Rusheed (A.)
(Inorganic Chemistry)
STUDIES OF THE AGGREGATION OF
MOLYBDATES

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By

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Isopolymolybdate ions in aqueous solution have been studied by means of an ion-exchange process, using mainly a liquid ion-exchange, tri-n-octylamine hydrochloride (TOAH.C1) in chloroform. From the exchange of chloride ions with the molybdate ions, the number of molybdenum(VI) atoms per unit charge (R value) is calculated. It has been found that there are two stages of condensation in molybdate solutions of pH below 5.0; one is represented by R = 2.0, which extends approximately from pH 4.8 to 3.5; and the other is represented by R = 2.5, and extends from pH 1.9 to 1.1. The ion of R = 2.0 was also isolated as a solid from the organic layer by precipitation with kerosene. The nature of these ions was further investigated by carrying out vapour pressure lowering measurements and infrared spectroscopy of the amine layer obtained after the extraction of isopolymolybdate ions from aqueous solution. Vapour pressure lowering measurements have given a measure of the degree of aggregation of molybdenum(VI), and also the charge on an isopolymolybdate species. From the information obtained it was concluded that...
the stage of condensation represented by \( R = 2.0 \), consists mainly of the ions \( H_3\text{Mo}_6\text{O}_{21}^{3-} \) and \( H_5\text{Mo}_6\text{O}_{22}^{3-} \) whilst the stage represented by \( R = 2.50 \), consists mainly of \( \text{Mo}_{10}\text{O}_{32}^{4-} \) ions. The structure of the postulated ions have been derived by deducing stability in terms of formal charge on the oxygen atoms and by a consideration of known structures.

From the available information the following scheme for the formation of isopolymolybdate ions in solution has been deduced:

\[
\begin{align*}
\text{MoO}_4^{2-} &\rightarrow \text{dimers} \rightarrow \text{trimers} \rightarrow \text{Hexamolybdate} \\
H_3\text{Mo}_6\text{O}_{21}^{3-} &\rightarrow \text{Mo}_{10}\text{O}_{32}^{4-} \\
H_5\text{Mo}_6\text{O}_{22}^{3-} &
\end{align*}
\]
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SECTION I

INTRODUCTION
I.1 HISTORICAL INTRODUCTION

The phenomenon of the aggregation of molybdates in acid solutions has been known for more than a century, but detailed investigations were started only in 1930. Since then research workers have used several methods to investigate the nature of these molybdate ions in aqueous solution but there is little agreement between the results of individual workers regarding the precise nature of the ions. It is well-known, however, that molybdate ions undergo aggregation in aqueous solutions at pH values below 7.

The methods used for the investigation of the aggregation of molybdate ions can be divided into the following categories:

(1) diffusion and dialysis,
(2) electrometric methods,
(3) spectrophotometry,
(4) cryoscopy,
(5) light scattering,
(6) paper chromatography and paper electrophoresis,
(7) polarography,
(8) ion exchange and solvent extraction studies,
(9) ultracentrifugation,
and (10) studies of the solid molybdate compounds.

(1) Diffusion and dialysis

The diffusion method was one of the earliest to be applied to the investigation of polymolybdate ions in solution. The theoretical basis of this method was deduced by Reicke\textsuperscript{[1]} from Graham's diffusion law and utilised the equation 

$$D_1 \sqrt{M_1} = D_2 \sqrt{M_2}$$

(where $D_1$ and $M_1$ = the diffusion coefficient (unknown) and the molecular weight of the substance under investigation, respectively, whilst $D_2$ and $M_2$ = the corresponding values for a standard substance of similar size and ionic charge to the substance under investigation).

Jander \textsuperscript{[2-5]} was one of the earlier workers to investigate the polymolybdate system and used various methods including diffusion, in which case, the equation $D_2 \sqrt{M} = \text{constant}$ (where $\zeta$ = the specific viscosity of the solution) was used. From the results of such experiments, it was concluded that the condensation of simple molybdate ions lead to the formation of the following species:

$$\text{MoO}_4^{2-}, \text{Mo}_3\text{O}_{11}^{4-}, \text{Mo}_6\text{O}_{21}^{6-}, \text{Mo}_{12}\text{O}_{41}^{10-}, \text{and Mo}_{24}\text{O}_{78}^{12-}$$
The work of Jander has been criticised by several other workers, but still it may provide some indication of the stages of condensation in molybdate systems.

Dialysis measurements were carried out by Brötzinger and Bertzinger[6] who used the equation, \( \lambda \sqrt{M} = \text{constant} \) (where \( \lambda \) = the dialysis coefficient and \( M \) = the molecular or ionic weight of the species). Their conclusions were similar to those of Jander, stating that the monomolybdate ion \( (\text{MoO}_4^{2-}) \) was present above pH 6.5. In more acid solutions condensation of this species takes place forming the trimolybdate ion \( (\text{Mo}_3\text{O}_{11}^{4-}) \) at pH 6.5-5.0, the hexamolybdate ion \( (\text{Mo}_6\text{O}_{21}^{6-}) \) at pH 4.5-2.0 and the dodecamolybdate ion \( (\text{Mo}_{12}\text{O}_{41}^{10-}) \) at pH 1.5-1.0. In a later paper[7] the dodecamolybdate ion was excluded from this scheme. A mixture of mono- and hexamolybdate ions were said to coexist over the pH range 1.2-6.42, with the hexamolybdate as the main species between pH 5.0 and 1.5.

The results of the diffusion and dialysis measurements are criticised largely because of the wrong assumptions made in the equation used[8,9]. The diffusion law is valid when it is applied to solutions of colloidal particles but not when applied to the diffusion of ions in electrolyte solution since ionic radius, ionic charges, solvation, and the effective
diffusing mass of the ions modify the Reicke-Graham relationship. Also, the assumption of the molecular weight of the reference ion MoO₄²⁻ is not correct since its degree of hydration is not known. Tourkay and Issa¹⁰ studied the isopolymolybdate ions by an ultrafiltration technique in which dialysis is performed by applying pressure so that the equilibrium on the two sides of the membrane is attained quickly. They found that the positions of the equilibria in which only a definite form of polymolybdate is formed do not exist below pH 7.5. The particles of colloidal dimensions were separated in quantities that increased with decrease in pH and indicated progressive condensation at any pH below 7.

Recently, Reznikov and Nachaeva¹¹ have studied the forms of molybdenum by an electrodialysis method (which is dialysis performed under the influence of electric current) and concluded that in natural waters, molybdenum is predominantly anionic at pH greater than 2, whilst at pH 1 it is in a cationic form.

(2) Electrometric Methods

Electrometric methods are by far the most widely used for the investigation of molybdate ions in solution.
These include conductometric and potentiometric titrations. When a solution containing the molybdate species is titrated with an acid or a base then, at equilibrium, the positions of breaks or inflections in the curve relating conductivity or pH to the volume of the titrant give an indication of the ions which are neutralised in that solution. The measurement of pH during a titration can be very useful since the formation of polymolybdate species should require the consumption of hydrogen ions in the following way:

\[ x\text{MoO}_4^{2-} + (2x-z)\text{H}^+ \rightleftharpoons \text{H}(2y-6x-z)\text{Mo}_x\text{O}_y^{2-} + (4x-y)\text{H}_2\text{O} \]

From the electrometric titration curves, the ratio \( \text{H}^+/\text{Mo} \) for the polymolybdate ion can be obtained.

In 1926, Travers and Malaparade\[12\] titrated solutions of molybdenum(VI) oxide with a base and found inflection points corresponding to \( \text{MoO}_4^{2-} \) and \( 4\text{MoO}_3\cdot\text{H}_2\text{O} \). They elaborated their results by precipitating the polymolybdates with metal ions.

Britton and German\[14\], from potentiometric and conductometric titrations of sodium molybdate with hydrochloric acid, found evidence for the formation of sodium polymolybdate in the solution. Jander\[3\] and Bertzinger et al.\[6,7\] also used electrometric methods to support their earlier results from the diffusion and dialysis experiments.
In 1939, Bye\textsuperscript{[15-18]} started an exhaustive series of experiments on the nature of the molybdate species in solution. From the neutralisation of molybdenum(VI) oxide and the conductometric titration of sodium molybdate with hydrochloric acid, he found the evidence for the formation of Na\textsubscript{2}MoO\textsubscript{4} and Na\textsubscript{2}MoO\textsubscript{4}\textsubscript{.13}\textsuperscript{[14]}. Later, he also claimed the existence of the ions [H\textsubscript{2}Mo\textsubscript{6}O\textsubscript{24}\textsuperscript{5-}] or [H\textsubscript{3}Mo\textsubscript{7}O\textsubscript{28}\textsuperscript{6-}]\textsuperscript{[16]}. His work up to 1945 is summarised\textsuperscript{[18]} and he concludes that from a combination of the results of conductometry and potentiometry together with the results from other methods, it seems that, in dilute solutions, Na\textsubscript{5}HMo\textsubscript{6}O\textsubscript{21} is formed first and then Na\textsubscript{3}H\textsubscript{3}Mo\textsubscript{6}O\textsubscript{21}, whilst in concentrated solutions, other ions may also be present.

Carpeni\textsuperscript{[19-33]} used electrometric titrations with a glass electrode to study the molybdate ions in solution. During the titration of a solution of MoO\textsubscript{3}.2H\textsubscript{2}O\textsuperscript{[19]} he found evidence for the presence of the ions MoO\textsubscript{4}\textsuperscript{2-} and MoO\textsubscript{4}\textsubscript{.13}\textsuperscript{2-} (or Mo\textsubscript{2}O\textsubscript{7}\textsuperscript{2-}, which was later rejected\textsuperscript{[21]}). He found that the addition of neutral salt resulted in an increased condensation of molybdate ions with the inflections becoming less sharp and the inflection point for MoO\textsubscript{4}\textsubscript{.13}\textsuperscript{2-} was found to be shifted. When inflection points were constructed by mixing MoO\textsubscript{3}.2H\textsubscript{2}O and sodium chloride,
equilibrium was found to be attained after four months\textsuperscript{[19]}. Carpeni has reviewed his work\textsuperscript{[21]} and has concluded that below 0.0003M molybdenum(VI) oxide only $\text{MoO}_4^{2-}$ exists, that $\text{H}_2\text{Mo}_4\text{O}_{13}^{2-}$ exists between 0.002-0.02M molybdenum(VI) oxide whilst at concentrations above 0.02M, complex ions containing eight or even sixteen molybdenum atoms per ion may be present. He also found\textsuperscript{[22]} that in the case of the titration of $\text{MoO}_3*2\text{H}_2\text{O}$ with a base, the equilibrium is reached only after 30-60 minutes and for this reason much of the work of earlier workers is suspected since the solutions were, probably, not at equilibrium. The equilibrium was, however, more rapid when neutral salts were added but the inflection points of sodium hydroxide/molybdenum(VI) oxide were shifted from 0.7 to 1.4. (Later workers\textsuperscript{[24,42]} have claimed that equilibrium in these titrations is attained quite rapidly even when the supporting electrolyte is absent.)

Rao and Banerji\textsuperscript{[24]} determined the electrical conductivity and pH of solutions of sodium molybdate and hydrochloric acid. They postulated that $\text{Na}_2\text{Mo}_2\text{O}_7$, $\text{Na}_2\text{Mo}_3\text{O}_{10}$, tetramolybdates, and higher aggregated molybdates were present and found no change in their results when the mixtures were
kept for 3 months, though a development of a yellow colouration was observed. This was also observed by Carpeni[^20] who ascribed it to the formation of silicomolybdic acid.

The potentiometric titration of molybdate solutions with hydrochloric acid was carried out by Pan and Co-workers[^25,26] and the results were the same as those by Jander[^2-5], whilst their conductometric studies gave evidence of the formation of the ions \( \text{Mo}_3^{4-}, \text{HMo}_{12}^{13-}, \text{HMo}_6^{5-}, \text{and H}_3\text{Mo}_6^{3-}. \)

In 1952, Ripan and Duca[^27-30] started investigations of the molybdate species in solution using mostly conductometric methods. From the conductometric titrations of sodium molybdate with silver(I) nitrate, lead(II) nitrate, and hydrochloric acid, they found confirmation of the existence of the \( \text{MoO}_4^{2-} \) ion. In 50% alcoholic solution the effect of ageing was observed. In the presence of nitric acid they found that \( \text{MoO}_4^{2-} \) ions were condensed to \( \text{Mo}_6^{6-}[27] \), the structure of which was given as \( [\text{MoO(MoO}_4)]_5^{6-} \). Later[^29,30], combining the results of the conductometric study and other methods they stated that \( \text{MoO}_4^{2-} \) ion condensed to \( \text{Mo}_6^{6-} \) which may polymerise and particularly dimerise depending upon the concentration and pH of the solution and that there must be hydrogen bonds present in the
isopolymolybdic acid to stabilize the condensed species.

Cannon[31], using E.M.F. and conductometric methods found evidence of only tetramolybdate (Mo$_4$O$_{13}^{2-}$) ions in solution. At the same time Richardson[32] prepared molybdic acid solutions of high molybdenum concentration by ion-exchange and his investigations showed that the nature of potentiometric and conductometric titration curves of molybdic acid depend upon the concentration of molybdenum.

The accumulation of the results of electrometric titrations gave an impetus to apply theoretical treatment to explain the presence of aggregated ions in solution. Thus, Carpeni[23] observed that at a certain base: acid ratio in solutions of constant ionic strength, there is a point at which the pH is independent of acid concentration. He called it "isohydric point" and thought that at this point a single equilibrium between two ionic species exists and applied this idea to explain the nature of the polygermanates and polyborates. In the case of molybdates, Bye and Schwing[33] studied the isohydric point and said that it only indicates the stage of maximum or minimum aggregation. It was found to be displaced with change in temperature or salt composition if the titration
was carried out with a recrystallised quinhydrone electrode. A theoretical treatment was given for these displacements.

Sillen\textsuperscript{[34]} has developed a theory for the formation of polynuclear species in solution and it is known as the "core plus link" hypothesis. The experimental results used were obtained by E.M.F. measurements. The theory can be described in the following way:

It is assumed that the composition of the polynuclear species in the solution can be described in terms of a core plus varying number of links. If the formation of a complex $\text{A}_p\text{B}_q$ can be expressed in the following way,

$$p\text{A} + q\text{B} \underset{\text{A}_p\text{B}_q}{\xrightarrow{\text{pA} + q\text{B}}}$$

(where $p$ and $q$ = positive integers, and $\text{A}$, $\text{B}$, and $\text{A}_p\text{B}_q$ may be electrically charged) the possible combinations of $p$ and $q$ to formulate a complex are limited by the "core plus link" method so that only those combinations in which $p$ is directly proportional to $q$ are possible. The complexes may be represented by a general formular $\text{A}_r(\text{A}_t\text{B})_n$ (where $r$ and $t$ = constants, whilst $n$ is any number which will make $p$ and $q$ integers). In such a complex $\text{A}_r$ is the core and $\text{A}_t\text{B}$ is the link. To apply this concept to the actual equilibria of a polynuclear species in
solution, experiments are carried out at constant ionic strength so that the activity coefficients of the ions remain effectively constant, and the concentration of ions (measured by E.M.F.) rather than the activities can be used to calculate the equilibrium constant from the following equation:

\[ [A^P B^q] = K \cdot a^p \cdot b^q \]

(where \( K \) = equilibrium constant of the reaction and \( a \) and \( b \) = free concentration of reactants \( A \) and \( B \).) Another parameter, \( Z \), is defined as the average number of \( A \) bound per \( B \), and applying this argument to the molybdate system it is the average number of hydrogen ions associated with each \( MoO_4^{2-} \) ion. Sasaki, Sillen, and Lindqvist\(^{35}\) studied the equilibrium of the molybdate species by this method and obtained a series of curves showing the variation in \( Z \) value with pH of the solution by keeping the metal concentration constant for a particular curve. Applying the "core plus link" treatment to these curves they found that with decreasing pH the following molybdate species are formed:

\[ HMoO_4^{2-}, Mo_7O_{24}^6, HMo_7O_{24}^{5-}, \text{ and, possibly, } H_2Mo_7O_{24}^4 \]

From the calculation of equilibrium constants of these species, \( Mo_7O_{24}^6 \) was found to be the most stable ion.
Yatmirskii and Alekseeva\textsuperscript{36} also gave a "core plus link" treatment to their results of the polymerisation of molybdates and obtained almost the same types of curves as obtained by Sillen and suggested a general form for the "core plus link" polymers of molybdates, namely

\[ (H_t\text{MoO}_4)_n\text{(OH)}_r \]

Sasaki and Sillen\textsuperscript{37} published further work on the molybdate system carrying out measurements over a wider pH range and also giving solubility data. They stated that there are strong indications that mono- and heptanuclear complexes are formed and also that there is evidence of the presence of a complex of the type \( H_{11}L_7^{3-} \) (where \( L = \text{MoO}_4^{2-} \)) and a further, larger complex. They have not yet published the full details of their work.

The "core plus link" method, although theoretically sound, fails to give a unique situation when applied to the experimental data, and conclusions other than those arrived at by Sillen may also be possible. Chojnacki\textsuperscript{38} has thrown serious doubts on the existence of paramolybdate ion as deduced from the "core plus link" treatment, but this may be possible with slight modification in the hypothesis. He proposed a mechanism by which molybdenum(VI) exists in a tetrahedral form, T,
in neutral or alkaline solution but on acidification, an octahedral species, $\text{Oh}$, is formed. Thus, at a certain pH, mixed complexes of general formula $\text{Oh}_p \text{T}_q$ may be present in the solution and the equilibrium between these will depend on the $\text{Oh}:\text{T}$ ratio. Chojnacki points out that this theory differs from that of Sillen only in that the total concentration of atoms and ligands is not independent, but their ratio $\text{Oh}:\text{T} = S(h)$ is a function of pH. He drew a graphical relationship between the pH of the solution and the ratio $\text{Oh}:\text{T}$ for the hypothetical isopolyacids and found that as the pH decreases the number of probable species present in equilibrium in the solution increases. The theory of Chojnacki is similar to that of Freedman$^{[39]}$ who proposed a mechanism of the formation of polytungstate ions in solution which could also be applied to polymolybdate systems.

Chojnacki and Oleksyn$^{[41]}$ carried out pH titrations of ammonium molybdate solution with nitric acid using quinhydrone and saturated calomel electrodes and partially eliminated their errors by carrying out blank titrations. The curves showing variation in Z (where $Z = \text{H}^+:\text{Mo}$ ratio) with pH had a common point of intersection at pH 3.75 and $Z = 1.45$ which indicates
that more than one species are present in the acidified solution
\(Z\) for \(\text{Mo}_7\text{O}_{24}^{6-} = 1.42\), and for \(\text{Mo}_4\text{O}_{13}^{2-}\) or \(\text{Mo}_8\text{O}_{26}^{4-} = 1.50\). They have interpreted these results according to the theory of Chojnacki and conclude that the core consists of the six-coordinate \(\text{Mo(OH)}_6^{2-}\) group and the links are formed from tetrahedral \(\text{HMoO}_4^{-}\) ions. They have also calculated the equilibrium constants and the energy of formation of the species in solution considering only dilute solutions where aggregates containing more than seven molybdenum atoms were not formed.

The literature of the electrometric work in recent years contains further work in which efforts were made to refine and improve the techniques of measuring \(\text{pH}\) and conductivity of the solutions. Schwarzenbach and Meier\(^{42}\) devised an apparatus for the continuous determination of \(\text{pH}\) as the hydrochloric acid and molybdate solutions are mixed. They found that \(\text{MoO}_4^{2-}\) ions first protonate to \(\text{HMOO}_4^{-}\) and then polymerise in less than \(10^{-2}\) seconds.

Saxena and Saxena\(^{43}\), carrying out \(\text{pH}\) titrations, using a glass electrode and conductometric titrations with a platinised electrode at a frequency of one kilocycle per second, found evidence for the presence of the ions \(\text{Mo}_6\text{O}_{21}^{6-}\), \(\text{H}_2\text{Mo}_6\text{O}_{21}^{4-}\), and \(\text{H}_3\text{Mo}_6\text{O}_{21}^{3-}\), with good evidence for the latter ion.
Beltran and Pureta[^44], from conductivity measurements, found the presence of most of the ions reported in the literature especially di-, tri-, and octamolybdate. Schwing[^45,46] studied isopolymolybdates by means of the progressive displacement of molybdic acid from sodium molybdate solutions with hydrochloric acid and measured pH using glass and gold-quinhydrone electrodes. He found evidence for the presence of ions Mo$_7$O$_{24}$$^{6-}$, Mo$_6$O$_{20}$$^{4-}$, and HMo$_6$O$_{20}$$^{3-}$, but could not detect HMo$_7$O$_{24}$$^{5-}$. Recently, Reingold and Nadol'skii[^47] have measured the electrical conductivity of sodium isopolymolybdate solutions using an alternating current frequency of one kilocycle per second with an oscillograph and a platinum sheet electrode. They have found that the electrical conductivity diminishes on polymerisation. Their isothermal conductivity curves show the presence of inflections corresponding to a mole ratio of molybdenum(VI) oxide and sodium oxide equal to 1, 2, 7/3, 12/5, and 3, indicating di-, para- and trimolybdate ions.

Many workers in recent years have developed new techniques for the investigation of polymolybdate ions in the solution and often have used these together with electrometric titrations.
Thus, Cooper and Salmon\(^\text{[48]}\), who studied isopolymolybdate ions by an ion-exchange method, also carried out glass electrode pH titrations of molybdic acid and found an inflection point corresponding to a hydrogen ion to molybdenum ratio = 1.5, which they attributed to the ion \(\text{Mo}_4^\text{O}_{13}^{2-}\). Similar results were obtained by Heitner-Wirguin\(^\text{[49]}\). Aveston and Co-Workers\(^\text{[50]}\) using an ultracentrifugation method supplemented their results with the potentiometric titration of isopolymolybdate solutions in media of 1M and 3M sodium chloride and lithium chloride. They found the presence of the species \(\text{Mo}_7^0\text{O}_{24}^6-\) and \(\text{Mo}_8^0\text{O}_{26}^4-\) along with some protonated forms of the monomeric and polymeric molybdates. This scheme is also the one given by Glemser, Holznagel and Ali\(^\text{[51]}\) who have used many techniques including pH titrations.

