considered to be bidentate in nature. In this way, the observations show that four co-ordination sites may be occupied by the co-ordination of phosphato ligands in the vanadyl complexes. As shown in section A, this is consistent with the structures of other vanadyl complexes which have been reported. Now, complexes of enhanced stability are considered to result when ligands form chelate rings. Since it has been shown in paragraph C.II(d)(ii) and figure 14 that the phosphato vanadyl complexes are of low stability, the lack of evidence for complexes containing more than two phosphate ligands in vanadyl/phosphate solutions may be explained because such species would necessarily involve the co-ordination of monodentate phosphate groups. Such species, therefore, would be of still lower stability.

The removal ratios shown in table C.2 indicate that vanadyl ion complexes with phosphate to an extent intermediate between that with tervalent and divalent metal ions. Thus, the oxide ion of the vanadyl group may be considered to reduce the formal quadripopositive
charge on the vanadium ion to below three units. However, as mentioned above, phosphato vanadyl complexes have been found to contain one or two phosphato ligands, while other workers have shown that tervalent cations may accommodate up to three such groups. For this reason, certain reservations are necessary when comparing the ratios of the various metal ions removed by the two acids. The changes in the absorption spectrum of the vanadyl ion on complexing with phosphate (figs. 13, 25, & 26) show that phosphato ligands give rise to stronger ligand-field forces than aquo ligands in the vanadyl complexes. Molar extinction coefficients of the bis-phosphato vanadyl species, at various wavelengths, have been presented in table E.4.

The observations from pH-titration studies, presented in table D.3 and figure 12, indicate that a green material was precipitated slowly from vanadyl/phosphate solutions of low hydrogen ion concentration. However, this was not accompanied by the levelling of the titration curve, which was found to characterise the precipitation of vanadyl hydroxide (fig. 10). More extensive studies of the properties of this green material were carried out as described in section F. As a result of these investigations, a polymeric structure has been postulated for the material, in which vanadyl ions are linked by hydroxyl and phosphate bridges. The occurrence and postulated structure of this material have not previously been reported in the literature.

Complexing of the vanadyl ion by thiocyanate in aqueous solution has previously been reported by Furman and Garner (91,92). As a result of their spectrophotometric studies, in which they employed Job's method of continuous variations, they reported that the species, VOCNS⁺, was the predominant complex formed in the solutions
and that other complexes are formed in comparatively small concentrations.

Studies, described in these pages, have confirmed that complex formation takes place in vanadyl/thiocyanate solutions, and the absorption spectra, presented in figures 15 and 16, show that this is most extensive in solutions of high thiocyanate concentration. Since thiocyanate ion is derived from a strong acid, the formation of thiocyanato complexes was found to be unaffected by pH under conditions in which hydrolysis of the vanadyl ion may be neglected (paragraph E.11(b)(ii)). However, the data presented in tables E.5 and 8 show that cationic complexes were not detected in these solutions, but anionic complexes accounted for a large percentage uptake of vanadyl ion from the solutions onto an anion-exchange resin. For this reason, the studies reported by Furman and Garner, using Job's method of continuous variations, were repeated. The data obtained from these studies are presented in table E.5 and figures 36 to 39. These contrast markedly with those previously reported (91) because the position of the maximum in the continuous variation curves was found to occur at 'x' values ranging from 0.55 to 0.64, depending on the wavelength of the light used.(paragraph E.11(d)). This shows that two or more complex species co-exist in vanadyl/thiocyanate solutions. For this reason, further quantitative deductions may not be justified from a study of this kind. The curves presented in figure 17 show that the thiocyanato complexes are of low stability. The large percentage uptake of vanadyl ion onto anion-exchange resin may, therefore, be explained by the sorption of a thiocyanato complex for which the resin has a high affinity, that is, a complex carrying a multiple negative charge. Since ligands have been shown to occupy four co-ordination sites in other
vanadyl complexes, the ion, \( \text{VO(CNS)}_4^- \), may be postulated to explain these phenomena. Such a formula would be consistent with the formulae of the thiocyanato vanadyl compounds which have been isolated by earlier workers (section A). Molar extinction coefficients for this ion, at various wavelengths, have been presented in table E.4.

The absorption spectra shown in figures 15 and 16, when considered in conjunction with the spectrochemical series of ligands discussed by Dunn (139), indicate that the thiocyanato ligands are bonded through the nitrogen atoms to the central vanadium ion in the complexes (paragraph E.11(a)(ii)). Unless specifically indicated in the foregoing discussion, the studies of the vanadyl/thiocyanate system are of an original nature.