The work described above shows the efforts made by various workers to apply electrometric methods to the investigations of isopolymolybdate ions in solution. As described earlier, it is not possible to draw a general conclusion from these results. The reasons for these disagreements are many. The pH and the conductivity measurements of molybdate solutions are liable to errors especially when the pH of the solution is low because of the presence of many foreign ions in the solution.
Aveston and Co-workers\textsuperscript{[50]} have pointed out some "over ambitious attempts" to interpret the breaks in the electrometric titration curves, since the difference of hydrogen ion to molybdenum ratio for some of the molybdate species is less than 1\% which is beyond the precision of the electrometric techniques. Also the hydrogen ion to molybdenum atom ratio found from the electrometric titrations is only a value from which it is not possible to obtain any idea of the exact degree of aggregation of molybdenum in the species and any such attempt is only a matter of speculation.

(3) Spectrophotometry

The ultraviolet spectra of solutions containing molybdate species have been studied by many workers who correlated changes in the nature of the absorption with variations in the degree of aggregation of the molybdate ion.

In 1930, Jander and Co-workers\textsuperscript{[2]} used ultraviolet absorption spectrophotometry along with the diffusion measurements to study isopolymolybdate ions in solution.

Carpeni in 1947\textsuperscript{[52]} studied the dependence of the wavelength of the maximum absorption and the molecular absorption coefficient on the concentration of molybdenum(VI) oxide, pH,
and the ionic strength of the solution. He found that the absorption curves shift towards higher wavelength as the solutions become more acidic. This is a common observation reported by many workers using the spectrophotometric method and indicate condensed species are being formed in the solution.

Lindqvist\textsuperscript{[53]} has devised a spectrophotometric method for studies of molybdate solutions. By considering the variation of the ratio \(\Delta E:(S-h)\) with \((S-h)\), (where \(\Delta E = \) the increase in extinction coefficient due to the hydrogen consumption \(S-h\)), he found breaks corresponding to \((S-h):C = 8/7\) and \(12/8\) (where \(C = \) concentration of molybdenum) which were assigned to the ions \(\text{Mo}_{7}^{024}\) and \(\text{Mo}_8^{026}\). These ions are formed in the solution in the following way:

\[
\begin{align*}
7\text{Mo}_4^{2-} + 8H^+ &\rightleftharpoons \text{Mo}_{7}^{024}^{6-} + 4H_2O \\
8\text{Mo}_4^{2-} + 12H^+ &\rightleftharpoons \text{Mo}_8^{026}^{4-} + 6H_2O
\end{align*}
\]

On further acidification the formation of larger complexes was postulated. The equilibrium constants of the abovementioned reactions were determined by Daniele\textsuperscript{[54]} who used the method of Lindqvist and found that the values of \(\log K_1(\text{Mo}_7^{024})^{6-} = 52.2\) and \(\log K_2(\text{Mo}_8^{026})^{4-} = 72.5\) at pH \(4.99-5.90\) and \(4.36-4.96\), respectively.
Chauvea, Schaal, and Souchay[55] have studied the absorption of molybdate cations in 5M perchloric acid between 2100 and 2500Å and have found that in 0.01M molybdenum solutions, the cations were bicondensed. Coope and Thistlewaite[56,57] have studied ultraviolet absorption spectra of molybdate solutions in hydrochloric, sulphuric, perchloric, and nitric acids. They observed a difference in the spectra in the case of nitric acid and ascribed it to some molybdate-nitric acid interaction. They have also observed a shift of the maxima from lower to higher wavelengths with increase in the acid concentration of the solution.

Rohwer and Cruywagen[58] determined the first protonation constant of molybdic acid at 218μ and found a value of 8.59 ± 0.20 for 0.0001M molybdenum(VI) in 0.7-0.01M perchloric acid solutions.

Reznikov and Tsyganok[59] have studied molybdophosphoric and molybdic acids between wavelengths 220 and 440μ and found maxima in the value of the extinction coefficient of molybdic acid solutions at pH 1.6. Beer's law was found to be obeyed by solutions of pH0.5 between 280-300μ.

Glemser, Holznagel, and Ali[51] observed a sudden change in the extinction coefficient in solutions containing
1.5 hydrogen ions per molybdenum atom. This was ascribed to
the ion \( \text{Mo}_8^{\text{O}_{26}}^{4-} \).

Many other workers have carried out ultraviolet
absorption spectrophotometry of polymolybdate solutions as a
supplementary technique[31,36,49].

(4) Cryoscopy

Cryoscopy is the measurement of the lowering of the
freezing point of a solvent in solution and is a function of
the activity of the solute. It provides a method of
determining the concentration of a solution in terms of the
average number of solute particles.

Carpeni[59] carried out freezing point determinations
of solutions of molybdic acid which led him to suggest that
molybdic acid had the formula \( \text{H}_2\text{Mo}_{4}^{\text{O}_{13}} \) and that it dissociates
to the extent of 50\% in a first stage to give \( \text{H}_2\text{Mo}_2^{\text{O}_7} \).

Doucet[161] described an apparatus for the accurate
measurement of the depression of freezing point using thermo­
couples and photographic recordings. The apparatus was tested
with potassium sulphate and the results were quite satisfactory.
Measurement of the freezing point of molybdic acid solutions in
which the molybdate ions were assigned the general formula 
(Mo\textsubscript{x}O\textsubscript{y})\textsubscript{H\textsubscript{2}} were carried out and the values for the depressions were extrapolated to infinite dilution which gave the composition of molybdic acid as (Mo\textsubscript{4}O\textsubscript{13})\textsubscript{H\textsubscript{2}}. Similar measurements using ammonium paramolybdate indicated the formula (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}, the anion of which dissociates at low concentrations into Mo\textsubscript{4}O\textsubscript{13}\textsuperscript{2-} and 3MoO\textsubscript{4}\textsuperscript{2-}. The discussion of these results was modified at a later date\textsuperscript{[62]} when the acid (MoO\textsubscript{3})\textsubscript{4}OH\textsubscript{2} was reported as the lowest polymer.

The dissociation of paramolybdate ion, Mo\textsubscript{7}O\textsubscript{24}\textsuperscript{6-}, in solutions of ammonium paramolybdate has also been reported recently by Guignard\textsuperscript{[63]} as a result of Cryoscopic measurements. The products of the dissociation were described as tetramolybdate and trimolybdate ions:

\[
\text{Mo}_7\text{O}_{24}^{6-} \rightleftharpoons \text{Mo}_4\text{O}_{13}^{2-} + \text{Mo}_3\text{O}_{11}^{4-}
\]

Since cryoscopy is carried out at the freezing point of the solvent it affords difficulties for the study of equilibria at very low temperatures. Another type of cryoscopy is known as "Salt Cryoscopy" in which the transition point of glauber's salt at 32.5°C is studied:

\[
\text{Na}_2\text{SO}_4(\text{aq}) \rightleftharpoons \text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}
\]
In the presence of molecules of some other substance the transition point is lowered by a value which is proportional to the number of foreign particles present.

Bye[64] measured the effect of mixtures of sodium molybdate and sulphuric acid solutions on the transition point of glauber's salt and found that the composition of the molybdate ion is \([\text{H}_8\text{Mo}_7\text{O}_{28}]^{6-}\), which on acidification in dilute solution becomes \([\text{H}_6\text{Mo}_4\text{O}_{16}]^{2-}\).

Martinez and Cabanes[65] studied the freezing point depression constant of sodium and ammonium molybdate in dilute sulphuric acid and ammonium hydroxide solutions in glauber's salt and found that it depends linearly on the solute concentration. As a result of this work, the following polymolybdate ions were reported:

\[
\text{Mo}_4\text{O}_{14}^{4-}, \text{Mo}_7\text{O}_{24}^{6-}, \text{Mo}_6\text{O}_{20}^{4-}, \text{Mo}_4\text{O}_{13}^{2-}, \text{HMo}_4\text{O}_{13}^{-},
\]

and \(\text{H}_2\text{Mo}_4\text{O}_{13}\)

Tobias[66] has discussed the limitations of salt cryoscopy and has questioned the interpretation of freezing point data for ions in aqueous solution in the same manner as that for non-ionised complexes in organic solvents. In the case of solutions of polyions, it has been shown that there is always a
considerable amount of hydroxide ion present which contributes significantly to the freezing point depression. Further, the assumption that solute activity coefficients are constant at high concentration of supporting electrolyte, whilst being a valid one for E.M.F. measurements, is a more complicated concept when applied to the analysis of cryoscopic data obtained in the presence of high concentrations of sodium sulphate because of the presence of three or more phases. Thus, Tobias suggested that "the results of cryoscopic measurements, particularly in case of systems with several complexes or polyions containing more than three or four metal atoms are best regarded as indicative rather than conclusive".

(5) Light scattering

The molecular weight of a solute present in a solution can be determined if the solution obeys the scattering law, which, for non-electrolytes is given by the following equation:

\[ \frac{Hc}{T} = \frac{1}{M_w} + \frac{2Bc}{RT} \]

(where \( H \) = function of the concentration \( c \) and the refractive index of the solution; \( T \) = turbidity of the medium; \( M_w \) = molecular weight of the solute; and \( B \) = characteristic for a given
solvent-solute system at a given temperature.) The same equation may be used for polyelectrolytes if measurements are made in the presence of high concentrations of a supporting electrolyte. If high concentrations of a polyelectrolyte are involved then the following modified equation is used:

\[
T = \frac{\phi \gamma_2^2}{1/m_2 + Z_2^2/2(m_3 + m_5)}
\]

(where \(\phi\) = volume fraction of the solvent; 
\(\gamma_2\) = refractive index increment of polymeric component; 
\(m_2\) = molarity of the polymeric component; 
\(m_3\) and \(m_5\) = molarities of supporting electrolyte salt and its acid respectively.)

The light scattering method was used for studies of the molybdate system by Kestigan, Coldony, and Stein[^67]. They measured the absolute turbidities of two sets of sodium molybdate solutions kept at an angle of 90° to the incident beam. These results indicate a molecular weight of 480 ± 10 for molybdate solutions of pH 6.5-7.5, and a value of 2500 ± 100 for solutions of pH 2.5-4.0. The precision of these results was described as rather low, but they confirm the greater association of molybdate ions at lower pH.
Katti and Wanchoo\cite{68} studied the depolarization $\rho_h$, (where $\rho_h$ = the ratio of intensities of the vertically polarized component and the horizontally polarized component when the incident beam is horizontally polarized) of sodium molybdate solution by sunlight and a green filter. They found that $\rho_h$ is 100% at pH 8.7, and 36% at pH 1.4. The size of the aggregates was 110$\mu\text{m}$ in the solutions of pH 1.4. In a later publication\cite{69} Wanchoo reported that in alkaline solution the size of the aggregates was less than 110$\mu\text{m}$ and the size increases as the pH decreases and reaches a maximum between pH 2.5-4.0.

Light scattering studies of molybdate solutions have also been carried out by Tyree and Co-workers\cite{70}. Apart from the measurements of turbidities, they have determined the refractive index and the density of such solutions. The variation in the polymerisation number of the polymeric component with the concentration of molybdenum for several possible $Z$ values (where $Z$ = number of sodium atoms per molybdenum atoms) were found to be the same for a variety of molybdic acid solutions prepared by different methods. These authors conclude that the ions $\text{Na}_5\text{Mo}_7\text{O}_{24}^{1-}$ and $\text{Na}_4\text{Mo}_7\text{O}_{24}^{2-}$ are the most
likely ones. A more condensed ion containing perhaps nine or ten molybdenum atoms was postulated.

When the light passes through a solution, a shift in the optical path may occur due to the "interference" of solute particles. These shifts may be measured by interferometers and provide a useful means of estimating small changes in concentrations of the solution. Plsko and Liska[71] found from the interferometric measurements of solutions of sodium molybdate in mineral acids that there was a sharp break in the titration curves when the ratio of molybdenum atoms to hydrogen ion was 2:3 which indicates the formation of isopolymolybdate ions. No further isopolymolybdate ion could be detected.

Variation of the degree of aggregation of aqueous solutions of sodium molybdate on the addition of nitric acid was studied by Pipan and Szekly[72] using interferometry and refractometry. The polymolybdate species reported by them are $2\text{Na}_2\text{O} \cdot 3\text{MoO}_3$ and $5\text{Na}_2\text{O} \cdot 12\text{MoO}_3$. Their results show no change in the condensation of molybdate ions in the presence of added electrolyte nor did it change with time.

Increases in the refractive index of molybdate solutions have been investigated by Aveston and Co-workers[50] using
sodium chloride, sodium perchlorate, and lithium chloride as supporting electrolytes. They observed an abrupt change in the increase in the refractive index per molybdenum atom when the hydrogen ion to molybdenum atom ratio of the solution was 1.15 and 1.50. They attributed these breaks, with some supporting evidence, to ions Mo$_{7}$$O_{24}^{6-}$ and Mo$_{8}$$O_{26}^{4-}$.

(6) Paper electrophoresis and chromatography

Studies of the migration of ions under the influence of an electric field over a strip of paper dipped in a solution of an electrolyte is commonly known as paper electrophoresis and is widely used for the separation of inorganic ions. In the case of polyions which are separable by this technique the degree of aggregation can also be identified by a consideration of the rate of the movement of ions.

Chojnacka$^{[38,39]}$ has described a theory for the formation of isopolymolybdate ions in solution, in which the formation of polymolybdates involves, first, the protonation of MoO$_{4}^{2-}$, and secondly the hydration of the protonated species. The concentration of the complexes formed by the protonation of MoO$_{4}^{2-}$ has been calculated from their ionic mobilities on a paper strip$^{[73]}$. Assuming that in extremely
dilute solution the ions are mainly in monomeric form, the equilibrium constant of the protonation reaction was determined and the following ions were found to predominate over a pH range:-

- at pH 7-5 $[\text{MoO}_4]^{2-}$; at 2.5 $\leq$ pH $\leq$ 4.5 $[\text{MoO}_4]^{2-}$ and $[\text{HMoO}_4]^{1-}$; and 1 $\leq$ pH $\leq$ 2.5 $\text{MoO}_6^{6-}$

In a later paper[74] the same author determined the cumulative equilibrium constant of the protonation of $\text{MoO}_4^{2-}$ ions in perchloric acid and nitric acid solutions from the mobility of ions for the following reactions:-

$$\text{MoO}_4^{2-} + \text{H}^+ \xrightleftharpoons{k_1} \text{HMOO}_4^{-}$$

$$\text{MoO}_4^{2-} + 2\text{H}^+ \xrightleftharpoons{k_2} \text{H}_2\text{MoO}_4$$

and $$\text{MoO}_4^{2-} + 3\text{H}^+ \xrightleftharpoons{k_3} \text{H}_3\text{MoO}_4^+$$

The value of $k$ was found to agree with those of other workers.

Blassius and Czekay[75] have used paper chromatography and paper electrophoresis for the investigation of the separation of molybdenum and tungsten and have studied the effect of paper type, pH, complexing agents, and solvent concentration. Different stages of the aggregation of the
separated ions were identified by their rate of movement and in case of molybdenum, the ions \( \text{MoO}_4^{2-} \) and \( \text{HMo}_6\text{O}_{21}^{5-} \) were identified.

Wendling, Rohmer, and Weiss\[^{76}\] postulated the existence of the ions \( \text{Mo}_2\text{O}_{11}^{2-} \) and \( \text{Mo}_4\text{O}_{13}^{2-} \) by making use of paper chromatography and ionophoresis.

Csyani\[^{77}\] investigating the aggregation of monomolybdate ions by paper chromatography found that instead of a single product, an equilibrium exists between different aggregates, the nature of which depends on the spatial arrangement of mono- and polymolybdic ions. The aggregates were also found to be liable to dissociation. He also stated that the hexamolybdate ion is the most stable ion observed under the experimental conditions employed.

Gaibakyan and Darbinyan\[^{78}\] have recently reported the investigation of molybdenum(VI) and rhenium(VII) in hydrochloric acid and sodium hydroxide solutions by means of paper electrophoresis. Their results indicate that, at pH 4.0, molybdenum(VI) forms complex anions which at pH 2.15 transform gradually into cationic forms and at pH 1.5 these cationic forms are the predominant ones.
(7) Polarography

Polarography is a method in which a gradually increasing potential is applied to an electrode dipped in a solution, causing movement of the ions. By constructing a curve of voltage and current, which is commonly known as polarogram, it is possible to determine the nature and the concentration of the solute.

Ripan, Duca, and Calu[79] have used the polarographic method to show that the hydrogen ion associated with a polymolybdate ion is reduced at a more negative potential than the hydrogen ion derived from strong acids. By making use of derivative polarography similarities in the polarographic behaviour of the following solutions were obtained:

(a) A solution of \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}\)

(b) A paramolybdate solution obtained at a mole ratio of sodium molybdate to nitric acid = 6:7 and between (a) a solution of molybdenum(VI) oxide in water concentrated by heating.

(b) A dodecamolybdcic acid obtained from a solution with a mole ratio of sodium molybdate to nitric acid of 6:12.
The conclusion from these observations was that an equilibrium exists between dodeca- and hexamolybdates.

It has been observed\(^{[80]}\) that during a polarographic study of sodium molybdate solutions in which hydrochloric acid was added in a way such that the mole ratio of hydrochloric acid to sodium molybdate was less or equal to 1.14, the diffusion current was approximately proportional to the Mo\(_7^0\)\(_{24}^6^-\) concentration formed in the hypothetical reaction:

\[
7\text{MoO}_4^{2-} + 8\text{H}^+ \rightleftharpoons \text{Mo}_7\text{O}_{24}^6^- + 4\text{H}_2\text{O}.
\]

By varying the molybdate concentration in a strongly buffered solution in such a way that only the ions postulated as Mo\(_4^0\)\(_{2}^2^-\) and Mo\(_7^0\)\(_{24}^6^-\) exist, the diffusion current was approximately proportional to the total molybdenum concentration. This was ascribed to the rapidity of the above-mentioned reaction in which decreases in the Mo\(_7^0\)\(_{24}^6^-\) concentration would be continuously compensated.

Other workers\(^{[81]}\) reported the ion H\(_3\text{Mo}_6\text{O}_{21}^3^-\) at pH 1.6-5.1, and the polarographic reduction process was described as:

\[
\text{H}_3\text{Mo}_6\text{O}_{21}^3^- + 18\text{e} + 21\text{H}^+ \rightleftharpoons 6\text{Mo(OH)}_3 + 3\text{H}_2\text{O}.
\]
Bodor and Co-workers\textsuperscript{[82]} used alternating current oscillographic polarography to identify a cathodic inflection at $10^{-7}$ M concentration of isopolyacid solution. This was ascribed to the catalytic evolution of hydrogen.

(8) Ion exchange and solvent extraction

The ion exchange process is usually used for the determination of the charge of a complex ion per metal atom in aqueous solution.

Nomitso and Hironacka\textsuperscript{[83]} found that during chloride: molybdate exchange on an anion exchange resin, the rate determining process was diffusion controlled and that the effective diffusion coefficient decrease as the pH of the solution is decreased in the range 8.0 to 3.8. At higher acidities the value of the diffusion coefficient was effectively constant. They have attributed these changes to the condensation of molybdate ions in acidic solution, and that the network of the resin is not larger than that of the paramolybdate ion in aqueous solution.

Kraus, Nelson, and Moore\textsuperscript{[84]} studied the ion exchange behaviour of molybdenum(VI) along with that of tungsten(VI) and uranium(VI) in hydrochloric acid and hydrofluoric acid
solution, and hydrochloric acid - hydrofluorofloric acid mixtures. They have observed a similarity in the extraction of uranium(VI) and molybdenum(VI) at low hydrochloric acid concentrations which may show that the complexes of these metals at these acid concentrations are similar. The slow anion exchange equilibria of molybdenum(VI) at low acidities was consistent with the postulated existence of polymeric species. It was concluded that these polymeric species depolymerise to dioxomolybdenum(VI) cation at higher acidities.

Babko and Nabivanets[85] studied the sorption of molybdenum(VI) by anion and cation exchange resins and found that molybdenum(VI) exists mainly in anionic form at a pH above 1, whilst below this pH, cationic species start to form, so that at pH near 0.7 a monomeric form of molybdenyl cations predominates.

Newman and Cook[86], studying the chloride species of molybdenum(VI), found that the species with a molybdenum to chloride ratio of 1:2 is the one which is extracted by ether and absorbed by ion-exchangers.

Some work on the nature of molybdate ions adsorbed by ion exchange resins has been carried out by Nomitsu and Fujimah[87] who have used the hydroxide form of an anion
exchange resin and found that in a solution of pH 5.0, the exchange of molybdenum is at a maximum and that it is exchanged as the ion \( \text{Mo}_4\text{O}_{13}^{2-} \).

The potentialities of ion exchange as a method for the investigation of polyions in solution have been described by Salmon and Co-workers\(^{[48,88]}\). Their work involves the determination of \( R \) value which is the ratio of metal atom and charge of an ion present in the solution. It is obtained from the exchange of metal oxyanions with the counter-ion of the resin. Harvey, Redfern, and Salmon\(^{[88]}\) have shown that a constant \( R \) value, obtained over a pH range, may indicate a single species in the solution and that the \( R \) value in such a region gives the correct value for the atom to charge ratio of known oxyanions. In the isopolymolybdate system, Cooper and Salmon\(^{[48]}\) have concluded from \( R \) values of 2.0 and 5.0 that a two stage condensation takes place and that a region of constant \( R \) value of 0.5 in alkaline region correspond to monomeric \( \text{MoO}_4^{2-} \) ions. The two condensed ions were separated by making use of the ionic sieve effect of the resins as a result of which bigger ions are excluded by a highly cross-linked resin. The formulae assigned to these ions were \( \text{Mo}_4\text{O}_{13}^{2-} \) and \( \text{H}_2\text{Mo}_{10}\text{O}_{32}^{2-} \). Similar
studies of isopolymolybdic acid by ion-exchange resins were carried out by Heitner-Wirguin and Cohen[49,89] who found evidence for the ion $\text{Mo}_{4}^{\text{O}_{13}}^{2-}$ by adsorption on highly cross-linked resins.