Complex formation has been detected in vanadyl/sulphate solutions of low pH by the greater removal of vanadyl ion effected from vanadyl-form, cation-exchange resin by sulphuric acid than by a solution of perchloric acid of the same pH (table C.1, fig.1). This is also shown by the pH-titration data presented in figures 8 and 9. Moreover, the absorption spectra of figures 21, 22, 31 and 32 indicate that complex formation is most extensive in solutions of high sulphate concentration and, since sulphuric acid is extensively dissociated in aqueous solution, is almost unaffected by pH, except in solutions of low hydrogen ion concentration. Ion-exchange studies have shown that anionic complexes are formed in vanadyl/sulphate solutions but were unable to detect the presence of cationic complexes (tables C.4 & 7). Interactions between vanadyl and sulphate ions were also found to take place in solutions of low hydrogen ion concentration because the precipitation of vanadyl hydroxide was found to require a higher pH in vanadyl/sulphate than in vanadyl/perchlorate
solutions (tables D.1, 2, & figs. 10,11). Furthermore, vanadyl/sulphate solutions of pH greater than 3 turned green slowly in a manner similar to the solutions of the perchlorate system (figs. 23, 24, 31, 32), but unlike the perchlorate solutions of higher pH, solutions of the vanadyl/sulphate system did not precipitate a gelatinous material on standing. This indicates, therefore, that polymeric, hydroxy, vanadyl species are formed in the solutions and that interactions between these species and sulphate ions prevent the formation and precipitation of species containing many metal ion units.

Other workers have used a wide variety of experimental methods to study the oxalato complexes of the vanadyl ion (41, 50, 55, 62-66). These investigations have been extended in the studies reported within these pages, for the absorption spectra of vanadyl/oxalate solutions, shown in figures 18 and 19, indicate that the formation of oxalato vanadyl species is most extensive in solutions containing the higher concentrations of oxalate. Furthermore, since the oxalato ligands are derived from the weak acid, oxalic acid, the absorption spectra of figures 29 and 30 were found to indicate that oxalato complexes are formed most extensively in solutions of low hydrogen ion concentration. Now, the visible absorption characters of the hydrated vanadyl ion are shown in these figures to become more distinct and to shift to longer wavelengths on complexing with oxalate. Moreover, new absorption bands were not observed in the near ultraviolet region of the absorption spectra. For this reason, oxalato, like phosphato, ligands appear to give rise to stronger ligand-field forces than co-ordinated water molecules in the complexes of the vanadyl ion (figs. 13, 25, & 26). A comparison of figures 14 and 20 shows that oxalato vanadyl
complexes are of moderate stability and, therefore, are more stable than the phosphato vanadyl species.

Ahrland, Noren, Kraus, and other workers have shown that complex formation between vanadyl and chloride ions takes place to a very small extent in solution (53, 86, 96, 97). However, Kraus has demonstrated that anionic chloro vanadyl complexes are formed in solutions which are concentrated in chloride ion. These conclusions have been substantiated by studies of the elution of vanadyl ion from cation-exchange resin with solutions of hydrochloric acid. The data obtained from these experiments are presented in table C.1, and figure 1. Furthermore, the absorption spectra shown in figures 18 and 19 indicate that complex formation takes place to only a small extent in vanadyl/chloride solutions. The shifts in the visible absorption characters of the hydrated vanadyl ion suggest that chloro ligands give rise to weaker ligand-field forces than co-ordinated water molecules. Complex formation between vanadyl and bromide ions has not previously been reported. The absorption spectra of figures 21 and 22, however, show that bromo vanadyl complexes are formed in solution and, like the chloro complexes, are apparently formed in low concentration. The shifts in the vanadyl absorption bands indicate that bromo ligands give rise to ligand-field forces similar in nature to those produced by chloro ligands.

Interactions between vanadyl and arsenate ions have also not been reported previously. This system has been studied in the experiments described in section E. The absorption spectra obtained in these studies, shown in figures 27 and 28, indicate that arsenato vanadyl complexes are formed in solution and that arsenato ligands...
give rise to ligand-field forces similar to those produced by phosphato ligands in complexes formed with vanadyl ion in solutions of low pH. However, vanadyl/arsenate solutions of higher pH were found to exhibit a new weak absorption band at a wavelength of 505 mp. This phenomenon is similar to that observed in vanadyl/perchlorate solutions of low hydrogen ion concentration (figs. 23, 24). For this reason, the vanadyl-containing species formed in these solutions appear to contain both arsenato and hydroxo ligands. Furthermore, these species may be polymeric in nature.