Solvent extraction studies of molybdates are usually confined to the separation of molybdenum from other metals. However, Neildov and Diamond[90] studied the extraction of molybdenum(VI) species from 6M hydrochloric acid into carbon tetrachloride, chloroform, and fluorite FS (which is a mixture of fluoro carbons) and obtained indirect evidence that the species are monomeric chloro complexes. Zeitsev and Co-workers[91] used trioctylamine in kerosene to separate molybdenum and rhenium from sulphuric acid solution. The organic phase species were shown to have metal to amine ratio of 1:2.

(9) Ultracentrifugation

Ultracentrifugation is a method which gives a weight average molecular weight of the solute in a solution. Aveston and Co-workers[50] have studied the sedimentation of molybdic acid in a solution containing supporting electrolyte at centrifuge speeds of 16200-23150 rotations per minute. Their
results indicate that ions with an average degree of aggregation of 6 to 9 are present when the p of the solutions lies within the range 1.2-1.5 (where p = number of hydrogen ions bound per molybdenum atom), and above p = 1.5, higher aggregates are present. These authors have chosen heptamers and octamers with formulae $\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{Mo}_8\text{O}_{26}^{4-}$, respectively, as the most likely species.

Glemser and Co-workers have carried out similar experiments on molybdic acid solutions and have arrived at similar conclusions.

(10) Preparation of solid molybdate compound

Some of the molybdate ions can be precipitated from aqueous solution on the addition of suitable cations. The structure of a solid obtained in this way is easier to determine than that of an ion in solution but the stoichiometry and structure of a crystalline salt need not necessarily be the same as those of a solution species. The preparation of these solids usually involves the addition of a solution of the salt of a heavy cation to an aqueous molybdate solution which is adjusted to a certain pH. Alternatively, oxides of molybdenum or a normal salt of molybdenum are fused with molybdenum(VI) oxide and then the product of the melt is crystallised.
Travers and Malaparade[12] reported the formation of barium tetramolybdate, $4\text{MoO}_3\cdot\text{BaO}\cdot4\text{H}_2\text{O}$ and suggested the formula of sodium paramolybdate is $7\text{MoO}_3\cdot3\text{Na}_2\text{O}\cdot22\text{H}_2\text{O}$ and postulated[92] that ammonium paramolybdate, $12\text{MoO}_3\cdot5(\text{NH}_4)_2\cdot7\text{H}_2\text{O}$ consists of the paramolybdate $7\text{MoO}_3\cdot30(\text{NH}_4)_6$ and a trimolybdate $3\text{MoO}_3\cdot0(\text{NH}_4)_3$.

Barium molybdate was also obtained by Bye[93] from a molybdate solution by precipitating with barium chloride. At different concentrations of hydrochloric acid, salts of the formulae $3\text{BaO}\cdot3\text{MoO}_3$, $\text{BaO}\cdot3\text{MoO}_3$, and $\text{BaMoO}_4$ were obtained. Later[18] the preparation of $\text{Ba}_2\text{H}_2\text{Mo}_6\text{O}_{21}$ was reported whilst the addition of ethyl alcohol to a solution of sodium molybdate produced the compounds $\text{Na}_2\text{MoO}_4$, $\text{Na}_5\text{HMo}_6\text{O}_{21}$, and $\text{Na}_3\text{H}_3\text{Mo}_6\text{O}_{21}$.

Other workers have characterised the following compounds:— $\text{K}_6\text{Mo}_7\text{O}_{24}$, $\text{Ba}_3\text{Mo}_7\text{O}_{24}$, $\text{H}_6\text{Mo}_7\text{O}_{24}$ [94], $\text{H}_4\text{Mo}_3\text{O}_{11}$, $\text{NH}_4\text{H}_5\text{Mo}_6\text{O}_{21}$ or $(\text{NH}_4)_2\text{H}_4\text{Mo}_7\text{O}_{24}$ [95] and salts of general formula $\text{MMoO}_4$ (where $\text{M} = \text{Ba}, \text{Sr}, \text{Cd})[96]$.

Crystal structure determinations of molybdate compounds have been carried out by Lindqvist[97]. The structure of the paramolybdate ion $\text{Mo}_7\text{O}_{24}^{6-}$ and the octamolybdate ion $\text{Mo}_8\text{O}_{26}^{4-}$ were shown to consist of $\text{MoO}_6$ octahedra which share edges to build up the polymeric unit. There is a common structural unit $\text{Mo}_6\text{O}_{22}^{8-}$. 
Molybdate compound with organic bases have also been reported. The compound formed by the addition of α-α' bipyridyl to a sodium molybdate solution in hydrochloric acid at pH 1.92, was reported to be \((\text{bipy. H}_2)_2\left(\text{H}_4\text{Mo}_7\text{O}_{24}\right)\) \(^{[98]}\). The same author also reported a molybdate compound of pyridine \(^{[99]}\) prepared at pH = 1.50 in the same way as was the bipyridyl compound. The formula for this compound was given as \((\text{pyH})_3\text{H}_3\text{Mo}_7\text{O}_{24}\). Similar compounds with quinoline and dimethyl aniline were also reported in the same publication. Other pyridinium compounds were prepared by Weill \(^{[100]}\) from the system \(\text{MoO}_3\cdot\text{C}_5\text{H}_5\text{N}\cdot\text{H}_2\text{O}\), which were assigned the formulae \(\text{Mo}_3\text{O}_{10}\left(\text{C}_5\text{H}_6\text{N}\right)_2\) and \(\text{Mo}_4\text{O}_{13}\left(\text{C}_5\text{H}_6\text{N}\right)_2\). The trimolybdate was stated to be metastable and hydrolyse to the tetramolybdate. The preparation of piperidine molybdate is reported \(^{[101]}\) and five solid phases, of formulae \(\text{Mo}_4\text{O}_{13}\left(\text{C}_5\text{H}_{12}\text{N}\right)_2\), \(\text{Mo}_3\text{O}_{10}\left(\text{C}_5\text{H}_{12}\text{N}\right)_2\cdot2\text{H}_2\text{O}\), \(\text{Mo}_7\text{O}_{24}\left(\text{C}_5\text{H}_{12}\text{N}\right)_6\cdot6\text{H}_2\text{O}\), \(\text{Mo}_2\text{O}_{7}\left(\text{C}_5\text{H}_{12}\text{N}\right)_2\cdot\text{H}_2\text{O}\), and \(\text{MoO}_4\left(\text{C}_5\text{H}_{12}\text{N}\right)_2\) are separable. The first four of these in aqueous piperidine with hydrochloric acid yield the tetramolybdate. The dietherate of a molybdenum(VI) hydrochloride \(\text{MoO}_3\cdot2\text{HCl}\cdot2\text{Et}_2\text{O}\cdot\text{H}_2\text{O}\) was prepared by Bye and Weill \(^{[102]}\). Removal of water from this compound gave an unstable product.
Ferric molybdate has been recently prepared by Koznelsova and Co-workers\textsuperscript{103} by the addition of a ferric chloride solution to a sodium molybdate solution at pH 7.0-7.1. The formula of the compound is given as $\text{Fe}_2(\text{MoO}_4)_3 \cdot 18\text{H}_2\text{O}$ and the structure has been determined by X-ray and differential thermal analyses, and confirmed by infrared spectroscopy.

**Miscellaneous Methods**

Das and Ray\textsuperscript{104} studied the magnetic susceptibility of sodium molybdate in aqueous nitric acid solution. The dependance of the susceptibility upon the pH of the solution shows four well defined inflections which correspond to the addition of 4, 7, 9, and 10.5 hydrogen ions per six molybdate ions and these were ascribed to di-, para-, and octamolybdates. The results were stated to agree with those of Jander\textsuperscript{2-5}.

Volumetric changes during the condensation of tungsten and molybdenum anions were studied by Liska\textsuperscript{105}. Positive volumetric changes were observed and the curves showing variation of dilation with the composition of the isopolymolybdate solution had a maximum at 1.5 hydrogen ions per molybdenum atom and indicated the formation of a metamolybdate anion.
<table>
<thead>
<tr>
<th>Degree of aggregation</th>
<th>Postulated Isopolyonol日期 Species</th>
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<tbody>
<tr>
<td>2</td>
<td>$\text{Na}_2\text{Mo}_2\text{O}_7$[El.24]; $\text{H}_2\text{Mo}_2\text{O}_7$[Cr.54]; $\text{Mo}<em>2\text{O}</em>{10}^5$[PC.76]; dimolybdate [El.44,47]; $\text{Mo}_2\text{O}_7(\text{C}<em>5\text{H}</em>{12}\text{N})_2$.H$_2$O[S.101]</td>
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<td>3</td>
<td>$\text{Mo}<em>3\text{O}</em>{11}^{4-}$[Dif. 2-5, Dia. 6, El. 25,26, Cr.65]; $\text{Na}_2\text{Mo}<em>3\text{O}</em>{10}^{5-}$[El.24]; 2$\text{Na}_2\text{Mo}_3\text{O}_3$[LS.72] trimolybdate[El. 44,47,63]; $\text{Ba}_2\text{Mo}_3\text{O}_3$[S18], $\text{H}_4\text{Mo}<em>3\text{O}</em>{11}$[S94], $\text{Mo}<em>3\text{O}</em>{10}(\text{C}<em>5\text{H}</em>{12}\text{N})_2$.2H$_2$O[S101], $\text{Mo}<em>3\text{O}</em>{10}(\text{C}<em>5\text{H}</em>{6}\text{N})_2$[S100]</td>
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<td>4</td>
<td>$4\text{Mo}_3\text{O}_3$.H$_2$O[El.12]; $\text{Mo}<em>4\text{O}</em>{13}^{2-}$[El.14,21,32,48,49, Cr.59,61,63,65, PC76,IE87, 48,49,89]; H$\text{Mo}<em>4\text{O}</em>{13}^{1-}$[Cr.65]; $\text{Mo}<em>4\text{O}</em>{13}(\text{C}<em>5\text{H}</em>{6}\text{N})_2$[S100]; $\text{Mo}<em>4\text{O}</em>{13}(\text{C}<em>5\text{H}</em>{12}\text{N})_2$[S101]</td>
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<tr>
<td>6</td>
<td>$\text{Mo}<em>6\text{O}</em>{21}^{6-}$[Dif.2-5,Dia.6,El.27,43]; $\text{HMo}<em>6\text{O}</em>{21}^{5-}$[El.18,25,26,PC.75]; $\text{H}_2\text{Mo}<em>6\text{O}</em>{21}^{4-}$[El.43]; $\text{H}_3\text{Mo}<em>6\text{O}</em>{21}^{3-}$[El.18,25,26,43,Pol.81]; $\text{H}_7\text{Mo}<em>6\text{O}</em>{24}^{4-}$[El.16]; $\text{H}_6\text{Mo}<em>6\text{O}</em>{20}^{4-}$[El.45,46, Cr.65]; $\text{HMo}<em>6\text{O}</em>{20}^{3-}$[El.45,46]; Hexa-[PC.77]; $\text{Ba}_2\text{H}_2\text{Mo}<em>6\text{O}</em>{21}$, $\text{Na}_3\text{H}_3\text{Mo}<em>6\text{O}</em>{21}$, $\text{Na}_5\text{H}_5\text{Mo}<em>6\text{O}</em>{21}$[S.18], $\text{NH}_4\text{H}_5\text{Mo}<em>6\text{O}</em>{21}$[S.94]</td>
</tr>
<tr>
<td>7</td>
<td>$\text{H}_8\text{Mo}<em>7\text{O}</em>{28}^{6-}$[El.16,Cr.64]; $\text{Mo}<em>7\text{O}</em>{24}^{6-}$[El.35,45,46,50,51,Sp.53,54,Cr.61,65, Pol.80,UC50,51,97]; $\text{Na}_4\text{Mo}<em>7\text{O}</em>{24}^{2-}$[LS.70]$\text{Na}_5\text{Mo}<em>7\text{O}</em>{24}^{1-}$[LS.70]; 7$\text{Mo}<em>7\text{O}</em>{24}^{3}$Na$_2$.H$_2$O[S.12]; K$\text{Mo}<em>7\text{O}</em>{24}^{3}$[S.94], $\text{H}_6\text{Mo}<em>7\text{O}</em>{24}^{3}$[S.94]; $\text{Mo}<em>7\text{O}</em>{24}^{3}$(C$<em>5$H$</em>{12}$N)$_6$6H$_2$O[S101]; (NH$_4$)$_2$H$_4$Mo$<em>7$O$</em>{24}^{3}$[S.95], (bip.H$_2$)$_2$($\text{H}_4\text{Mo}<em>7$O$</em>{24}^{3}$)[S.98]; (PYH)$_3$H$_3$Mo$<em>7$O$</em>{24}^{3}$[S.99]; para - [El.47]</td>
</tr>
</tbody>
</table>

(contd....)
<table>
<thead>
<tr>
<th>Degree of aggregation</th>
<th>Postulated Isopolymolybdate Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>( \text{Mo}<em>8\text{O}</em>{26}^{4-} )[El.50,51,Sp.53,54,51,UC.50,51,S.97]; Octa.[El.44,21]; 3BaO.8MoO(_3)[S.93]</td>
</tr>
<tr>
<td>&gt;8</td>
<td>( \text{Mo}<em>{10}\text{O}</em>{32}^{4-} )[IE.48]; ( \text{Mo}<em>{12}\text{O}</em>{41}^{10-} )[Dif.2-5], ( \text{Mo}<em>{24}\text{O}</em>{78}^{12-} )[Dif.2-5]; ( \text{Mo}<em>{12}\text{O}</em>{40}^{13-} )[El.25,26]; 5Na(_2).12MoO(_3)[LS.72]</td>
</tr>
</tbody>
</table>

Dif. = diffusion; Dia. = dialysis; El. = electrometric; Sp. = spectrophotometry; Cr. = cryoscopy; LS = light scattering; PC = paper chromatography; Pol. = polarography; IE = ion exchange; SE. = solvent extraction; UC = ultracentrifugation; S. = solids.
1.2 SCOPE OF THE WORK

The survey of the work described in section 1.1 and the number of postulated ions listed in Table 1 reveals the numerous attempts made to determine the nature of aggregated molybdate ions in solution. In spite of such an immense quantity of work there is not yet general agreement. The reasons for this have been mentioned in part in the previous section.

It seems that one of the major disadvantages in the studies of polymolybdates is that most of the methods give an indirect result since only a ratio, say, the number of hydrogen atoms bound per molybdenum atom of the ionic species, is obtained. The derivation of a single formula of an ion, from such a ratio is obviously not possible.

The methods which give a more direct result, in the sense that they give an indication of the number of ions present, are those which are based on the colligative properties of a solution (e.g., cryoscopcy, ebullioscopy, and vapour pressure lowering). Such methods, however, may suffer from the disadvantage that the polar character of the aqueous phase has an adverse effect on the results of the number of
molybdate ions obtained. Sillen [106] has discussed the drawbacks of the various methods employed to study polyions and commented on the reliability of the results. Because of uncertainty in the conclusions drawn from these results, Sillen suggested that in order to avoid unwarranted speculation from a single series of experiments it may be more desirable instead to discuss the polymerisations in terms of observation which indicate that a certain species is predominant.

This evidence suggests that there is a need to investigate those systems involving polyions in which the factors which may lead to disagreement are avoided. The present work was undertaken to re-investigate the isopoly-molybdate ions using the technique of two phase liquid ion-exchange. Because of the stoichiometric nature of the ion-exchange process, the counter ions are released in the solution in an amount equivalent to the charge of the exchanged molybdate ions, and from the amount of molybdenum lost from the aqueous solution, the ratio of metal to charge on the ion, which is defined as the R value, may be obtained.

In order to arrive at a particular formula of the extracted ion, measurements of the properties of the extracted
species were thought ot be necessary. For this reason, in the major part of the present work, these extractions have been carried out by means of an organic phase anion exchanger though some preliminary work with ion exchange resins was thought necessary. The presence of aggregated molybdate species in the non-polar organic phase provides the facility of studying the colligative properties of this solution with a minimum of possible errors. The property chosen for study was vapour pressure lowering since there was the advantage that measurements could be made on solutions at near to room temperature (25°C) by means of a thermoelectric method using thermistors. From such measurements the number of molybdenum atoms in an aggregated species was obtained. Combining this value with the R values, a more precise formula of the extracted ion was determined.

The work was further supplemented by infrared spectrophotometric measurements of the organic as well as the aqueous layers, and by the preparation of some solids. A combination of these various methods is considered to be essential for the investigation of these complicated polymolybdate systems.
I.3 METHODS OF STUDY AND THEIR DISCUSSION

I.3.a Ion Exchange Resins

Adams and Holmes made the first ion exchange resins in 1935 by the condensation of polyhydric phenols with formaldehyde, and on charging the resins with cations it was found that these would exchange with other cations in solution. They prepared anion exchange resins by the condensation of polyamines with formaldehyde and then treatment with alkali converted this material into free base form.

The first polymerisation resin based on cross linked polystyrene were made in 1944 by D'Alelio and were found to be chemically more stable than the phenol-formaldehyde resins. These resins are produced in the form of beads by polymerising a suspension of styrene monomer and a crosslinking agent such as divinylbenzene in water. After agitating the mixture at 85°C for about 6-8 hours, the polymerised material solidifies and transparent spherical beads are formed. Treatment with sulphuric acid or oleum results in the introduction of sulphonic groups, and the product is known as sulphonated crosslinked polystyrene. In the case of anion exchange resins, the introduction of basic groups is a two stage process.
(i) Chloromethyl groups are introduced into the polystyrene polymers by reaction with chloromethyl ether in the presence of a catalyst.

(ii) The chloromethylated product is then reacted with an amine. Primary and secondary amines give rise to weak base resins whilst tertiary amines form strong base resins.

Cation exchange resins contain acidic groups, e.g., -SC\(_3\)H, -COOH, or a phenolic, -OH, group. The acidic hydrogen in these groups may be replaced by another cation. The acidic group may be classified to give strongly acidic resins. Anion exchange resins contain either strongly basic quaternary groups, e.g. -N\(^+\)(CH\(_3\))\(_3\)OH\(^-\) or weakly basic groups, e.g. -NH\(_2\), -NH.CH\(_3\), or -N(CH\(_3\))\(_2\).

The crosslinked polystyrene is hydrophobic but attains a hydrophilic character after the introduction of functional groups. It swells in water and the degree of swelling depends upon the degree of crosslinking of the resin matrix which in turn, depends on the percentage of divinylbenzene (D.V.B.) added. The degree of swelling also depends upon the concentration and nature of the functional groups and on the nature of the exchangeable ion. For cation exchange resins, the mean pore size may be determined as a reciprocal nominal per cent D.V.B.
content of the resin. In the case of anion exchange resins, the additional crosslinking occurs during the introduction of functional groups and therefore the mean porosity is given by water regain values which are defined as the weight of water (g) in a fully swollen resin taken up by 1g of dry resin.

(i) Ion-exchange equilibria:

The ion exchange reaction may be represented in the following way:

\[ A + B^-(aq) \rightleftharpoons \bar{B} + A^+(aq) \]  \hspace{1cm} (i)

(where A and B = the exchangeable ions, and barred formulae refer to resin phase). The exchange is reversible and stoichiometric. The mechanism of ion exchange is explained by the concept of "film theory", according to which, in an instantaneously stirred solution, there is a thin film of immobile solution around a resin bead which is known as "Nernst layer". The ion in solution first diffuses into this thin layer and then into the resin bead (which may also be called a particle). The exchange reaction then takes place at the resin functional groups and the exchanged ion diffuses out of the particle and then through the film whence it enters the solution. In the case of strongly acidic or
strongly basic resins and for simple inorganic ions "film diffusion" is the rate controlling step whilst in the presence of high ionic concentrations or large ions, the rate controlling step is "particle diffusion". The diffusion process in turn is controlled by the concentration gradient.

One of the interesting properties of ion exchange resins is selectivity. In such an ion-exchange reaction as is described in equation (i) the position of equilibrium depends upon the relative proportions of $A$ and $B$ but it also depends on the nature of ions $A$, $B$, and on the resin employed. These observations show that the resin exhibits some sort of preference for one ion relative to another. This is known as the selectivity of an ion-exchange resin. The phenomenon of selectivity may be considered in an approximate way by treating the ionic equilibrium according to the law of mass action by which the equilibrium constant of the reaction (i), also known as the selectivity coefficient, $K_{cA}^B$, may be described by the equation:

$$K_{cA}^B = \frac{[B][A]}{[A][B]} \quad \text{............... (ii)}$$

Numerical values of $K_{cA}^B$ give a valuable practical measure of the preference of a resin for one ion over another. If $K_{cA}^B > 1$, 

then there is a selective sorption of B as compared with A. $K_{c_A}^B$ is only constant for a given set of conditions, and it varies appreciably with the ionic composition of the aqueous phase.

An improved treatment, which has been used to calculate the selectivity coefficient, regards the solutions as non-ideal and introduces thermodynamic activities, $a$. Thus,

$$K_{c_A}^B = \frac{[B][A]}{[A][B]} = \frac{\bar{a}_B a_A}{\bar{a}_A a_B} \cdot \frac{\gamma_A \gamma_B}{\gamma_B \gamma_A} \quad \ldots \ldots \ldots \quad (iii)$$

(where $\gamma =$ activity coefficient)

Ion-exchange resins may be regarded as concentrated solid electrolyte solution so that the Dorman equilibrium theory may be applied according to which the ionic activity products of an electrolyte inside and outside of non-permeable membrane are equal. Therefore for an anion $X^-$ and a cation $Y^-$,

$$\frac{\bar{a}_x a_y}{\bar{a}_y a_x} = \frac{\bar{a}_x a_y}{\bar{a}_y a_x}$$

If there are two anions $A^-$ and $B^-$, and one cation $Y^+$, then,

$$\frac{\bar{a}_A a_y}{\bar{a}_y a_A} = \frac{\bar{a}_A a_y}{\bar{a}_y a_A}$$

$$\frac{\bar{a}_B a_y}{\bar{a}_y a_B} = \frac{\bar{a}_B a_y}{\bar{a}_y a_B}$$

or

$$\bar{a}_B a_A = \bar{a}_A a_B$$
therefore, equation (iii) becomes,

$$K_c^B = \frac{\gamma_A \cdot \gamma_B}{\gamma_B \cdot \gamma_A}$$

This simplification was suggested by Baumann and Eichhorn[111].

An alternative theory of selectivity was presented by Gregor[112] who placed emphasis upon the strain energy of a resin which will lead to a resin preferring the smaller of a pair of ions. This factor would account for the order of affinity for alkali metal cations which falls into the order of decreasing size of the hydrated ions, but would not account for the high affinity of silver(I) and thallium(I) cations.

It seems, therefore, that allowance must be made both for activity coefficient and strain energy effects. A complete expression, derived from the Donnan theory is given by the following equation:

$$\ln K_c^B = \ln \left( \frac{\gamma_B}{\gamma_A} \right) - \left( \ln \frac{\gamma_B}{\gamma_A} \right) + \frac{\pi}{RT} \left( v_A - v_B \right) \ldots \ldots (v)$$

(where $\pi$ = the swelling pressure, and $v$ = partial molar volume.)
It has usually been observed that the values $K_{A}^{B}$ decrease markedly as the ionic fraction increases. Therefore a resin which is predominantly in the A form exhibits a greater affinity for ion A than does the same resin when it is in predominantly the B form. This has been explained by the possibility that the resin has a microheterogenous structure.

(ii) Effect of pH on ion exchange equilibrium.

With weakly acidic or weakly basic resins, pH plays a special role because hydrogen ions are considered to be held by a covalent bond. In solutions of low pH a weakly acidic resin is mostly in an undissociated form and cannot exchange cations whilst a weakly basic resin is in an undissociated form at high pH and does not exchange anions under these conditions. The strongly acidic or strongly basic resin remain dissociated at all pH values.

(iii) Applications of ion exchange resins

The earliest and one of the main uses of ion-exchange resins is in the softening and deionisation of water. Apart from this, they have been used exhaustively in analytical chemistry for the separation of elements. In this respect ion exchange has provided such a powerful tool that similar series elements, such as lanthanides and actinides, may
be separated from one another. This facility for separating ions is utilised frequently in the fabrication and re-fabrication of the fuel elements of nuclear reactors, and principally for the separation of uranium and plutonium. The separation of materials of biological importance, such as proteins and amino acids, may be mentioned among many of the uses of ion exchange resins.

Ion exchange resins have also provided a method to study equilibria in solutions of inorganic complex ions. The ionic composition of the solution of a complex may be studied by means of its ion-exchange behaviour. For example, it has been shown that zirconium sulphate solutions contain negligible concentrations of the zirconium(IV) cation because negligible amount of zirconium(IV) were adsorbed on cation exchange resins. However, in order to get a more detailed information, a more quantitative treatment of the data is needed.

The mean ionic charge of a complex may be determined by its adsorption on ion-exchange resins, since equivalent amounts of counter ions are released by the resin. This fact has been utilised by Salmon and Co-workers[88] to determine the atom to charge ratio, which is known as the R value, of oxyanion and polyanions in solution.
I.3.b Liquid-liquid Phase Ion Exchange

(i) Tertiary aliphatic amines and their salts

Aliphatic amines are a class of compounds which may be regarded as derived from ammonia by the successive replacement of one, two, or three hydrogen atoms by monovalent aliphatic groups giving rise to primary amines $RNH_2$, secondary amines $R_2NH$, and tertiary amines, $R_3N$. The closely related quaternary ammonium compounds $[R_4N]^+X^-$ are regarded as analogous to ammonium salts $NH_4^+X^-$. Primary, secondary, and tertiary amines may be separated from involatile quaternary salts by distillation in alkaline solution. A tertiary amine can be separated from primary and secondary amines by treatment of the mixture with acetic anhydride with which a tertiary amine does not react whilst the other two classes are converted to non-basic amides.

The alkylamines are all basic in aqueous solution and the order of basicity is secondary $\succ$ primary $\succ$ tertiary $\succ$ ammonia. The basicity of an amine derives from the capability of forming a coordinate link between the proton and the nitrogen atom through the unshared electrons on nitrogen. The enhanced
basicity of primary amines compared with ammonia is attributed to the electron repelling nature of the alkyl group which increases the electron density on nitrogen and thus the capability to attract a proton. The fall of basicity in the case of tertiary amines is attributed to the steric effects due to the accumulation of alkyl groups on the nitrogen atom which imposes a restriction on the molecule to attain a tetrahedral structure by the addition of a proton. That both the steric and inductive effects play significant roles in determining the basicity of amine is evident from the decrease of basicity with the increase of chain length and with the branching of alkyl groups attached to the nitrogen atom.

The accumulation of alkyl groups on the nitrogen atom may also cause interference in the interaction with water molecules to form a solvated ion and supplies an alternative explanation for the decrease of basicity of tertiary aliphatic amines. In aprotic solvents, such as chloroform and chlorobenzene, where solvation energies are expected to be small, trimethylamine is the strongest base of the methylated amines. This emphasizes the fact that the basicity of amines may vary in different solvents.
Because of the lower basicity of tertiary amines in water, they probably do not form highly ionised hydroxides of the type \([R_3NH]OH\). It was postulated by Moore and Winmill in 1912 \([113]\) that amines and water form an unstable hydrate in which hydrogen bonding occurs between nitrogen and oxygen,

\[
R_3N \quad \text{----} \quad H \quad O \quad H \quad \text{or} \quad R_3N^+ \quad H \quad \text{----} \quad O^- \quad H
\]

and only to a small extent does the nitrogen atom fully withdraw a proton from water to give the hydroxide \([R_3NH]OH\).

Quaternary ammonium hydroxides \([R_4N]OH\) are completely ionised and strongly basic since nitrogen is tetracovalent and cannot expand its covalency and there is no hydrogen available for hydrogen bonding so that the association of ions is very low. The configuration of nitrogen in quaternary ammonium compounds \(R_4NX\) is tetrahedral and the configuration of the cation is independent of the associated anion.

In the infrared absorption spectrum tertiary amines lack the strong, characteristic band of an N-H stretching vibration \([114]\). In quaternary ammonium salts, however, N-H stretching is evident at 2250-2700 cm\(^{-1}\), and there is also a band at 1400-1440 cm\(^{-1}\) which is characteristic of C-H bending in a methylene group adjacent to a nitrogen atom.
(ii) Liquid-liquid extraction by amines and their salts

The partition of a substance between two immiscible liquids has been well-known for many years. As long ago as 1842, the extraction of uranyl nitrate from aqueous solutions by ether was described[115]. During World War II, the advent of atomic energy programmes in many countries brought about the use of solvent extraction of inorganic substances on a large scale. The main use of solvent extraction remains in the separation of elements from each other and only recently had it been used for the investigation of the nature of metal ions in solution. The extractants used for this purpose include a variety of substances, such as ethers, esters, and acids, but amines have found much wider application in recent years.

The amines used as extractants include primary, secondary, and tertiary amines. These extractants are usually converted into quaternary ammonium salts before use and anionic aqueous phase species are then extracted by means of an ion-exchange process. Among the most widely used amines in recent years is trioctylamine \((C_8H_{17}N)_3N\) because of its low cost, low solubility in water, and high solubility in most of the organic solvents.
An organic, inert solvent, such as carbon tetrachloride, chloroform, benzene, xylene, or kerosene is used as a diluent for the amine. Sometimes, as may happen in the case of kerosene, an amine salt is not soluble and therefore a small amount of a long-chain alcohol is added to increase the solubility.

The extraction of simple acids from aqueous solution into an organic solution of an amine has been extensively studied and is usually followed by a study of the extraction of metal complexes from acidic solutions.

(iii) Extraction of acids by trioctylamine (TOA)

Anion extraction from aqueous phases by organic solutions of high molecular weight amine salts was first reported in 1948, by Smith and Page[116]. They used salts of methyldioctylamine with chloroform as diluent, and described extraction by amine salts as being analogous to sorption by ion-exchange resins. A study of the extraction of uranium from its ores was undertaken at the Oak Ridge National Laboratories, using various amines including tri-iso-octylamine, which was described as a mixture of isomers of \(C_8\) alkyls obtained from a commercial process[117]. Studies of amine
extraction were mainly centered around their extractive power for uranium and other nuclear fuels because of their high efficiency and the low cost. Since such extractions were carried out in acidic solutions, studies of the extraction of acids were also reported simultaneously. Afterwards, studies of the mechanism of the extraction of acids aroused great interest because it was found that the fundamental processes were not easy to explain.

Usually, the law of mass action is applied to the equilibrium of the two phases and chemical analysis can thus provide useful fundamental data about the values of the distribution coefficient. Various attempts have been made to solve the more difficult problem of the nature of the organic phase species and these include the use of E.M.F. titrations, cryoscopy, polarography, and spectrophotometry.

In 1956, Allen[118] attempted to provide a quantitative theoretical treatment for the extraction from aqueous solution of sulphuric acid by TOA in benzene solution, and took into consideration the earlier qualitative work. He found that the amine sulphate and bisulphate species remain in the organic phase and the data was interpreted on the basis of the polymerization of these salts. Cryoscopic studies have shown the
presence of dimers or trimers in TOA dissolved in benzene\textsuperscript{[119]}.

The earlier work was confined to the studies of dilute solution of acids\textsuperscript{[120]}. Bertocci and Rolandi\textsuperscript{[121]} have described the extraction from up to 10M nitric, hydrochloric, hydrofluoric, and sulphuric acids, using TOA dissolved in xylene. In the case of hydrochloric acid, the compound extracted into the aqueous layer was found to have a composition of HCl : TOA = 1:1, up to 3.5M aqueous phase acid concentration. At higher concentration, excess acid over and above a 1:1 ratio was extracted into the organic phase. The extraction of acid in an amount excessive to that required by the stoichiometry of the amine salt is a commonly observed phenomenon. In the case of hydrochloric and sulphuric acids, this has been observed at a high acid concentration (\(>3M\)) in the aqueous phase, whilst in the case of nitric acid excessive extraction is observed even at low acid concentration. The mechanism of this phenomenon is described in terms of the production of ions of the type HX\textsubscript{2}\textsuperscript{−} (where X = Cl, NO\textsubscript{3}, etc.,) which are formed in the organic layer, and is supported by infrared evidence\textsuperscript{[122,123]}.

\[
\begin{align*}
R_3\text{N(\text{org.})} + H^+(\text{aq.}) + X^-(\text{aq.}) & \rightarrow R_3\text{NHX(\text{org.})} \\
R_3\text{NHX(\text{org.})} + HX(\text{aq.}) & \rightarrow R_3\text{NH}_2HX(\text{org.})
\end{align*}
\]
The mechanism of the extraction of sulphuric acid, before it extracts excessively in the organic phase, is described in terms of the formation of sulphate and bisulphate salts of the amine.

\[ 2R_3N(\text{org.}) + 2H^+(\text{aq.}) + SO_4^{2-}(\text{aq.}) \rightleftharpoons (R_3NH)_2SO_4(\text{org.}) \]

\[ (R_3NH)_2SO_4(\text{org.}) + 2H^+(\text{aq.}) + SO_4^{2-}(\text{aq.}) \rightleftharpoons 2(R_3NH)\cdot HSO_4(\text{org.}) \]

It has been reported\cite{121} that at low acid concentration, sulphate ion was extracted in the organic phase as a mixture of sulphate and bisulphate species, then, with the increase of the concentration of acid, only as bisulphate ion. The formation of amine sulphate at concentrations lower than 0.019M, was also observed by Verstegen and Co-workers\cite{124} who used benzene as the diluent for TOA, and also calculated the heat and entropy of the formation of \((TOAH)_2SO_4\). Sato\cite{125}, using benzene as the diluent, reported the formation of amine sulphate as \((TOAH)_2SO_4\cdot 4\text{H}_2\text{O}\). As the acidity of the aqueous phase increased, the amine sulphate was gradually replaced by unhydrated amine bisulphate \((TOAH)\cdot HSO_4\). This scheme was supported by infrared studies of the organic phase.
(iv) **Extraction of metal complexes by amine salts**

The normal salt of an amine in an organic diluent exists as an ion pair and may be used to extract metal ions from the aqueous phase. It is expected that by analogy with the sorption by solid anion exchangers, information about the nature of metal complexes may be obtained from the extraction equilibria. A typical reaction may thus be represented in the following way:

\[ zR_3NHX_(org.) + MeL_n^{2-}_(aq.) \rightleftharpoons (R_3NH)_2MeL_n_(org.) + zX^-(aq.) \]

The amine salt may interact with a metal salt either by an anion exchange mechanism or by an addition mechanism. Instances of both types of reaction have been reported. In the case of extraction by the anion exchange mechanism, the stability of the extracted compound depends upon the stability of the bond between the cation and anion, which, in turn, depends on factors such as ionisation potential of the amine salt and the electron affinity of the anions, whilst the charge and size of the cation and anion also decides to a certain extent the stability of the extracted compound[126].
(v) **Relationship between the structure of amine and the extracted salt**

It is quite interesting and of great practical importance to find some sort of correlation between the structure of the amine and the nature of the salt formed after extraction. Some work has been done on this aspect\[126\], but still it is difficult to predict definitely the nature of the extracted salt and the extractive power of an amine for a certain solute.

Many factors are involved in deciding the nature of the amine salt formed. One of the most important factors is the basicity of amine which has been described briefly in section I.3.b(i). When a strong acid and a strong base (amine) interact, a complete transfer of protons takes place from acid to amine so that a compound $\text{RNH}^+-\text{A}^-$ is formed which will be polar in nature. When either the amine or the acid is weak, which means that the electron donating power of nitrogen atom is weak, or that the proton liberating power of the acid is low, then the bond formed between the cation and anion of the amine salt will be through hydrogen bonding, i.e. without a complete transfer of a proton to nitrogen. Such a compound will be non-ionic in character.
Evidence for intramolecular hydrogen bonding may be obtained by infrared spectroscopy, conductivity, dielectric constant measurements. The number of possible hydrogen bonds increases in the order primary > secondary > tertiary. Thus it has been shown that the stability constant of the compounds of acetic acid is higher with dibutylamine than the corresponding compound of tertiary amine.
I.3.c Thermoelectric methods for the determination of the lowering of vapour pressure

The saturated vapour pressure of a solution is lower than the saturated vapour pressure of the pure solvent. This lowering of vapour pressure is a useful parameter since it is proportional to the number of solute molecules present in the solution (Raoult's law).

A direct measurement of the vapour pressure lowering afford difficulty because it is usually a very small quantity. However, a thermoelectric method to measure this quantity is finding increasing application.

Hill[127] reported a thermal method for the measurement of vapour pressure lowering of aqueous solutions which was developed from an investigation of the increase of heat generation derived from nitrogen stimulation of isolated muscles. A multijunction thermopile which was covered on both the sides with filter paper was used for temperature detection. One of the sides of the thermopile was moistened with the solvent or a solution of known composition whilst the other was moistened with a solution of unknown composition. The whole system was thermostatted and after fifteen minutes a
steady temperature difference between the two sides of thermopile was attained.

Baldes and Johnson\textsuperscript{[128,129]} replaced the thermopile by a thermocouple which was in the form of fine wire loops, one of which held a drop of a standard solution whilst the other, a drop of the solution of unknown composition. The thermocouple assembly was thermostatted and was found to be much more efficient in measuring the difference in temperature than the former method. The fine wire loops used in Baldes and Johnson's apparatus could not be used for organic liquids which have a lower surface tension than water. The apparatus used by Taylor and Hall\textsuperscript{[130]} had platinum foil cups in which organic solutions could be used, but it was not suitable for aqueous solutions.

The thermopiles and thermocouples need highly sensitive galvanometers and were not convenient for routine use. The use of thermistors in the place of thermopiles or thermocouples was reported in 1951 by Brady and Co-workers\textsuperscript{[131]} and these have the advantage that they do not need highly sensitive galvanometers since small temperature changes give rise to proportionally high resistance differences.
The apparatus used by Muller and Stolten[132] also employed thermistors and could be used for aqueous as well as organic solutions. The two thermistors were in the form of beads which were dipped in the standard and test solutions which were contained in stainless steel cups. The difference in the temperature between the thermistors and consequently the difference in their resistance was measured by means of a Wheatstone bridge.

Muller and Stolten's apparatus required about 30 minutes before the stainless steel cup and the solutions therein reached a maximum temperature. A modification of this apparatus[133] enabled the solutions to reach a maximum temperature in 3 minutes. In the new apparatus the thermistors were covered by platinum wire coils in which the solvent could be readily placed by means of elongated medicinal droppers inserted into the chamber. This method was found to have a relative error of less than 2%. In another modification of the Muller-Stolten apparatus[134] the chamber was evacuated to remove permanent gases and hence to remove gas phase diffusion barriers. Furthermore, the solvent and solution were continuously stirred to maximise the composition and thermal homogeneties. Different methods for calibrating the instrument are reported[135].
An apparatus for measuring vapour pressure lowering by the thermoelectric method is commercially available and is known as the Vapour Pressure Osmometer (Mechrolab model 301A). The construction of this apparatus is described in section II.6.a.

A systematic study of the thermodynamic properties of aqueous solutions using the Vapour Pressure Osmometer was started by Burge [136]. With the assumption that the change in the resistance obtained by the Vapour Pressure Osmometer is proportional to the difference of chemical potential ($\Delta \mu$) between the pure solvent and that of the solvent in the solution, he calculated the molar osmotic coefficients, $\bar{\phi}$, by means of the following equation:

$$\Delta \mu = \frac{vW\bar{\phi}RTm_2}{1000}$$

(where $v$ = total number of ions given by one mole of electrolyte, $W$ = molecular weight of the solvent, and $m_2$ = concentration of the solute.)

Burge found that the osmotic coefficients of a wide variety of electrolytes obtained by means of the Vapour Pressure Osmometer were accurate and agreed with other published
values. Although the precision of this method was found to be fairly low, the speed and the convenience of the measurements were useful for many studies.

For the organic solvents, chloroform, benzene, and ethanol, Kume and Kobayashi have determined the calibration constant $K$ using known solutes. They observed that the values of change in resistance ($\Delta T$) depend on time. Determinations of the molecular weights of polybutadienes were obtained with a 10% error for benzene and a 3% error for chloroform. The errors were obtained with a 95% confidence limit. The authors state that good reliability is difficult to obtain from the Vapour Pressure Osmometer for the measurement of the molecular weights greater than 10,000.

Tridodecylammonium salts with hydrochloric acid and nitric acid were prepared by Scibona, Basol, and Danesi and the aggregation of these salts in benzene was studied using the Vapour Pressure Osmometer. The degree of aggregation found experimentally agreed well with some theoretical considerations and their experimental data predicts a monomer-dimer equilibrium for the chloride salts and a dimer-trimer equilibrium for the nitrate salts.
I.3.d Infrared Spectrophotometry

(i) The origin of infrared spectra

Absorption in the infrared region of the electromagnetic spectrum often results from the interaction of the radiation and the vibrations of the constituent atoms in a molecule. Vibrational spectra may be observed between about 10,000 and 1 cm\(^{-1}\) although the range 4000-400 cm\(^{-1}\) is more usually used by inorganic chemists. Allowing for translational and rotational degrees of freedom a non-linear molecule has 3N-6, and a linear molecule 3N-5 (where N = number of atoms) degrees of vibrational freedom. Vibrations which are infrared active are those which involve a change in dipole moment during the particular vibration. The positions of absorption are proportional to the force constants of particular bonds. Thus, the vibration associated with the stretching of the bond in nitrogen molecules will fall at a higher energy than that of oxygen molecules since the force constant of the former molecule is the greater. For the molybdate system, polymerisation would be expected to produce a reduction in the bond order of some of the molybdenum-oxygen linkages and thus some reduction in the frequency of absorption may be
observed whilst those bonds not concerned in the polymerisation process may produce absorptions at similar positions to those observed for the simple molybdate ion, $\text{MoO}_4^{2-}$.

The vibrational modes of molecules frequently occur as doubly or triply degenerate absorptions. The number of absorptions to be expected from a molecule or ion is governed by the overall symmetry of that group. For instance, the nine vibrational modes of a tetrahedral, molybdate ion, $\text{MoO}_4^{2-}$, would give rise to one non-degenerate, one doubly-degenerate, and two triply-degenerate absorptions in the infrared spectrum. A reduction of symmetry in this ion would partially or totally lift these degeneracies.

(ii) Some experimental considerations

Solid, liquid, or gaseous samples may be studied by infrared spectroscopy. Solids may be filmed, melted, and dispersed either in viscous liquids or in an inorganic halide disc or pellet. Mulling is a common practice and a refined mineral oil, Nujol, is often used. This mixture of aliphatic hydrocarbons absorbs in the regions associated with the vibrations of C-H bonds and therefore a fully-chlorinated hydrocarbon is a useful mulling agent for the study of these
regions. Spectra may be obtained from thin films of pure liquids and from their solutions. The compensation for strong solvent absorptions may cause difficulties but intermolecular solute interactions may be reduced in this way. Aqueous solutions are particularly difficult to handle because of the general, high absorption of water. Water also attacks some of the materials commonly employed as cell windows. However, silver(I) chloride, calcium fluoride, and barium fluoride are not attacked by water and are useful window materials. The attenuation of the reference beam partially reduces the absorption of water. Deuterium oxide, D₂O, is more transparent to infrared radiation than water. For aqueous solutions, D₂O and H₂O may sometimes form a useful pair of complementary solvents.