Finally, complex formation has been detected in the vanadyl/acetate system. The elution data shown in table C.1 and figure 1 indicate that vanadyl ion is removed to only a small extent from cation-exchange resin by solutions of acetic acid and that this is brought about to the greatest extent by dilute solutions of the acid. These phenomena may be explained by the formation of cationic acetato vanadyl species which are sorbed onto the cation-exchange resin in addition to hydrated vanadyl ions and hydrogen ions.
SECTION H.

REFERENCES.


5. A. Holroyd & J.E. Salmon.  
J.C.S. 1956, 269.


7. J.M. Harrison.  

8. K.A. Jensen.  
Z. Anorg. Chem. 1934, 221, 1.

J.C.S. 1952, 2316.

10. J.E. Salmon.  
J.C.S. 1953, 2644.


J.C.S. 1954, 4013.

J.C.S. 1955, 360.

J.C.S. 1957, 256.

J.C.S. 1958, 1128.
    J.C.S. 1959, 1459.
    J.A.C.S. 1951, 73, 5646.
    J.C.S. 1955, 1444.
19. O.T. Quinby.
20. J. West.
22. L. Pauling.
23. C. Duc-Mange.
25. W.L. Groeneveld.
    J.A.C.S. 1949, 71, 3135.
27. D. Cozzi & S. Cecconi.
    Ricerca Sci. 1953, 23, 609.
    J.C.S. 1958, 1687.
29. G.W.A. Fowles & C.M. Pless.
30. L.E. Orgel.
    J.A.C.S. 1954, 76, 4281.
32. A. Yakimach.


33. R. Hoppe.


34. V. Gutmann.

Monatsh. 1954, 85, 286.

35. V. Gutmann.


36. J. E. Carpenter.

J.A.C.S. 1934, 56, 1847.

37. ***


Z. Physik. 1928, 48, 716.

39. E. Wedekind & C. Horst.

Ber. 1912, 45, 262.

40. F. J. C. Rossotti & H. S. Rossouti.


41. J. J. Ligane & L. Meites.

J.A.C.S. 1947, 69, 1021.

42. G. Jones & W. A. Ray.

J.A.C.S. 1944, 66, 1571.

43. L. Meites.

J.A.C.S. 1953, 75, 6059.

44. L. G. Sillen.

Quart. Revs. 1959, 13, 146.

45. L. G. Sillen.


46. C. Cabannes-Ott.


47. H. T. S. Britton & G. Welford.

J.C.S. 1940, 758 & 764.

48. L. P. Ducret.

49. H.T.S. Britton.
    J.C.S. 1934, 1842.
50. I. Koppel & R. Goldmann.
    Compt. Rend. 1930, 190 25.
52. W. Rudorff, G. Walter, & H. Becker.
53. R. Santini, J. F. Hazel, & W. M. McNabb.
54. E. Vernazza.
    Industria Chimica. 1934, 9 1616.
55. L. P. Ducret.
56. E. Schulek, I. Pais, & L. Pataki.
57. C. D. Coryell & D. M. Yost.
    J.A.C.S. 1933, 55 1909.
59. G. Lundgren.
60. G. Anderson.
61. C. K. Jørgensen.
    Naturviden. 1952, 6 61.
63. H. Brintzinger & F. Jahn.
64. R. Trujillo, & F. Brito.
    Anales real soc. fis y quim. 1956, 52B 157.
65. V.L.Zolotavin & N.N.Kalugina. 
    Zhur. Obshchei Khim. 1956, 1 703.
66. R.I.Walter. 
67. O.Samuelson. 
    Z.Electrochem. 1953, 57 207.
68. V.L.Zolotavin & N.N.Kalugina. 
69. C.Heitner & D.Friedman. 
70. M.Zeigler. 
    Naturwissenschaften. 1959, 46 492.
71. G.A.Barbieri. 
    Atti. acad. nazl. Lincei. 1914, (2)23 47.
72. A.Rosenheim & H.Y.Mong. 
73. V.L.Zolotavin & H.I.Sintsov. 
74. H.Brintzinger & F.Jahn. 
75. R.Trujillo & F.Torres. 
    Anales real soc. espan. fis y quim. 1958, 548 377.
76. P.Braumann. 
    Compt. Rend. 1934, 198 1237.
77. P.Braumann. 
    Ann. 1957, 605 117.
80. M.M.Jones. 
    J.A.C.S. 1954, 76 5995.
81. E. Parisi.