In the present work, infrared investigation has proved to be a useful, complementary technique. It was not possible, however, to obtain conclusive, structural evidence as the symmetry of the absorbing ions is not known and the spectra are, in general, extremely complex.
SECTION II

PART A. EXPERIMENTAL
(i) **Sodium molybdate**

Sodium molybdate, $\text{Na}_2\text{MoO}_4\cdot2\text{H}_2\text{O}$, which used as the source of molybdic acid, was of 'Analar' quality (B.D.H.).

(ii) **Tri-n-octylamine (abbreviated here to TOA)**.

TOA (Koch-Light Ltd.) was repeatedly shaken with equal volumes of water before use. The amine layer was carefully removed and the titration of aliquots against standard perchloric acid in non-aqueous media indicated 89% purity. In later stages, when high purity amine was required for the vapour pressure lowering measurements, a product from Eastman Kodak was obtained which had approximately 100% purity and a molecular weight of 352.4 (calc. M.Wt. for $\text{C}_{24}\text{H}_{51}\text{N} = 353.65$).

(iii) **Chloroform**

Chloroform was used as the diluent for TOA. Laboratory grade chloroform was shaken five times with equal volumes of water to remove alcoholic impurities. Freshly washed chloroform was used to prepare the solutions of TOA.
(iv) Other reagents

All the reagents used for the preparation of the molybdenum solutions, as well as for the analyses, were of analytical grade wherever possible.

All the original solutions were made up in deionised water obtained by passing distilled water through a mixed-bed ion-exchange column.

II.2. PREPARATION OF MOLYBDIC ACID SOLUTIONS

Solutions of molybdic acid were prepared from sodium molybdate by cation exchange. About 250g. of ZeoKarb 225, a cation exchange resin, was washed with water until the supernatant liquid was clear. It was then treated with mild chromic acid solution to remove any reducing matter and then with water to produce shining yellow beads. These were transferred to an ion-exchange column, fitted with a porous disc, and backwashed with water for several hours to remove the smaller resin particles. The column was now ready to be used for the preparation of molybdic acid. First, all the
resin was converted to the hydrogen form by passing 2M hydroch­
chloric acid through the column until the effluent was acidic and free from ferric ions. A further 500ml 2M hydrochloric acid was then passed through the column so that the resin was converted completely into the hydrogen form. The column was then washed with deionised water until the effluent was free from chloride ions. A solution of sodium molybdate (72-144g/l) was then passed through the column to produce a molybdic acid solution through the exchange of hydrogen for sodium ions. The effluent solution was collected in a clean conical flask at pH = 1.5. When all the hydrogen ions of the resin were exchanged the effluent becomes neutral or slightly alkaline to pH paper, at which point, the collecting vessel was removed. The column was then washed free of sodium molybdate with deionised water. The resin was now in the sodium form and could be re-used for the preparation of molybdic acid solutions once it was reconverted to the hydrogen form.

The molybdic acid solution collected in this way had a pH = 1.45 and solutions of any other pH were made by adding hydrochloric acid or sodium hydroxide. The solution was usually colourless or had a very faint bluish colouration.
On keeping it for a long time, the solution acquires a faint yellow colour, possibly by reaction with silica of the glass vessel and therefore for each experiment fresh solutions were made. The molybdic acid solutions were stored in the dark since they are prone to reduction by sunlight.

II.3. EXPERIMENTS WITH ION-EXCHANGE RESINS

The experiments with ion-exchange resins were carried out using seven laboratory-prepared anion exchange resins.

The water regain values of these resins were checked by the method of Pepper and Co-workers [139]. About 1g. conditioned and air-dried resin in the chloride form was allowed to swell in water for about 24 hours. A clean glass tube (4cm x 1cm dia.) with a porous disc at the bottom was dried in an oven at 95°C and then weighed after allowing it to cool in a desiccator (weight A). The swollen resin was then transferred to the glass tube and the excess water was removed. The tube was then fitted into a centrifuge tube of appropriate size and covered with a rubber cap to prevent evaporation.
It was centrifuged for 1 hour at 2,000 rotations per minute, after which the tube was weighed (weight B). The tube was then dried to constant weight at 95°C (weight C). The water regain value was then calculated in the following way:

$$\text{water regain} = \frac{\text{weight of water in the resin (g)}}{\text{weight of dry resin (g)}}$$

$$= \frac{B-C}{C-A}$$

II.3.a. **Determination of R Value**

Batch experiments were carried out by equilibrating ion-exchange resins with molybdic acid solutions in order to determine R values, i.e., the number of molybdenum atoms per unit charge of a molybdate ion. About 0.5g of the chloride form of a laboratory-prepared anion exchange resin was weighed into a conical flask and a known volume of molybdic acid (100-150ml) of the required pH was added. The flasks were kept in the dark for 20-30 days which time was found to be sufficient for the solutions to reach equilibrium with the resin[48]. Each experiment was performed in duplicate, but the time of equilibrium for two identical flasks varied by a few days so that a consistent analysis of the two flasks
could be used to indicate that sufficient time was allowed for equilibration.

When the solutions reached equilibrium the pH of a small amount of solution was measured using a Pye "Dynacap" pH meter fitted with a glass electrode and a saturated calomel electrode. Subsequently, the total volume of the solution was poured into a 250ml volumetric flask. The solution remaining on the resin beads was removed by filtration and the resin was washed quickly with water one or two times and the filtrate was quantitatively transferred to the volumetric flask. The solution in the volumetric flask was then made up to the mark. Aliquots from it were taken for analysis of molybdenum and chloride ion from which R values for each solution were determined in the following way:-

\[
R = \frac{\text{g atoms of molybdenum entering the resin}}{\text{g equivalents chloride released by resin}}
\]
II.4. EXPERIMENTS WITH TOA AND TOAH\textunderscore Cl

II.4.a. Preparation of Aqueous Layers

The aqueous layer was a solution of molybdic acid which was prepared as described in Section II.2.

II.4.b. Preparation of Organic Layers

The organic layer was either a solution of TOA or TOAH\textunderscore Cl in chloroform. TOA was washed with water, separated, and filtered to obtain a clear liquid. Approximately weighed quantities of the amine were dissolved in washed chloroform and the solution was made up to a certain volume. Aliquots from this solution were withdrawn for titration against standard perchloric acid solution in glacial acetic acid in order to determine the exact concentration of amine (section II.5.c.).

For the experiments that involved the exchange of molybdate ions with chloride ions and the subsequent determination of R values, the amine was first converted to the hydrochloride form (TOAH\textunderscore Cl). TOA solutions in chloroform were shaken with 2M hydrochloric acid in the volume ratio of 1:2 for five minutes in a separatory funnel. On allowing to
stand for sometime, the two layers separated clearly and the lower organic layer was carefully withdrawn after removing drops of water from the stem of the funnel by means of a piece of filter paper.

II.4.c. **Equilibration of the Aqueous and Organic Layers**

Aliquots from the aqueous layer (molybdic acid) and the organic layer (TOA or TOAH.C1 solution) in the ratio of 2:1 by volume was pipetted into a 250ml "Quickfit" conical flask provided with polythene stopper which was fastened tightly by means of a copper wire. The stoppered flask was placed in a trolley-type shaker which contained a specially made frame to hold ten flasks at a time. For solutions of molybdic acid of pH near 1, it was found that equilibrium reached after shaking for 20 hours, but for higher pH solutions the time was less than that, and for solutions of pH 4.0, the equilibration time was found to be only 4 hours. In each experiment two flasks contained similar solutions so that the reproducibility of the results could be checked.

After the equilibrium between the two layers was reached, the flasks were removed from the shaker and stored overnight. The two layers separated quite clearly and were
removed from each other by pouring the contents of the flask in a separatory funnel and collecting the organic and aqueous layers in dry glass stoppered conical flasks.

II.5. ANALYSIS OF THE SOLUTIONS

The aqueous layer was analysed for molybdenum and chloride ion whilst the organic layer was analysed for TOA and chloride ions. In the case of the extractions involving sulphuric acid and oxalic acid, the anions of these acids were analysed in the aqueous phase only.

II.5.a. Analysis of Molybdenum

Molybdenum was analysed volumetrically by the Jones reductor method[140]. A Jones reductor column was prepared by placing about 500g amalgamated zinc shots in a glass column fitted with a stopcock in a long stem. Some glass wool and a perforated disc was placed beneath the zinc shots to prevent the shots flowing out of the column. The stem of the column was fitted with a fitter flask by means of a tightly fitting rubber bung. About 50ml 2N sulphuric acid solution was poured
on top of the zinc amalgam and this solution was removed by suction until the zinc shots were just covered. The column was further washed with 50ml 2N sulphuric acid so that it became sufficiently activated for reduction of the molybdenum solution. Care was taken to keep the zinc shots under solution to prevent the oxidation of zinc by the atmosphere.

In order to analyse molybdenum, an aliquot of the aqueous solution was heated to fuming with 15ml 1M sulphuric acid solution in order to remove any chloride ion. The solution was then allowed to cool to room temperature. Meanwhile, a solution of excess ferric ion in the form of ammonium ferric sulphate containing a small quantity of syrupy phosphoric acid, which decolourised the ammonium ferric sulphate and also decreased the redox potential of ferric-ferrous system, was prepared. The filter flask, containing this solution, was then fitted with an activated Jones reductor, care being taken that the stem of the column remained beneath the surface of the solution. The cooled molybdenum solution was then poured on the top of the zinc bed, the stopcock was opened and the solution was drawn down the activated zinc bed when the colourless molybdenum(VI) solution was reduced to a
green molybdenum(III) solution. The reduced solution ran into the ammonium ferric sulphate solution where it reduced an equivalent amount of ferric to ferrous ions. The column was repeatedly washed with 1M sulphuric acid and then with distilled water so that all of the molybdenum was quantitatively reduced and collected in the ferric solution. The filter flask was detached from the column and the washings from the stem of the column were collected in the same flask. The contents of the filter flask were then titrated against a standard solution of potassium permanganate. This titre was used to calculate the molybdenum concentration.

II.5.b. Analysis of Chloride Ion

Chloride ion was analysed volumetrically by the Volhard method using nitrobenzene\textsuperscript{[140]}. A suitable aliquot of the aqueous layer was taken and the same volume of 6M nitric acid was added followed by a known volume of excess standard silver nitrate solution. A small quantity of nitrobenzene was then added and the flask was shaken so that the nitrobenzene formed a layer around the silver chloride precipitate. The amount of free silver nitrate was then titrated against
standard ammonium thiocyanate solution using a ferric indicator (consisting of 40% acidic ammonium ferric sulphate solution) until a faint brown colouration was observed.

For the analysis of chloride ion in the organic layer, a suitable aliquot was first diluted with 75% ethyl alcohol and then treated as described above.

II.5.c. Analysis of TOA

The strength of amine in TOA solutions in chloroform was determined by titrating the aliquots of this solution against standard perchloric acid solution in glacial acetic acid.

A standard solution of perchloric acid was prepared by dissolving perchloric acid (70%) in glacial acetic acid and adding enough acetic anhydride in order to convert the water present in it into acetic acid. The solution was kept for 24 hours before using it, and was standardised by a potassium hydrogen phthalate solution, also made in glacial acetic acid, using crystal violet as indicator.

A TOA solution in chloroform was first diluted with a neutral acetic acid solution (green colour with crystal violet) and then titrated against standard perchloric acid solution in
the presence of crystal violet as indicator until a permanent green colouration was obtained.

II.5.d. Analysis of Sulphate and Oxalate

Sulphate was analysed by precipitation as barium sulphate with barium chloride in a hot solution.

The solution of oxalate was mixed with 1M sulphuric acid and heated to 50-60°C. It was then titrated whilst still hot against standard potassium permanganate.

II.6. PHYSICAL MEASUREMENTS

II.6.a. Use of Vapour Pressure Osmometer

The Vapour Pressure Osmometer consists essentially of two components (Figure 1). One of these is a solvent chamber which remains saturated with solvent vapour and is thermostatted at a particular temperature (25°C in the present work) at an accuracy of ± 0.001°C. The second contains the necessary electronic circuits and controls for the Wheatstone bridge device.
Fig. 1

VAPOUR PRESSURE OSMOMETER

- SYRINGES 1-6
- GALVANOMETER
- DECADE RESISTANCE DIAL
- ΔT-T SWITCH
- BRIDGE ON/OFF
- BALANCE CONTROL
- POTENTIOMETER DIAL
- THERMOSAT ON/OFF
- ZERO CONTROL
- NULL DETECTOR ON/OFF
- THERMISTOR BEADS
- MIRROR
- SOLVENT CUP
A probe containing two matched thermistor beads which are used as the temperature-sensing elements is mounted on the top of the solvent chamber. One of the thermistor beads holds a drop of the solvent whilst the other holds a drop of the solution. Since the saturated vapour pressure of the solution is lower, solvent vapour condenses into it and thus produces a temperature increase. Because of the difference in temperature of the two thermistor beads a difference in their resistance is recorded by a Wheatstone bridge device which is maintained in the second portion of the apparatus.

Apart from the thermistor probe, the chamber holds six guarded holes through which six syringes, fitted with needles, pass into the chamber and are held in a constant position. These syringes may be filled with the solution or the solvent. One of the syringes supplies the solvent thermistor bead whilst the remaining five supply the sample bead. The accuracy of this instrument is reported by the manufacturers[141] as greater than 95% for substances of molecular weights between 10,000-12,000. The reproducibility of repetitive readings was said to be better than 1%.
In order to use the Vapour Pressure Osmometer, the cup in the solvent chamber was filled with chloroform and the chamber was closed. The instrument was thermostatted overnight to ensure that the solvent chamber became saturated with the solvent vapour and the instrument attained thermal equilibrium. The instrument was then calibrated. A series of benzil solutions in chloroform were prepared at various solute concentrations. The chloroform was previously shaken five times with water to remove alcoholic impurities. Four of the syringes were filled with benzil solutions and were placed in the solvent chamber in order of increasing concentration (syringes 3-6 in Figure 1). Syringes 1 and 2 were filled with solvent. After positioning the syringes, about 10 minutes were allowed before the thermal stability of the instrument was checked. This was done by putting the ΔT-T switch to the T position. The galvanometer zero was then set by pressing and holding the button zero whilst centering the needle with the zero control knob. The zero button was released and the needle was again set to zero by rotating the potentiometer knob T. The instrument was then left for 30 minutes. If the drifting of the needle was less than 8 small divisions of the
galvanometer scale in 30 minutes then the instrument was considered to have acquired thermal equilibrium.

Before carrying out the measurements, the Wheatstone bridge circuit must be balanced. This was done by placing solvent drops on each thermistor bead by means of syringes 1 and 2. The syringe was lowered into the solvent chamber and the piston was screwed slowly in a clockwise direction so that a drop of the liquid adhered to the thermistor bead. This operation could be observed by means of the mirror (see Figure 1). When both the beads hold a solvent drop, the $\Delta T$ control was turned to the $\Delta T$ position. After making sure that the decade resistance dials were at zero, the galvanometer needle was set to zero, first by the zero control and then by the balance control. After 2 or 3 minutes, the needle was again set to zero until no further adjustment was necessary. The bridge was now balanced.

The measurements on the solutions were then carried out by rinsing and replacing the drop on the sample bead by the most dilute of the solutions. Because of the lower vapour pressure above the solution drop, the solvent condenses into it which leads to a rise of temperature which resulted in a
change in the resistance of the thermistors and hence the Wheatstone bridge becomes unbalanced. The zero of the galvanometer was checked after one minute and the bridge was rebalanced by rotating the decade resistance dials (ΔT). Such values of ΔT were obtained after 2, 3, 4, and 5 minutes. It was found that the ΔT readings after 4 minutes were quite reproducible and in all the subsequent work the values of ΔT refer to the reading after 4 minutes. A duplicate reading was taken by replacing the drop on the sample bead with a fresh solution drop, and the two readings were found to be within 0.1 ΔT. The readings for the next solution may be taken by replacing the solution drop with a drop of the new solution and repeating the whole procedure.

A calibration curve was constructed from ΔT measurements and the corresponding solute concentrations. In order to carry out the measurements on solutions of unknown molecular weight or concentrations, the next run was set up by filling the solution syringes with the unknown solutions, which, in this work, were the extracted organic layers containing TOA salts of molybdic, sulphuric, and oxalic acids, dissolved in chloroform.
II.6.b. **Infrared Spectrophotometry**

(i) **Organic layer:**

Infrared absorption spectra of the organic layer containing extracted molybdate species were recorded on a Unicam SP200 spectrophotometer. A few drops of the organic layer were taken in a liquid cell having silver chloride windows. The path length between the two silver chloride plates was .013 mm for 0.25M TOA solutions, but varied according to the concentration of TOA in the organic layer.

(ii) **Aqueous layer**

The infrared spectra of aqueous layer cannot be obtained because of the strong absorption by water. Therefore, sodium molybdate was dissolved in deuterium oxide (D₂O) and the pH of the solution was adjusted between 1 and 7 by adding concentrated sulphuric acid. The pH of these solutions was recorded on a Pye "Dynacap" pH meter, using a glass electrode and was corrected for D₂O by the following relationship[142]:

\[
pL = (\text{meter reading}) + 0.3314n + 0.0766n^2
\]

(where L = isotopically different hydrogen ion, and 
n = fraction of deuterium atoms present).
The spectra of the solutions were recorded on a Unicam SP 200 spectrophotometer as well as on a Grubb-Parsons spectromaster in order to verify the absorption peaks in the region 8 to 15μ. The windows of the cell were made of silver chloride and the path length was 0.025mm. An attenuator made of wire mesh was placed in the reference beam to cut down the absorption by D₂O to about 20%.
SECTION II

PART B. RESULTS
11.7. EXPERIMENTS WITH ION-EXCHANGE RESINS

In the early stages of the present work, experiments involving the exchange of molybdate ions with ion exchange resins of varying water regain values were carried out in order to study the effect of crosslinking of the resin on the exchange of polymolybdate ions of different R values. These experiments were similar to those of Cooper and Salmon [48] who found that highly crosslinked resins prevent the entry of large ions and in this way obtained an ionic sieve separation of R = 2 and R = 5 ions.

In the present work, seven laboratory prepared resins of water regain values ranging from 1 to 11 were used. Molybdic acid solutions (0.21M-0.25M Mo) were prepared from AnalaR sodium molybdate by ion exchange (see section II.2.). The pH of a fresh solution was usually 1.4-1.5, and from such stock solutions addition of hydrochloric acid or sodium hydroxide produced solutions of a required pH. Four experiments were carried out using molybdic acid solutions of pH 1.26 to 2.61. All the experiments were carried out in the batch form, i.e. a certain amount of resin was equilibrated in molybdic acid solutions.
The results of this series of experiments are shown in Table IIA-IID and in Figure 2. It may be seen that the ionic sieve effect for the $R = 2.0$ ion is not well defined in the region of low water regain values. The tendency to reach $R = 5.0$ may be observed in the solutions of low pH and this occurs in resins of water regain values greater than 3.0. With the increase of initial pH, the maximum $R$ value decreases. This shows that the ion of $R = 5.0$ becomes less abundant as the pH increases and the value of $R$ moves towards 2.0. The solution of low acidity had a pH 2.61 and still contained some $R = 5.0$, and therefore at higher value of water regain, a constant value of $R = 3.0$ was observed.

These experiments have confirmed, within their limits, the work of Cooper and Salmon[48]. They found that there were two stages of condensation of molybdate ions, one of which was represented by $R = 2.0$, and the other by $R = 5.0$. The $R = 2.0$ ion could not be observed in the present series of experiments because of the lack of a sufficient number of low water regain value resins, but the $R = 5.0$ ions was observed quite clearly.

No further conclusion may be derived from ion exchange resin work since the species sorbed on the resin cannot be
studied by other physical methods. Further work was thus carried out using a liquid anion exchanger, TOA.H.Cl, which is a salt of a tertiary base, dissolved in chloroform. It dissociates completely in an acidic environment and the chloride ion is exchanged with ionic species in the aqueous solution when the two solutions are agitated vigorously. The organic layer thus obtained provides the facility of carrying out physical measurements on the extracted species in an inert media.
Fig. 2

VARIATION OF R VALUE WITH WATER REGAIN
TABLE IIA

Variation of $R$ Value with Water Regain

Initial pH of the solution $= 1.26$
150ml molybdic acid (0.248M Mo) equilibrated with ~0.5g resin.
Equilibrium time $= 38-39$ days.

<table>
<thead>
<tr>
<th>Water regain</th>
<th>Final pH</th>
<th>Equilibrium concentration Mo(aq.), Mole/l</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
<td>1.26</td>
<td>0.138</td>
<td>2.15</td>
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<tr>
<td>1.01</td>
<td>1.22</td>
<td>0.138</td>
<td>1.93</td>
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<td>2.36</td>
<td>1.24</td>
<td>0.114</td>
<td>4.72</td>
</tr>
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<td>2.36</td>
<td>1.23</td>
<td>0.114</td>
<td>4.61</td>
</tr>
<tr>
<td>3.20</td>
<td>-</td>
<td>0.115</td>
<td>4.88</td>
</tr>
<tr>
<td>3.20</td>
<td>1.23</td>
<td>0.114</td>
<td>5.19</td>
</tr>
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<td>1.19</td>
<td>0.112</td>
<td>4.89</td>
</tr>
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<td>1.22</td>
<td>0.110</td>
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<td>0.112</td>
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</tr>
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<td>5.00</td>
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<td>0.111</td>
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<td>11.05</td>
<td>1.23</td>
<td>0.109</td>
<td>5.37</td>
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</table>
## TABLE IIB

**Variation of R Value with Water Regain**

*Initial pH of the solution = 1.47*

100ml molybdic acid (0.213M Mo) equilibrated with ~0.5g resin.

*Equilibrium time = 31-32 days.*

<table>
<thead>
<tr>
<th>Water regain</th>
<th>Final pH</th>
<th>Equilibrium concentration Mo(aq.), Mole/l</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
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<td>0.071</td>
<td>2.25</td>
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<td>0.043</td>
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<td>0.98</td>
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<td>1.06</td>
<td>0.044</td>
<td>4.68</td>
</tr>
<tr>
<td>4.93</td>
<td>0.89</td>
<td>0.044</td>
<td>4.73</td>
</tr>
<tr>
<td>6.62</td>
<td>1.05</td>
<td>0.040</td>
<td>5.15</td>
</tr>
<tr>
<td>6.62</td>
<td>0.86</td>
<td>0.044</td>
<td>5.15</td>
</tr>
<tr>
<td>11.05</td>
<td>0.84</td>
<td>0.041</td>
<td>5.00</td>
</tr>
<tr>
<td>11.05</td>
<td>0.83</td>
<td>0.041</td>
<td>5.00</td>
</tr>
</tbody>
</table>
TABLE IIC

Variation of R Value with Water Regain

Initial pH of the solution = 1.98
100ml molybdic acid (0.262M Mo) equilibrated with ~0.5g resin.
Equilibrium time = 25-39 days.

<table>
<thead>
<tr>
<th>Water regain</th>
<th>Final pH</th>
<th>Equilibrium concentration Mo(aq.), Mole/l</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
<td>1.95</td>
<td>0.147</td>
<td>2.17</td>
</tr>
<tr>
<td>1.01</td>
<td>1.98</td>
<td>0.144</td>
<td>1.08</td>
</tr>
<tr>
<td>2.36</td>
<td>1.96</td>
<td>0.129</td>
<td>3.75</td>
</tr>
<tr>
<td>2.36</td>
<td>1.98</td>
<td>0.130</td>
<td>3.79</td>
</tr>
<tr>
<td>3.20</td>
<td>1.94</td>
<td>0.130</td>
<td>4.21</td>
</tr>
<tr>
<td>3.20</td>
<td>1.98</td>
<td>0.130</td>
<td>4.50</td>
</tr>
<tr>
<td>4.29</td>
<td>1.92</td>
<td>0.125</td>
<td>4.08</td>
</tr>
<tr>
<td>4.93</td>
<td>1.95</td>
<td>0.113</td>
<td>4.27</td>
</tr>
<tr>
<td>4.93</td>
<td>1.98</td>
<td>0.125</td>
<td>4.52</td>
</tr>
<tr>
<td>6.62</td>
<td>1.92</td>
<td>0.125</td>
<td>4.81</td>
</tr>
<tr>
<td>6.62</td>
<td>1.98</td>
<td>0.125</td>
<td>4.74</td>
</tr>
<tr>
<td>11.05</td>
<td>1.92</td>
<td>0.123</td>
<td>4.88</td>
</tr>
<tr>
<td>11.05</td>
<td>1.96</td>
<td>0.123</td>
<td>4.66</td>
</tr>
</tbody>
</table>
**TABLE IID**

**Variation of R Value with Water Regain**

Initial pH of the solution = 2.61

150ml molybdic acid (0.254M Mo) equilibrated with ~0.5g resin.

Equilibrium time = 25-26 days.

<table>
<thead>
<tr>
<th>Water regain</th>
<th>Final pH</th>
<th>Equilibrium concentration Mo(aq.), Mole/l</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
<td>2.56</td>
<td>0.142</td>
<td>2.00</td>
</tr>
<tr>
<td>1.01</td>
<td>2.54</td>
<td>0.141</td>
<td>2.08</td>
</tr>
<tr>
<td>2.36</td>
<td>2.64</td>
<td>0.131</td>
<td>2.89</td>
</tr>
<tr>
<td>2.36</td>
<td>2.62</td>
<td>0.131</td>
<td>2.89</td>
</tr>
<tr>
<td>3.20</td>
<td>2.63</td>
<td>0.133</td>
<td>3.00</td>
</tr>
<tr>
<td>3.20</td>
<td>2.63</td>
<td>0.133</td>
<td>3.20</td>
</tr>
<tr>
<td>4.29</td>
<td>2.64</td>
<td>0.130</td>
<td>3.00</td>
</tr>
<tr>
<td>4.29</td>
<td>2.63</td>
<td>0.130</td>
<td>3.05</td>
</tr>
<tr>
<td>4.93</td>
<td>2.63</td>
<td>0.131</td>
<td>2.94</td>
</tr>
<tr>
<td>4.93</td>
<td>2.62</td>
<td>0.130</td>
<td>3.00</td>
</tr>
<tr>
<td>6.63</td>
<td>2.62</td>
<td>0.131</td>
<td>3.12</td>
</tr>
<tr>
<td>6.63</td>
<td>2.61</td>
<td>0.131</td>
<td>3.25</td>
</tr>
<tr>
<td>11.05</td>
<td>2.62</td>
<td>0.129</td>
<td>3.17</td>
</tr>
<tr>
<td>11.05</td>
<td>2.62</td>
<td>0.130</td>
<td>3.11</td>
</tr>
</tbody>
</table>
II.8 EXPERIMENT WITH TOAH.C1

II.8.a. Conversion of TOA into its Chloride Salt

TOA is a tertiary base which is insoluble in water but soluble in most organic solvents. It was converted to its chloride salt by shaking a solution of the base in chloroform with an aqueous solution of hydrochloric acid. It may be assumed that the base would be completely converted to its salt if sufficient acid is present in the aqueous solution \([121]\). There is, however, a possibility that the amine salt may extract some extra acid from the aqueous phase (section I.3.b.). In the case of TOA in xylene solution, it is reported that the extraction of excess acid occurs if the acid concentration of the aqueous phase is more than \(3M\) \([121]\). A series of experiments were carried out to check the conditions in which the base is present in the organic layer.

The results of equilibrating 0.1M TOA solutions in chloroform with 0.5-2.5M hydrochloric acid solutions, are reported in Table III. The mixing was carried out by shaking the two layers for 5 minutes in a separatory funnel. The acidity of the aqueous layer was determined by titration with standard alkali. The results indicate that as the amount
TABLE III
Conversion of TOA to TOAH.Cl

TOA concentration in the organic phase = 0.1M
Initial aqueous phase hydrochloric acid concentration = 0.5 to 2.5M.
Shaking time = 5 minutes.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.103</td>
<td>0.107</td>
<td>1.07</td>
<td>1.07</td>
</tr>
<tr>
<td>0.643</td>
<td>0.108</td>
<td>1.08</td>
<td>1.08</td>
</tr>
<tr>
<td>1.179</td>
<td>0.107</td>
<td>1.07</td>
<td>1.07</td>
</tr>
<tr>
<td>2.169</td>
<td>0.094</td>
<td>0.94</td>
<td>0.94</td>
</tr>
</tbody>
</table>

*K obtained by the difference in the initial acid concentration and the final acid concentration of aqueous phase.
of acid increases in the aqueous layer there is no corresponding increase in the amount of acid going into the organic phase so that the ratio $[\text{HCl}]_{\text{org.}} : [\text{TOA}]_{\text{org.}}$ remained almost constant at 1. Therefore a 2M hydrochloric acid solution can be conveniently used to convert the TOA to the chloride form. In all future experiments, TOAH.Cl solutions were prepared by equilibration with 2M hydrochloric acid.

II.8.b. Determination of the time of equilibrium for the extraction of molybodic acid solutions by TOAH.Cl

Chloroform solutions of TOAH.Cl were used to extract isopolymolybdate ions from aqueous solutions of molybdic acid. Under sufficiently acidic conditions, the chloride ions of TOAH.Cl are capable of replacement by other anions so that the overall process is that of anion exchange. The equilibrium time of the ion exchange process is important and was determined in a series of experiments.

Solutions of TOAH.Cl in chloroform at two different concentrations were equilibrated with molybdic acid solutions of pH near 1.0. Since these were preliminary experiments different concentrations of TOAH.Cl solutions were also utilised
in finding suitable concentrations for the examination of the organic layer by infrared spectroscopy.

The organic phase and the aqueous phase, usually in a ratio of 1:2, were contained in polythene-stoppered flasks and were shaken in an 8-arm Griffin flask shaker. The results, given in Table IV, indicate that in the course of 30 hours, although the R values were constant, there was not good reproducibility of the results obtained at similar shaking times. It was thought that in an arm-like shaker the vibrations were not mixing the two layers efficiently as the heavier chloroform layer always remains at the bottom. To be more certain of a proper mixing, a more vigorous type of shaker was used. This consisted of a wooden box which was mounted on electric motor, producing a vigorous motion in a horizontal plane. A specially constructed frame was fitted, which allowed up to ten flasks to be shaken simultaneously in horizontal positions. The results of the determination of equilibrium time with this shaker are given in Table V. It is obvious that the equilibrium was reached after 15 hours, and accordingly, in the subsequent experiments the flasks were shaken for 20 hours to ensure complete equilibration.
### TABLE IV

**Determination of Equilibrium Time Using Griffin Flask Shaker**

<table>
<thead>
<tr>
<th>Organic layer</th>
<th>Aqueous layer</th>
<th>Shaking time</th>
<th>Final pH of the aqueous layer</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.074M TOAH.Cl</td>
<td>Molybdic acid (0.25M Mo) pH=0.95</td>
<td>20 minutes</td>
<td>0.90</td>
<td>2.19</td>
</tr>
<tr>
<td>do.</td>
<td>do.</td>
<td>20 minutes</td>
<td>0.87</td>
<td>2.12</td>
</tr>
<tr>
<td>do.</td>
<td>do.</td>
<td>8 hours</td>
<td>0.83</td>
<td>2.50</td>
</tr>
<tr>
<td>0.253M TOAH.Cl</td>
<td>Molybdic acid (0.35M Mo) pH=1.04</td>
<td>8 hours</td>
<td>0.83</td>
<td>2.31</td>
</tr>
<tr>
<td>do.</td>
<td>do.</td>
<td>14 hours</td>
<td>0.82</td>
<td>2.41</td>
</tr>
<tr>
<td>do.</td>
<td>do.</td>
<td>30 hours</td>
<td>0.81</td>
<td>2.48</td>
</tr>
</tbody>
</table>
TABLE V

Determination of Equilibrium Time Using Box-Type Shaker

<table>
<thead>
<tr>
<th>Organic layer</th>
<th>Aqueous layer</th>
<th>Shaking time (hrs.)</th>
<th>Final pH of the aqueous layer</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.249M</td>
<td>Molybdic acid (0.375M Mo)</td>
<td>4</td>
<td>0.83</td>
<td>2.56</td>
</tr>
<tr>
<td>do.</td>
<td>do.</td>
<td>8</td>
<td>0.86</td>
<td>2.71</td>
</tr>
<tr>
<td>do.</td>
<td>do.</td>
<td>15</td>
<td>0.86</td>
<td>2.79</td>
</tr>
<tr>
<td>do.</td>
<td>do.</td>
<td>29</td>
<td>0.88</td>
<td>2.81</td>
</tr>
</tbody>
</table>
The molybdic acid solutions used for the determination of the equilibrium time had a pH near 1.0 and were expected to take a long time to reach equilibrium since highly aggregated species are expected in the region of such a pH. Solutions of higher pH were expected to reach equilibrium more quickly and therefore in some of the later experiments involving solutions of higher pH, the time of shaking was less than 20 hours, but since duplicate experiments were performed at different shaking times, a consistent final pH and R value indicated that sufficient time was allowed for the solutions to equilibrate.

II.8.c. Variation of R Value with the pH of Molybdate Solutions

TOAH.Cl solutions in chloroform were used to extract molybdate species from aqueous molybdic acid solution of pH 1 to 7. From the exchange of chloride ions with the molybdate ions, R values were calculated according to the
following equation:-

\[ z\text{TOAH}_2\text{Cl} \text{(org.}) + H_w \text{Mo}_{n} O_y^Z \text{(aq.)} \rightarrow (\text{TOAH})_2 \text{Mo}_{n} O_y \text{(org.)} + z\text{Cl}^- \text{(aq.)} \]

Since \( R = n/z \)

\[ \therefore \quad R = \frac{g \text{ atoms of Mo entering organic phase}}{g \text{ equivalentsof Cl released in the aqueous phase}} \]

It was ensured, beforehand, that chloroform itself does not extract any molybdenum(VI) by shaking molybdate solutions of pH between 1 and 7 with chloroform. No molybdenum(VI) was found to enter into the organic layer from the analysis of the initial and final aqueous layers. Also on evaporating a small portion of chloroform layer, no residue was left which was also an indication that no molybdenum(VI) was extracted by chloroform.

The R values thus calculated, are reported in Table VI, and their dependence on the pH of the aqueous phase is drawn in Figure 3. A steep fall in R value in the solutions of pH higher than 5.0 may be noticed and is attributed to the hydrolysis of TOAH₂Cl. Excess chloride ion is thus released in the aqueous phase and gives rise to very low R values. Because of this, R values for the solutions of pH > 5.0 are not reliable.
Fig. 3

VARIATION OF R VALUE WITH pH
### TABLE VI

**Variation of R Value with pH**

Organic layer: 0.236M TOAH Cl in Chloroform.
Aqueous layer: Molybdic acid (0.32-0.37M Mo), pH 1 to 7
Equilibration: 25ml organic layer equilibrated with 50ml aqueous layer for 20 hours.

<table>
<thead>
<tr>
<th>Initial pH of aqueous layer</th>
<th>Final pH of aqueous layer</th>
<th>% organic phase chloride exchanged</th>
<th>Equilibrium R concentration Mo(Aq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.14</td>
<td>0.93</td>
<td>89.8</td>
<td>0.064</td>
</tr>
<tr>
<td>1.14</td>
<td>0.92</td>
<td>89.8</td>
<td>0.066</td>
</tr>
<tr>
<td>2.20</td>
<td>2.38</td>
<td>98.3</td>
<td>0.102</td>
</tr>
<tr>
<td>2.20</td>
<td>2.38</td>
<td>98.3</td>
<td>0.100</td>
</tr>
<tr>
<td>2.94</td>
<td>3.62</td>
<td>98.3</td>
<td>0.100</td>
</tr>
<tr>
<td>2.94</td>
<td>3.60</td>
<td>98.3</td>
<td>0.100</td>
</tr>
<tr>
<td>4.22</td>
<td>5.22</td>
<td>91.5</td>
<td>0.132</td>
</tr>
<tr>
<td>4.22</td>
<td>5.22</td>
<td>91.5</td>
<td>0.130</td>
</tr>
<tr>
<td>5.19</td>
<td>5.69</td>
<td>84.7</td>
<td>0.162</td>
</tr>
<tr>
<td>5.19</td>
<td>5.71</td>
<td>86.4</td>
<td>0.160</td>
</tr>
<tr>
<td>6.08</td>
<td>6.10</td>
<td>79.7</td>
<td>0.226</td>
</tr>
<tr>
<td>7.06</td>
<td>6.58</td>
<td>84.7</td>
<td>0.344</td>
</tr>
<tr>
<td>7.06</td>
<td>6.57</td>
<td>86.4</td>
<td>0.326</td>
</tr>
</tbody>
</table>
It may be seen in Figure 3, that there is a well-defined plateau of \( R = 2.0 \), extending from pH \( \approx 3.5 \) to 4.8. Below pH 3.5, the R value starts to increase and a further constant R value of approximately 2.5 is reached. It was observed that in the solutions of pH 2.0, molybdic acid has a tendency to precipitate, and this inhibits the determination of R values. In order to ascertain the correct position of \( R = 2.5 \) plateau, a series of experiments were carried out using molybdic acid solutions of pH \( > 2.0 \).

II.8.d. **Investigation of \( R = 2.5 \) plateau**

Solutions of polymolybdate species of pH \( > 2.0 \) were extracted by TOAH.Cl solutions in chloroform. The results of such an experiment are given in Table VIIBA and VIIB.

For the extractions into 0.244M TOAH.Cl it may be seen that only the solutions of pH = 0.81 do not precipitate, otherwise all the solutions up to pH 1.80 produced precipitates. The average R value for the solutions which did not precipitate was 2.47.
TABLE VIIA

Investigation of R = 2.5

Organic layer: - 0.249M TOAH.Cl in chloroform
Aqueous layer: - Molybdic acid (0.33M Mo), pH 0.81 to 1.8
Equilibration: - 25ml organic layer equilibrated with
50ml aqueous layer for 20 hours.

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Final pH</th>
<th>% organic phase chloride exchanged</th>
<th>Equilibrium Mo concentration (Mole/l)</th>
<th>R</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.81</td>
<td>0.68</td>
<td>77.4</td>
<td>0.094</td>
<td>2.48</td>
<td>Solution clear</td>
</tr>
<tr>
<td>0.81</td>
<td>0.69</td>
<td>77.4</td>
<td>0.096</td>
<td>2.46</td>
<td>do.</td>
</tr>
<tr>
<td>1.28</td>
<td>0.98</td>
<td>95.2</td>
<td>0.042</td>
<td>2.51</td>
<td>Slight turbidity</td>
</tr>
<tr>
<td>1.28</td>
<td>0.96</td>
<td>91.9</td>
<td>0.042</td>
<td>2.60</td>
<td>do.</td>
</tr>
<tr>
<td>1.49</td>
<td>1.11</td>
<td>93.5</td>
<td>0.044</td>
<td>2.53</td>
<td>Some precipitation</td>
</tr>
<tr>
<td>1.49</td>
<td>1.12</td>
<td>93.5</td>
<td>0.044</td>
<td>2.53</td>
<td>do.</td>
</tr>
<tr>
<td>1.80</td>
<td>1.26</td>
<td>95.2</td>
<td>0.042</td>
<td>2.56</td>
<td>do.</td>
</tr>
<tr>
<td>1.80</td>
<td>1.27</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Heavy precipitation</td>
</tr>
</tbody>
</table>
TABLE VIIB

Investigation of R = 2.5

Organic layer: - 0.100M TOAH.Cl in chloroform.
Aqueous layer: - Molybdic acid (0.33M Mo), pH 0.12 to 2.11.
Equilibration: - 25ml organic layer equilibrated with 50ml aqueous layer for 20 hours.

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Final pH</th>
<th>% organic phase chloride exchanged</th>
<th>Equilibrium Mo concentration (Mole/l)</th>
<th>R</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.12</td>
<td>5.7</td>
<td>0.332</td>
<td>5.00</td>
<td>Solution clear do.</td>
</tr>
<tr>
<td>0.12</td>
<td>0.10</td>
<td>6.2</td>
<td>0.330</td>
<td>11.00</td>
<td>do.</td>
</tr>
<tr>
<td>0.55</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Precipitation do.</td>
</tr>
<tr>
<td>0.55</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>do.</td>
</tr>
<tr>
<td>1.34</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Solution precipitated do.</td>
</tr>
<tr>
<td>1.34</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>do.</td>
</tr>
<tr>
<td>1.92</td>
<td>1.43</td>
<td>64.9</td>
<td>0.132</td>
<td>2.59</td>
<td>Solution clear do.</td>
</tr>
<tr>
<td>1.92</td>
<td>1.43</td>
<td>64.4</td>
<td>0.134</td>
<td>2.57</td>
<td>do.</td>
</tr>
<tr>
<td>2.11</td>
<td>1.84</td>
<td>64.9</td>
<td>0.132</td>
<td>2.59</td>
<td>do.</td>
</tr>
<tr>
<td>2.11</td>
<td>1.84</td>
<td>64.4</td>
<td>0.134</td>
<td>2.52</td>
<td>do.</td>
</tr>
</tbody>
</table>
It was thought that a high concentration of TOAH.Cl may account for the precipitation in the molybdate solutions, since it would disturb the equilibrium of the species in the aqueous layer to a great extent. With this view in mind, a lower concentration of TOAH.Cl (0.1M) was used in a further experiment, but almost the same sort of behaviour was observed as in the previous experiment (Table VIIIB). Solutions of initial pH = 0.12 are quite clear after shaking, but the accurate determination of R value for these solutions were not possible because of the very low extraction of molybdenum. This is because of the high initial content of chloride ions in the aqueous phase since hydrochloric acid was added to reduce the pH from 1.5 to 0.12. Further, at such a low pH, some cationic species would be expected which would not be exchanged by TOAH.Cl. For these reasons, the R values at pH = 0.12 are not reliable. Among the remaining solutions, only those of initial pH = 1.92 and 2.11 were without precipitates after shaking and these showed R value of 2.52 to 2.59.

It is clear from these experiments that the concentration of TOAH.Cl is not important in the precipitation reaction. However, these experiments show that molybdate solutions
precipitate if the initial pH lies between approximately 1.1 and 1.9. From the few experiments in which R values could be determined accurately, it became clear that the maximum R value is 2.50 and this value is probably maintained for pH 0.81 to 2.11.

The R values determined from the extraction data are merely ratios of the metal to charge of the ions present in the aqueous phase. To obtain more precise information about the ionic species it is necessary to determine either the number of metal atoms contained in the aggregated species or the charge by an independent method. Therefore, it was decided to carry out physical measurements on the organic phase containing extracted molybdate ions. The physical measurements include the determination of lowering of vapour pressure and infrared spectrophotometric measurements.
II.9. VAPOUR PRESSURE LOWERING MEASUREMENTS

Lowering of the vapour pressure is a colligative property of a solution, i.e. it depends on the total number of molecules present in the solution. The measurement of this property of organic layers containing extracted molybdate species thus provides a direct method of determining the number of molybdenum atoms in an aggregated molybdate species. The apparatus used for the measurements of vapour pressure lowering, the Vapour Pressure Osmometer, has been described in detail in section II.6.a.