82. R. Trujillo & F. Brito.
   Anales real soc. espan. fis y quim. 1956, 528 407.

   Anales real soc. espan. fis y quim. 1956, 528 589.

84. G. Schwarzenbach & J. Sandera.

85. F. B. Martinez & Q. P. Bouza.

86. S. C. Furman & C. S. Garner.
   J. A. C. S. 1950, 72 1785.

87. F. Rivenq.


89. A. Cioci.

90. A. Scaglierini & G. Tartanini.

   J. A. C. S. 1951, 73 4528.

   J. A. C. S. 1952, 74 2333.

93. P. Job.

94. L. Meites.

95. H. I. Feinstein.

96. S. Ahrland & B. Noren.

98. A. Morette.  
Compt. Rend. 1957, 244, 611.

99. A. Morette.  

100. S.I. Sinyakova & N.P. Ivanov.  

101. C. Eichner.  
Compt. Rend. 1927, 185, 1200.

102. V. Auger & C. Eichner.  
Compt. Rend. 1927, 185, 208.

103. M. Zeigler.  
Naturwissenschaften. 1959, 46, 353.

104. B.S. Evans.  
Analyst. 1938, 63, 870.

105. F. Rivenq.  


J.C.S. 1952, 2324.


I.M. Kolthoff & E.B. Sandell.

110. R. Gangin.  

111. W.C. Baumann & J. Eichhorn.  
J.A.C.S. 1947, 69, 2830.

112. H.P. Gregor.  
J.A.C.S. 1948, 70, 1293.
    J.C.S. 1958, 4708.

114. J.E.Salmon.

    J. Biol. Chem. 1950, 185 387.

116. L.F.Nims.
    J.A.C.S. 1934, 56 1110.

117. Bottger.

118. J.H.Hildebrand.
    J.A.C.S. 1913, 35 847.

119. H.T.S.Britton.
    J.C.S. 1925, 2110.

120. R.Abegg & G.Bodlander.

121. N.Bjerrum.

122. J.Bjerrum.
    Chem. Revs. 1950, 46 381.

123. "Metal Ammine formation in Aqueous Solution".
    J.Bjerrum. P.Haase & Son, Copenhagen, 1941.

124. I.Leden.

125. J.Bjerrum.
    Kgl. Danske Videnskab Selskab. 1944, 21 No.4.

126. J.Bjerrum.

127. S.Fronaeus.

128. S.Fronaeus.
129. H.M.Irving & H.S.Rossotti.
    J.C.S. 1953, 3397.
130. H.M.Irving & H.S.Rossotti.
    J.C.S. 1954, 2904.
131. F.J.C.Rossotti & H.S.Rossotti.
133. J.C.Sullivan & J.C.Hindmann
    J.A.C.S. 1952, 74 6091.
134. J.N.Bronsted.
    J. Appl. Chem. 1958, 8 141.
    J. Appl. Chem. 1958, 8 151.
137. L.E.Orgel.
    Quart. Revs. 1954, 8 422.
138. H.Hartmann.
    J. Inorg. & Nucl. Chem. 1958, 8 64.
139. "Modern Co-ordination Chemistry, Principals & Methods".
140. L.E.Sutton.
141. C.Furlani.
    Ricerca Sci. 1957, 1141.
142. M.B.Palma-Vittorelli et al.
    Nuovo Cimento. 1956, 3 718.
143. M.M.Jones.
    J.C.S. 1958, 457.
145. S.R. Cohen.

146. H.S. Frank & R.L. Oswalt.

147. W.C. Vosburgh & G.R. Cooper.
   J.A.C.S. 1941, 63 437.

   Anales real soc. espan. fis y quim. 1957, 53B 253.

149. "The Chemistry of Co-ordination Compounds",
    J.C. Bailar.

150. P. Pfeiffer.
   Ber. 1907, 40 4036.

151. H. Basset.
   Quart. Revs. 1947, 1 246.

152. A. Werner.
   Ber. 1914, 47 3087.

153. A. Werner.
   Compt. Rend. 1914, 159 426.

154. A. Gouy.
   Compt. Rend. 1889, 109 935.

155. A. Earnshaw.

156. "Magnetic and Atomic Structure".

157. S.S. Bhatnagar & K.N. Mathur. "Physical Principles and

158. R.S. Nyholm.
   Quart. Revs. 1953, 7 377.

159. R.S. Nyholm.

160. "Magnetochemistry"