II.9.a. Calibration of Vapour Pressure Osmometer

The calibration of the Vapour Pressure Osmometer is important since it forms the basis for the measurements on solutions of unknown concentration. It was carried out by preparing solutions of benzil in chloroform (section II.6.a.), since benzil is monomeric in most of the organic solvents, including chloroform.

A typical calibration graph is shown in Figure 4 (Table VIII) in which the variation of ΔT with the
CALIBRATION OF VAPOUR PRESSURE OSMOMETER

- BENZIL 16.3.1966
- " 9.5.1966
- " 23.5.1966
- NAPHTHALENE 12.5.1966
- TOA (89%) 15.5.1966

\[ \Delta T \]

\[ \text{CONCENTRATION (moles/L)} \]
### TABLE VIII
Calibration of Vapour Pressure Osmometer

Solvent in the chamber: - chloroform  
Temperature of the chamber: - 25°C

<table>
<thead>
<tr>
<th>Date</th>
<th>Concentration of solute (Mole/1)</th>
<th>ΔT (4 minutes)</th>
<th>Concentration of solute (Mole/1)</th>
<th>ΔT (4 minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solute = Benzil</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.3.1966</td>
<td>0.0077</td>
<td>3.24</td>
<td>0.0479</td>
<td>18.11</td>
</tr>
<tr>
<td></td>
<td>0.0312</td>
<td>12.09</td>
<td>0.0717</td>
<td>26.93</td>
</tr>
<tr>
<td>9.5.1966</td>
<td>0.0097</td>
<td>3.79</td>
<td>0.0875</td>
<td>32.31</td>
</tr>
<tr>
<td></td>
<td>0.0416</td>
<td>15.78</td>
<td>0.1034</td>
<td>37.70</td>
</tr>
<tr>
<td></td>
<td>0.0583</td>
<td>21.78</td>
<td>0.2111</td>
<td>79.82</td>
</tr>
<tr>
<td>23.5.1966</td>
<td>0.105</td>
<td>4.57</td>
<td>0.0893</td>
<td>34.06</td>
</tr>
<tr>
<td></td>
<td>0.0406</td>
<td>16.02</td>
<td>0.1972</td>
<td>79.45</td>
</tr>
<tr>
<td></td>
<td>0.0595</td>
<td>23.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solute = Naphthalene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.5.1966</td>
<td>0.0117</td>
<td>4.60</td>
<td>0.0864</td>
<td>31.39</td>
</tr>
<tr>
<td></td>
<td>0.0407</td>
<td>15.02</td>
<td>0.1501</td>
<td>54.11</td>
</tr>
<tr>
<td></td>
<td>0.0547</td>
<td>19.95</td>
<td>0.1869</td>
<td>66.26</td>
</tr>
<tr>
<td>Solute = TOA (89% pure)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.5.1966</td>
<td>0.0476</td>
<td>22.10</td>
<td>0.100</td>
<td>47.05</td>
</tr>
<tr>
<td></td>
<td>0.0800</td>
<td>33.65</td>
<td>0.124</td>
<td>55.61</td>
</tr>
<tr>
<td></td>
<td>0.0938</td>
<td>43.98</td>
<td>0.146</td>
<td>67.725</td>
</tr>
<tr>
<td></td>
<td>0.0980</td>
<td>45.71</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
concentration of benzil is shown. The measurements were carried out three times over a period of 2 months. In Figure 4, the behaviour of solutions of naphthalene is shown in order to show that another solute of different molecular weight behaves similarly (Mol.wts., benzil = 210, naphthalene = 128). The solvent used in all these measurements was pre-treated chloroform. Figure 4 shows that the calibration of the Vapour Pressure Osmometer is dependable and that a substance of different molecular weight does not appreciably alter the calibration. Although the calibration did not vary over a period of 2 months, a new calibration line was constructed on each occasion the apparatus was used to ensure accuracy of the results. The calibration curve was initially linear but continuous use of the instrument over one year produced a slight curvature in the line.

The behaviour of TOA solutions is also shown in Figure 4, and it can be observed that TOA does not follow the calibration line of benzil. The points lie above the line and diverge rapidly at concentrations greater than 0.1M. This may be because the amine used had a purity of only 89%. For this reason, for accurate work and for all the work
involving the extraction of molybdate species a sample of amine with almost 100% purity was used. The behaviour of this amine is shown in Figure 5 (Table IX), where it can be seen that the amine follows closely the calibration line of benzil. Some scattering of points may be seen at concentrations greater than 0.1M and for this reason the final concentration of the organic layer used in subsequent experiments was usually below 0.1M.

Before studying the organic layers containing the extracted molybdate species it was considered useful to study the extraction of some simple acids such as hydrochloric, sulphuric, and oxalic acids. The studies of these acids, would, then, form a basis for the studies of more complicated equilibria of the aggregated molybdate species.

II.9.b. Vapour Pressure Lowering Studies of the TOA Extraction of Hydrochloric Acid

Vapour pressure lowering studies of TOAH·Cl were necessary because it formed the original organic layer with which the extractions of molybdate ions were carried out. Solutions of various concentrations of TOA in chloroform were
VAPOUR PRESSURE OSMOMETER

VARIATION OF ΔT WITH CONCENTRATION AT 23°C USING WATER SAT'D CHLOROFORM AS SOLVENT
**TABLE IX**

Vapour Pressure Lowering Measurements for TOA

Solvent: - chloroform
Temperature of the chamber: - 25°C

<table>
<thead>
<tr>
<th>Concentration of solute (Mole/1)</th>
<th>ΔT (4 minutes)</th>
<th>Concentration of solute (Mole/1)</th>
<th>ΔT (4 minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solute: - benzil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0079</td>
<td>3.54</td>
<td>0.0772</td>
<td>30.13</td>
</tr>
<tr>
<td>0.0342</td>
<td>13.82</td>
<td>0.1076</td>
<td>41.48</td>
</tr>
<tr>
<td>0.0485</td>
<td>19.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solute: - TOA (100% pure)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0100</td>
<td>4.41</td>
<td>0.974</td>
<td>39.83</td>
</tr>
<tr>
<td>0.0308</td>
<td>12.74</td>
<td>0.145</td>
<td>59.98</td>
</tr>
<tr>
<td>0.0788</td>
<td>31.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solute: - TOAH.Cl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0104</td>
<td>5.62</td>
<td>0.0890</td>
<td>33.62</td>
</tr>
<tr>
<td>0.0355</td>
<td>13.76</td>
<td>0.1102</td>
<td>41.77</td>
</tr>
<tr>
<td>0.0511</td>
<td>20.42</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
equilibrated with half the volume of 2M hydrochloric acid. The organic layer was analysed for chloride content and measurements of ΔT were carried out. Table IX and Figure 5 show the results obtained. It may be seen that the values of ΔT for TOAH·Cl and benzil are the same at equivalent concentrations. Hence, TOAH·Cl is monomeric, like benzil, and does not dissociate throughout the concentration ranges studied in these experiments.

II.9.c. Vapour Pressure-Lowering Studies of TOA Extraction of Sulphuric Acid

Sulphuric acid solutions (1 to 4M) were extracted by TOA solutions (0.1 to 0.15M in chloroform) and the analytical results are reported in Table X. The chemical analysis of the aqueous layer gives a value of

\[ \frac{[TOA]_{\text{org.}}}{[H_2SO_4]_{\text{org.}}} \]

close to 1, which indicates that bisulphate ions (HSO₄⁻) are extracted by the amine. The value \[ [H_2SO_4]_{\text{org.}} \] could also be obtained from the calibration curve of the Vapour Pressure Osmometer on substituting ΔT values obtained for the organic layers. This value was called \[ [QAS]_{\text{org.}} \]. Since it was assumed that the amine was completely
TABLE X
Extraction of Sulphuric Acid by TOA

Organic layer: - 0.098 to 0.146M TOA in chloroform
Aqueous layer: - 1 to 3M sulphuric acid solutions
Equilibration: - 20ml organic layer equilibrated with 40ml aqueous layer for 30 minutes.

<table>
<thead>
<tr>
<th>Concentration of TOA (Mole/1)</th>
<th>Eqbm. acid concn. in aqueous phase (Mole/1)</th>
<th>Eqbm. acid concn. in organic phase (Mole/1)</th>
<th>[TOA]org.</th>
<th>[H₂SO₄]org.</th>
<th>[QAS]org.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.098</td>
<td>0.985</td>
<td></td>
<td>-</td>
<td>0.97</td>
<td>1.18</td>
</tr>
<tr>
<td>0.098</td>
<td>1.905</td>
<td>0.101</td>
<td>0.94</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>0.098</td>
<td>2.705</td>
<td>0.104</td>
<td>1.13</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>0.124</td>
<td>0.975</td>
<td>0.1095</td>
<td>0.99</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>0.124</td>
<td>1.894</td>
<td>0.125</td>
<td>1.01</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>0.124</td>
<td>2.686</td>
<td>0.123</td>
<td>1.12</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>0.146</td>
<td>0.966</td>
<td>0.130</td>
<td>0.98</td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td>0.146</td>
<td>1.884</td>
<td>0.149</td>
<td>0.95</td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td>0.146</td>
<td>2.673</td>
<td>0.153</td>
<td>0.99</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td>0.100</td>
<td>3.485</td>
<td>0.101</td>
<td>0.98</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>0.100</td>
<td>3.811</td>
<td>0.1015</td>
<td>0.98</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>0.100</td>
<td>4.401</td>
<td>0.102</td>
<td>0.98</td>
<td>1.29</td>
<td></td>
</tr>
</tbody>
</table>
converted to the quaternary ammonium salt. This assumption was verified by the fact that on increasing the acid concentration of the aqueous layer there was no corresponding increase in the amount of acid entering organic phase.

It may be noticed that the value of \([\text{TOA}]_{\text{org.}} / [\text{QAS}]_{\text{org.}}\) is near 1.2. These initial experiments were carried out using amine of 89% purity. It was realised that the purity of amine, though not so important in \(R\) value measurements, may be an important factor for the vapour pressure measurements. For this reason all the later work was carried out with an amine of 100% purity.

The use of the Vapour Pressure Osmometer has been restricted, so far, to studies of amine salts completely saturated with the exchanged species, and these organic phases were obtained by neutralising the amine completely with the acid under investigation. The amine solution requires a high acidity (of \(\text{pH} \leq 1\) for \(0.1\text{MTOA}\)) to convert it to the quaternary ammonium salt. Since the molybdic acid solution which contained aggregated anions, have a \(\text{pH} 1\) to \(7\), they could not be used to saturate the amine solution and for this reason the amine had to be first converted into the
hydrochloride, and then the chloride ions were exchanged by polymolybdate ions. It was decided to simulate the same process for the extraction of known oxyanions. Thus the anions of sulphuric acid were extracted by the amine hydrochloride in chloroform and from the exchange of chloride ions with the oxyanion, R values could be calculated. Such an extraction would provide the benefit of using solutions of pH = 5.0, so that non-protonated ions of higher charges may also be studied. A method was, therefore devised to calculate the charge of the extracted species (z) from the Vapour Pressure Osmometer measurements of the organic layers.

II.9.d. Method to Determine z Values of the Extracted Species

The extraction of a species $X^{z-}$ by means of TOAH.C1 takes place by its exchange with the chloride ions according to the following reactions:-

$$ z\text{TOAH.Cl}^{\text{org.}} + X^{z-}^{\text{aq.}} \rightleftharpoons (\text{TOA})_z^{\text{org.}}X + z\text{Cl}^{-}^{\text{aq.}} $$

The final organic layer contains molecules of the exchanged salt $(\text{TOA})_z^X$ and the unexchanged TOAH.C1. Therefore, $\Delta T$ values of the organic layer obtained from the Vapour Pressure Osmometer and called $\Delta T_{\text{total}}$ consist of a $\Delta T$ component
due to exchanged molecules, $\Delta T_x$, and a $\Delta T$ component due to the chloride compound, $\Delta T_{Cl}$, therefore,

$$\Delta T_{\text{total}} = \Delta T_x + \Delta T_{Cl} \quad \text{(i)}$$

Since the chloride concentration of the organic layer is known from chemical analysis, the corresponding value of $\Delta T_{Cl}$ was read from the calibration curve and $\Delta T_x$ was determined from equation (i). The corresponding concentration of the extracted quaternary ammonium salt was then calculated from $\Delta T_x$ by reading the calibration curve and this concentration was termed $[X]_{\text{org}}$. Now, the amount of TOA which is combined with the exchanged quaternary ammonium compound was also known since it is equal to the amount of chloride released by the organic layer into the aqueous layer and was denoted by $[\text{TOA}_x]_{\text{org}}$. It is evident now that the ratio $[\text{TOA}_x]_{\text{org}}/[X]_{\text{org}}$ is the number of TOA molecules per exchanged ion and is termed $z$, since it is also the charge of the extracted anion.

II.9.e. Vapour Pressure Lowering Studies of TOAH.C1 Extraction of Oxyanions of Sulphuric Acid

Solutions of sulphuric acid of pH = 3.8 were prepared by mixing solutions of sodium sulphate and sulphuric acid. From
ion exchange experiments[88] it is known that bisulphate ions are present in such solutions at pH<2.0, whilst above this pH sulphate ions are present. Aqueous solutions of sodium sulphate and sulphuric acid (pH = 3.8) were equilibrated with TOAH.Cl solutions in chloroform. From the exchange of chloride ions by the oxyanion, R values were calculated in the following way:-

\[
R = \frac{\text{g. atoms of sulphate entering organic phase}}{\text{g. eq. of chloride released}}
\]

The final organic layer was studied by means of the Vapour Pressure Osmometer and z values were calculated. In this case X was a quaternary ammonium compound of sulphuric acid and was termed QAS, thus:-

\[
z = \frac{[\text{TOA}_{\text{QAS}}]_{\text{org.}}}{[\text{QAS}]_{\text{org.}}}
\]

The results are given in Table XI. It may be seen that the exchange of chloride ions is very low, i.e. 18% for a single stage extraction. The percentage exchange was increased by repeated extractions, i.e. after separating the organic layer, it was re-equilibrated with a fresh aqueous layer and this process was repeated until the final and the initial pH of the solution were the same. Even by repeated extraction the percentage exchange
**TABLE XI**

**Extraction of Sulphuric Acid by TOAH.Cl**

Organic layer: 0.113M TOAH.Cl in chloroform

Aqueous layer: 0.5M sodium sulphate solution, pH adjusted by adding 0.5M sulphuric acid.

Equilibration: 20ml organic layer equilibrated with 40ml aqueous layer for 2 hours in each stage of extraction.

<table>
<thead>
<tr>
<th>pH of the solution</th>
<th>%org. phase chloride exchanged</th>
<th>R</th>
<th>$\frac{[\text{TOA}<em>{\text{org}}]}{[\text{QAS}</em>{\text{org}}]}$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.82</td>
<td>24</td>
<td>0.53</td>
<td>1.28</td>
<td>Single stage extraction</td>
</tr>
<tr>
<td>3.82</td>
<td>46</td>
<td>0.63</td>
<td>1.30</td>
<td>3 stage extraction</td>
</tr>
<tr>
<td>3.82</td>
<td>47</td>
<td>0.45</td>
<td>1.25</td>
<td>do.</td>
</tr>
</tbody>
</table>
was only 46%. Further, the repeated extractions had an adverse effect on the determination of $R$ values since there was some unavoidable loss of solution during separation and re-mixing of the two layers. With such a possibility of error in $R$ values, they may be considered to be very near to 0.50, which indicates that $SO_4^{2-}$ ions are being exchanged by the chloride ions of the organic phase. However, the vapour pressure lowering measurements gave $z = 1.25$ to 1.3, instead of the value 2.0 predicted for $SO_4^{2-}$ ions. Two explanations may be advanced for low $z$ values.

(1) The low percentage of the extraction gives rise to the presence of a large quantity of unexchanged molecules of $TOA\cdot Cl$ and their elimination in the calculation gives rise to large errors.

(2) There seems to be a charge separation in the $TOA$-sulphate molecule, represented by $(R_3NH)^{++} \cdots \cdots SO_4^{-}$. Since $TOA$ sulphate is the salt of a strong acid and a tertiary base, the proton of the acid is strongly bound to the nitrogen of the amine and this may give rise to some dissociation. Hence, a molecule of $TOA$-sulphate does not behave as a single entity. This argument has been supported in the literature by work on the extraction of sulphuric acid by methyldioctylamine.
in chloroform\[^{[123]}\], where it was found that the infrared spectra of the sulphate ion in the organic layer indicated some degree of ion-dissociation. As a matter of fact, these two reasons may reinforce one another as an ionic compound would have a low solubility in chloroform and may not form in large amounts in the organic layer. It was, therefore, decided to extract the anions of a weaker dibasic, oxalic acid, so that the resulting salt would be less ionic.

II.9.f. \textbf{Vapour Pressure Lowering Studies of \textit{TOAH}.Cl Extraction of Oxalic Acid}

Solutions of oxalic acid (pH = 1 to 5) were prepared from potassium oxalate and oxalic acid. The results of the extraction of these ions by \textit{TOAH}.Cl are given in Table XII, and indicate clearly that the percentage extraction has increased, over sulphate extraction, to 62\%. The results of the vapour pressure measurements are, accordingly, altered. Up to pH = 3.0, R values are near 1.0, and indicate that only biocxalate species are being extracted. The values of \( z \) calculated from the \textit{Vapour Pressure Osmometer} are also near to 1.0. At pH = 4.0, however, the R values
**TABLE XII**

**Extraction of Oxalate Ions by TOAH.Cl**

Organic layer: - TOAH.Cl in chloroform

Aqueous layer: - 0.25 to 0.5M potassium oxalate solutions, pH adjusted by adding oxalic acid of similar concentration.

Equilibration: - 20ml organic layer equilibrated with 40ml aqueous layer for 2-4 hours.

<table>
<thead>
<tr>
<th>Concentration of TOAH.Cl in organic phase (Mole/l)</th>
<th>Initial pH of aq. phase</th>
<th>Final pH of org. phase</th>
<th>Eqbm. time (hours)</th>
<th>%org. chloride exchanged</th>
<th>R</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.076</td>
<td>0.98</td>
<td>0.94</td>
<td>2.0</td>
<td>55.1</td>
<td>0.91</td>
<td>1.05</td>
</tr>
<tr>
<td>0.076</td>
<td>3.04</td>
<td>3.08</td>
<td>2.0</td>
<td>66.0</td>
<td>0.98</td>
<td>0.89</td>
</tr>
<tr>
<td>0.076</td>
<td>5.08</td>
<td>4.90</td>
<td>2.0</td>
<td>61.3</td>
<td>0.41</td>
<td>1.02</td>
</tr>
<tr>
<td>0.104</td>
<td>4.20</td>
<td>4.23</td>
<td>2.5</td>
<td>62.7</td>
<td>0.74</td>
<td>1.21</td>
</tr>
<tr>
<td>0.104</td>
<td>4.20</td>
<td>4.22</td>
<td>4.0</td>
<td>63.2</td>
<td>0.74</td>
<td>1.22</td>
</tr>
</tbody>
</table>
indicate that the species being extracted was a mixture of biroxalate (\(\text{HC}_2\text{O}_4^-\)) and oxalate (\(\text{C}_2\text{O}_4^{2-}\)) ions. Similarly, the \(z\) values rise to 1.2. At pH = 5.0, the results obtained were not so reliable since hydrolysis of amine hydrochloride sets in.

The improvement in the results for the extraction of oxalate ions as compared to the results of sulphuric acid anion extraction emphasises that the final organic layer should contain a very high percentage of exchanged molecules for good vapour pressure lowering measurements. One of the reasons for the increase in the exchange of ions may be the affinity of the amine for particular ions, since it was found that the polymeric ions of molybdenum exchange more than 95% of the chloride of the organic phase.

II.9.g. Vapour Pressure Lowering Studies of TOAH.C1 Extraction of Molybdate Species

The extraction of molybdate ions from aqueous solutions by TOAH.C1 was carried out. \(R\) values were calculated as described in section II.8.c., and the method for the calculation of \(z\) values is given in section II.9.d. In this case \(X\) is a quaternary ammonium compound of the molybdate ion and is
denoted by QAM, therefore, \( z = \frac{[\text{TOA}_{\text{QAM}}]_{\text{org.}}}{[\text{QAM}]_{\text{org.}}} \). Since the extracted species are polymeric, another parameter, \( n \), or the degree of aggregation was calculated from the relationship, \( n = \frac{[\text{Mo}]_{\text{org.}}}{[\text{QAM}]_{\text{org.}}} \); where \( n \) may be defined as number of molybdenum atoms present in each condensed ion extracted into the organic phase.

(i) **Preliminary experiments**

Preliminary experiments involved vapour pressure lowering studies of organic layers containing molybdate species which were obtained by the exchange of molybdate ions for chloride ions in the organic layer. The aqueous molybdate solutions were of pH 0.8 and 4.2 and covered the region of the two plateaus of constant R value (see Figure 3). The TOAH.CI solutions used for the extraction were of three different concentrations. The results are given in Table XIII. It may be observed that for equilibrium pH 0.8 solutions, the R value lies between 2.50 and 2.66, while the values of \( z \) and \( n \) are between 3.5 and 4.7, and 9 and 11.7, respectively. The region for pH = 4.2 gives more consistent results as the R value is constant at 2.0, while \( z \) and \( n \) vary between 2.2 and 2.8, and 5.0 and 5.8, respectively.
### TABLE XIII

**Extraction of Molybdic Acid by TOAH.Cl**

Organic layer: - TOAH.Cl in chloroform
Aqueous layer: - molybdic acid solutions (≈0.25M Mo)
Equilibration: - 25ml organic layer equilibrated with 50ml aqueous layer for 12 to 20 hours.

<table>
<thead>
<tr>
<th>Concentration of TOAH.Cl in organic layer (Mole/1)</th>
<th>Initial pH of aq. phase</th>
<th>Final pH of aq. phase</th>
<th>% org. layer chloride exchanged</th>
<th>Final Mo concn. in aq. layer (Mole/1)</th>
<th>R</th>
<th>z</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.098</td>
<td>0.93</td>
<td>0.87</td>
<td>84.0</td>
<td>0.160</td>
<td>2.66</td>
<td>4.00</td>
<td>10.67</td>
</tr>
<tr>
<td>0.126</td>
<td>0.93</td>
<td>0.85</td>
<td>87.1</td>
<td>0.132</td>
<td>2.59</td>
<td>3.48</td>
<td>9.03</td>
</tr>
<tr>
<td>0.150</td>
<td>0.95</td>
<td>0.86</td>
<td>73.7</td>
<td>0.100</td>
<td>2.50</td>
<td>4.66</td>
<td>11.67</td>
</tr>
<tr>
<td>0.098</td>
<td>3.37</td>
<td>4.14</td>
<td>96.0</td>
<td>0.176</td>
<td>2.04</td>
<td>2.82</td>
<td>5.76</td>
</tr>
<tr>
<td>0.126</td>
<td>3.37</td>
<td>4.26</td>
<td>100.0</td>
<td>0.150</td>
<td>2.00</td>
<td>2.48</td>
<td>4.96</td>
</tr>
<tr>
<td>0.150</td>
<td>3.66</td>
<td>4.21</td>
<td>97.4</td>
<td>0.092</td>
<td>2.03</td>
<td>2.18</td>
<td>5.77</td>
</tr>
<tr>
<td>0.098</td>
<td>7.37</td>
<td>6.32</td>
<td>92.0</td>
<td>0.276</td>
<td>0.09</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.126</td>
<td>7.37</td>
<td>6.30</td>
<td>93.5</td>
<td>0.274</td>
<td>0.10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.150</td>
<td>6.77</td>
<td>6.40</td>
<td>84.2</td>
<td>0.228</td>
<td>0.16</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
This preliminary experiment was carried out with TOA of 89% purity. In these measurements, $\Delta T$ due to the impurity was eliminated from $\Delta T_{\text{total}}$ by subtracting the value of deviation for TOA from the calibration line of benzil (see Figure 4).

Some useful information was obtained from this experiment. For example, it was found that the species of $R = 2.5$ has a molecular weight of more than 2,000 so that the results of the vapour pressure lowering for this ion may not be very accurate. Furthermore, precipitation near the pH region of $R = 2.5$ ion (section II.8.d.) does not facilitate the investigation. It may also be noticed that regions of $R = 2.0$ give more consistent results and it was decided to investigate this area (pH = 3.5 to 4.8) more carefully. Further studies in this region were carried out with an amine of high purity (about 100%). The concentration range for the amine solutions was chosen such that the values of $\Delta T$ for the final organic layer should lie in that region of the calibration line which is the most reliable.

(ii) Vapour pressure lowering studies of $R = 2.0$ ion

In the first series of experiments for the investigations of this ion, molybdate solutions of a wide pH
range (3.6 to 5.3, Table XIV) were extracted by TOAH·Cl. This was in order to ascertain the limits of the constancy of $R = 2.0$, and to see whether the vapour pressure lowering measurements also show some sort of constancy. The results in Table XIV show that the $R$ values vary between 2.2 and 2.0 whilst the variation in $z$ and $n$ is from 3.4 to 2.5, and from 7.50 to 4.9, respectively. This indicates that some sort of equilibrium exists in these solutions between species of similar $R$ value, but different aggregation number. There seemed to be a need to investigate the region more closely and it was thought that the study of a series of solutions of constant pH and containing ions of $R = 2.0$, by extraction with different concentrations of TOAH·Cl in chloroform would provide useful results. In this way, if a mixture of species of similar $R$ values is present, then it is likely that one of them would be more soluble in the organic phase than the others and thereby some separation of these species would be achieved.

In the next series of experiments, molybdic acid solutions of pH 4.45 were extracted by TOAH·Cl (0.02 to 0.078M) in chloroform solution (Table XV). It was found that the extraction into TOAH·Cl solutions of various concentrations
**TABLE XIV**

Extraction of Molybdic Acid by TOAH(Cl)

Organic layer: 0.0996M TOAH,Cl in chloroform
Aqueous layer: molybdic acid (~0.25M Mo)
Equilibration: 20ml organic layer equilibrated with 40ml aqueous layer for 4½ to 9 hours.

<table>
<thead>
<tr>
<th>Initial pH of aq. layer</th>
<th>Final pH of aq. layer</th>
<th>%org. phase chloride exchanged</th>
<th>Final Mo concn. in aq. layer (Mole/l)</th>
<th>R</th>
<th>z</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.26</td>
<td>3.63</td>
<td>97.0</td>
<td>0.157</td>
<td>2.21</td>
<td>3.45</td>
<td>7.50</td>
</tr>
<tr>
<td>3.26</td>
<td>3.63</td>
<td>97.9</td>
<td>0.157</td>
<td>2.21</td>
<td>3.36</td>
<td>7.24</td>
</tr>
<tr>
<td>3.98</td>
<td>4.37</td>
<td>98.0</td>
<td>0.160</td>
<td>2.10</td>
<td>2.38</td>
<td>4.93</td>
</tr>
<tr>
<td>3.98</td>
<td>4.37</td>
<td>96.5</td>
<td>0.157</td>
<td>2.10</td>
<td>2.91</td>
<td>6.12</td>
</tr>
<tr>
<td>5.01</td>
<td>5.34</td>
<td>93.0</td>
<td>0.172</td>
<td>2.00</td>
<td>2.50</td>
<td>4.86</td>
</tr>
<tr>
<td>5.01</td>
<td>5.34</td>
<td>91.9</td>
<td>0.172</td>
<td>2.00</td>
<td>2.47</td>
<td>4.89</td>
</tr>
<tr>
<td>7.36</td>
<td>6.39</td>
<td>37.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
TABLE XV

Extraction of Molybdic Acid by TOAH.C1

Organic layer:— TOAH.C1 in chloroform
Aqueous layer:— Molybdic acid solutions (~0.25M Mo), pH = 4.45.
Equilibration:— 20ml organic layer equilibrated with 40ml aqueous layer for 4½ to 8 hours.

<table>
<thead>
<tr>
<th>Conc. of TOAH.C1 in org. layer (Mole/1)</th>
<th>Final pH of aq. layer</th>
<th>%org. chloride exchanged</th>
<th>Final Mo concn. in aq. layer</th>
<th>R</th>
<th>z</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0205</td>
<td>4.54</td>
<td>96.0</td>
<td>0.249</td>
<td>2.19</td>
<td>2.70</td>
<td>5.92</td>
</tr>
<tr>
<td>0.0205</td>
<td>4.54</td>
<td>96.7</td>
<td>0.249</td>
<td>2.24</td>
<td>3.15</td>
<td>7.09</td>
</tr>
<tr>
<td>0.041</td>
<td>4.63</td>
<td>95.0</td>
<td>0.229</td>
<td>2.09</td>
<td>3.27</td>
<td>6.83</td>
</tr>
<tr>
<td>0.041</td>
<td>4.64</td>
<td>96.0</td>
<td>0.230</td>
<td>2.04</td>
<td>3.15</td>
<td>6.44</td>
</tr>
<tr>
<td>0.060</td>
<td>4.73</td>
<td>96.1</td>
<td>0.211</td>
<td>2.04</td>
<td>2.90</td>
<td>5.92</td>
</tr>
<tr>
<td>0.060</td>
<td>4.72</td>
<td>94.5</td>
<td>0.211</td>
<td>2.03</td>
<td>3.22</td>
<td>6.52</td>
</tr>
<tr>
<td>0.079</td>
<td>4.82</td>
<td>95.3</td>
<td>0.193</td>
<td>2.01</td>
<td>3.04</td>
<td>6.14</td>
</tr>
<tr>
<td>0.079</td>
<td>4.81</td>
<td>96.2</td>
<td>0.193</td>
<td>2.00</td>
<td>3.00</td>
<td>6.00</td>
</tr>
</tbody>
</table>
gives equilibrium aqueous layers of different molybdenum concentration with the result that the pH of the aqueous phases at equilibrium is not constant. It may be noticed that within a difference of 0.3pH unit, n varies between 5.9 and 7.0, z varies between 2.7 and 3.3 while the R values vary between 2.0 and 2.2.

In order to eliminate the variation in n due to the changes in the final pH of the aqueous layer, it was decided to keep the final pH constant by means of the approximate relationship that 0.02M TOAH.Cl increases the pH of the aqueous layer by 0.1pH unit. This relationship was estimated from the available data concerning the increase in pH after equilibration of the molybdate solutions with the TOAH.Cl solutions. This is not a general rule, since the rate of change in pH varies for different pH regions.

Table XVI shows the results of the extraction of molybdate ions by TOAH.Cl when the final pH of the aqueous layer is constant. It is evident that in most of the solutions the pH remained reasonably constant at 4.8. The average degree of aggregation, n, in twelve solutions is 5.8, whilst z is 3.0 and R remains constant at 2.0. This experiment
indicates that in molybdate solutions of pH 4.8, the predominant species have an aggregation number 6.0, and charge 3.0.

Studies of the abundance of the hexamolybdate ions over the whole range of $R = 2.0$, were undertaken. The next series of experiments were thus designed to investigate molybdic acid solutions which would have an equilibrium pH = 3.8 after extraction into TOAH·Cl solutions of different concentrations. This pH region lies at the lower pH end of the $R = 2.0$ plateau. The final pH of the aqueous phase was maintained at 3.8 by varying the initial pH and as is evident from Table XVII that this was achieved satisfactorily. $R$ values are again constant at 2.0, whilst the degree of aggregation, $n$, has an average value of 6.55 and $z$ has an average value of 3.25. This experiment also demonstrates the abundance of an ion of $n = 6.0$, and $z = 3.0$. It is, however, to be noticed that a slight increment in the values of $n$ and $z$ is evident. In order to check further the presence of hexamolybdate ion in the $R = 2.0$ region, another experiment was carried out using aqueous molybdate solutions of final pH 4.3, which lies near the centre of the $R = 2.0$ plateau. The results given in Table XVIII confirm those of the previous experiments as the prevailing ion has $n = 6.0$, $z = 3.0$, and $R = 2.0$. 
Vapour pressure studies of the organic phase have given more precise information concerning the ions exchanged by TOAH.Cl as they have provided a direct measurement of \( n \) and \( z \) rather than \( R \) value which is a ratio of \( n \) and \( z \). The 10% variation in \( n \) and \( z \) at lower pH may indicate the presence of an ion in very small amounts which has an \( R \) value close to 2.0 but is quite different in its degree of aggregation. Such a possibility is discussed in the next section.
# TABLE XVI

**Extraction of Molybdic Acid by TOAH.Cl**

Organic layer: TOAH.Cl in chloroform

Aqueous layer: Molybdic acid solution (0.25M Mo)

Equilibration: 20ml organic layer equilibrated with 40ml aqueous layer for 4 to 8 hours.

<table>
<thead>
<tr>
<th>Conc. of TOAH.Cl in org. layer (Mole/l)</th>
<th>Initial pH of aq. layer</th>
<th>Final pH of aq. layer</th>
<th>% org. phase chloride exchanged</th>
<th>Final Mo concn. in aq. layer (Mole/l)</th>
<th>R</th>
<th>z</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.041</td>
<td>4.65</td>
<td>4.85</td>
<td>95.7</td>
<td>0.205</td>
<td>2.10</td>
<td>3.29</td>
<td>6.40</td>
</tr>
<tr>
<td>0.041</td>
<td>4.65</td>
<td>4.84</td>
<td>96.7</td>
<td>0.206</td>
<td>2.02</td>
<td>3.20</td>
<td>5.96</td>
</tr>
<tr>
<td>0.084</td>
<td>4.48</td>
<td>4.87</td>
<td>96.3</td>
<td>0.167</td>
<td>2.01</td>
<td>3.20</td>
<td>5.96</td>
</tr>
<tr>
<td>0.084</td>
<td>4.48</td>
<td>4.88</td>
<td>96.0</td>
<td>0.167</td>
<td>1.99</td>
<td>3.19</td>
<td>5.96</td>
</tr>
<tr>
<td>0.122</td>
<td>4.40</td>
<td>5.00</td>
<td>94.8</td>
<td>0.130</td>
<td>1.99</td>
<td>3.06</td>
<td>5.90</td>
</tr>
<tr>
<td>0.122</td>
<td>4.40</td>
<td>5.02</td>
<td>94.8</td>
<td>0.132</td>
<td>1.93</td>
<td>2.97</td>
<td>5.62</td>
</tr>
<tr>
<td>0.162</td>
<td>4.42</td>
<td>5.20</td>
<td>92.3</td>
<td>0.098</td>
<td>1.97</td>
<td>2.89</td>
<td>5.46</td>
</tr>
<tr>
<td>0.162</td>
<td>4.42</td>
<td>5.19</td>
<td>92.1</td>
<td>0.097</td>
<td>2.00</td>
<td>2.86</td>
<td>5.46</td>
</tr>
<tr>
<td>0.121</td>
<td>4.32</td>
<td>5.04</td>
<td>95.1</td>
<td>0.119</td>
<td>2.00</td>
<td>2.91</td>
<td>5.69</td>
</tr>
<tr>
<td>0.121</td>
<td>3.32</td>
<td>5.04</td>
<td>94.7</td>
<td>0.119</td>
<td>2.00</td>
<td>2.95</td>
<td>5.76</td>
</tr>
<tr>
<td>0.162</td>
<td>4.32</td>
<td>4.86</td>
<td>95.2</td>
<td>0.079</td>
<td>1.98</td>
<td>2.90</td>
<td>5.70</td>
</tr>
<tr>
<td>0.162</td>
<td>4.02</td>
<td>4.86</td>
<td>95.2</td>
<td>0.077</td>
<td>2.00</td>
<td>2.93</td>
<td>5.69</td>
</tr>
</tbody>
</table>
TABLE XVII

Extraction of Molybdic Acid by TOAH.C1

Organic layer: - TOAH.C1 in chloroform
Aqueous layer: - Molybdic acid solutions (0.25M Mo)
Equilibration: - 20ml organic layer equilibrated with 40ml aqueous layer for 4 to 8 hours.

<table>
<thead>
<tr>
<th>Conc. of TOAH.C1 in org. phase (Mole/l)</th>
<th>Initial pH of aq. layer</th>
<th>Final pH of aq. layer</th>
<th>% org. layer chloride exchanged</th>
<th>Final Mo concn. in aq. layer (Mole/l)</th>
<th>R</th>
<th>z</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.041</td>
<td>3.74</td>
<td>3.84</td>
<td>97.4</td>
<td>0.225</td>
<td>2.02</td>
<td>3.42</td>
<td>6.48</td>
</tr>
<tr>
<td>0.041</td>
<td>3.74</td>
<td>3.84</td>
<td>97.2</td>
<td>0.225</td>
<td>2.07</td>
<td>3.42</td>
<td>6.56</td>
</tr>
<tr>
<td>0.083</td>
<td>3.58</td>
<td>3.83</td>
<td>98.2</td>
<td>0.182</td>
<td>2.11</td>
<td>3.42</td>
<td>6.70</td>
</tr>
<tr>
<td>0.083</td>
<td>3.58</td>
<td>3.83</td>
<td>97.8</td>
<td>0.180</td>
<td>2.12</td>
<td>3.40</td>
<td>6.80</td>
</tr>
<tr>
<td>0.123</td>
<td>3.50</td>
<td>3.88</td>
<td>97.8</td>
<td>0.141</td>
<td>2.07</td>
<td>3.21</td>
<td>6.67</td>
</tr>
<tr>
<td>0.123</td>
<td>3.50</td>
<td>3.91</td>
<td>98.3</td>
<td>0.141</td>
<td>2.08</td>
<td>3.31</td>
<td>6.86</td>
</tr>
<tr>
<td>0.162</td>
<td>3.36</td>
<td>3.90</td>
<td>97.0</td>
<td>0.100</td>
<td>2.06</td>
<td>3.13</td>
<td>6.31</td>
</tr>
<tr>
<td>0.162</td>
<td>3.36</td>
<td>3.94</td>
<td>97.0</td>
<td>0.100</td>
<td>2.06</td>
<td>3.22</td>
<td>6.52</td>
</tr>
</tbody>
</table>
TABLE XVIII

Extraction of Molybdic Acid by TOAH.Cl

Organic layer: - TOAH.Cl in chloroform
Aqueous layer: - Molybdic acid solutions (0.28M Mo)
Equilibration: - 20ml organic layer equilibrated with 40ml aqueous layer for 4 to 8 hours.

<table>
<thead>
<tr>
<th>Conc. of TOAH.Cl in org. layer (Mole/l)</th>
<th>Initial pH of aq. layer</th>
<th>Final pH of aq. layer</th>
<th>% org. layer</th>
<th>Final Mo chloride exchanged in aq. layer (Mole/l)</th>
<th>Final Mo concn. (Mole/l)</th>
<th>R</th>
<th>z</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.082</td>
<td>4.02</td>
<td>4.30</td>
<td>97.7</td>
<td>0.200</td>
<td>2.01</td>
<td>3.20</td>
<td>6.42</td>
<td></td>
</tr>
<tr>
<td>0.082</td>
<td>4.02</td>
<td>4.34</td>
<td>97.2</td>
<td>0.200</td>
<td>1.98</td>
<td>3.24</td>
<td>6.40</td>
<td></td>
</tr>
<tr>
<td>0.163</td>
<td>3.76</td>
<td>4.34</td>
<td>96.7</td>
<td>0.119</td>
<td>1.99</td>
<td>3.06</td>
<td>6.09</td>
<td></td>
</tr>
<tr>
<td>0.163</td>
<td>3.76</td>
<td>4.35</td>
<td>96.7</td>
<td>0.118</td>
<td>2.03</td>
<td>3.02</td>
<td>6.13</td>
<td></td>
</tr>
</tbody>
</table>
II.10 STUDIES OF THE INFRARED SPECTRA

II.10.a. Infrared Spectra of Organic Layers

Table XIX shows the infrared absorption spectra of the organic layers containing molybdate species. The main features of the spectra are outlined as follows:

(All the pH refer to the equilibrium pH of aqueous layer)

(1) A weak shoulder at 720 cm\(^{-1}\) on the 760 cm\(^{-1}\) broad peak of chloroform is visible clearly in the solutions of pH = 6.08 and 5.69. In the spectra of other solutions it is not seen, probably because it is a weak absorption.

(2) A shoulder at 805-810 cm\(^{-1}\) appears on the broad peak 760 cm\(^{-1}\) of chloroform at pH = 3.62 and becomes stronger at lower pH's.

(3) A distinct peak at 840-850 cm\(^{-1}\) gets weaker with the decrease of pH, so that at pH = 2.38, it is a weak shoulder on the broad peak, 760 cm\(^{-1}\), of chloroform.

(4) Two distinct peaks, at 920 cm\(^{-1}\) and 950-960 cm\(^{-1}\) are observed throughout the pH region studied. But the strength of 950-960 cm\(^{-1}\) peak increases in relation to 918-920 cm\(^{-1}\) peak, so that at pH 5.69 both the peaks are equal in intensity and below this pH, 950-960 cm\(^{-1}\) peak is stronger.
<table>
<thead>
<tr>
<th>CHCl₃</th>
<th>760 (vs,b)</th>
<th>1220 (vs)</th>
<th>3050 (vw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOAH·Cl</td>
<td>760 (w) 935 (vs) 1212 1235 1380 1470 (vw,b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.25M</td>
<td>2400-2475 2870 2950 3050</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE XIX**

Infrared Spectra of Organic Layer (cm⁻¹)

**TOA-molybdates in CHCl₃:**

<table>
<thead>
<tr>
<th>pH of</th>
<th>CHCl₃ layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.58</td>
<td>663 720 760 (w) (s) - 850 920 950 1200 1300 1460 (m) (vw) (vw,920) (s) (vw) (s) -</td>
</tr>
<tr>
<td>6.08</td>
<td>665 705 720 760 (s) (vs,b) - 845 920 950 1205 1370 1460 1600 (m) (s,920)(vs) (w) (s) (vw) (vw) -</td>
</tr>
<tr>
<td>5.69</td>
<td>670 700 720 760 (s) (vs,b) - 845 920 950 1205 1370 1460 1595 (m) (s) (s,920)(vs) (w) (s) (vw) (vw) -</td>
</tr>
<tr>
<td>5.22</td>
<td>665 700 760 (s) (vs,b) - 845 920 950 1205 1370 1460 1595 (m) (s) (s,920)(vs) (w) (s) (vw) (vw) -</td>
</tr>
<tr>
<td>3.62</td>
<td>670 705 810 845 (s) (vs,b) - 920 955 1210 1375 1460 1600 (m) (s) (s,920)(vs) (w) (s) (vw) (vw) -</td>
</tr>
<tr>
<td>2.68</td>
<td>670 700 805 840 (s) (vs,b) (w) (vs) (s) (s) (vw) (vw) (vw) (vw) (vw) -</td>
</tr>
<tr>
<td>0.92</td>
<td>670 700 806 850 (s) (vs,b) (w) (s) (vs) (vs) (w) (s) (vw) (vw) (vw) (vw) -</td>
</tr>
</tbody>
</table>
II.10.b. **Infrared Spectra of Molybdate Species in D₂O**

Table XX shows the absorption intensities of the infrared spectra obtained by dissolving sodium molybdate in D₂O, whilst altering the pH by adding small quantities of concentrated sulphuric acid. The main features of the spectra are as follows:

1. A strong peak at 844 cm⁻¹ in the solutions of pH 7.80 becomes weaker and shifts to a slightly higher wave number with the decrease of pH.

2. A weak absorption at 915 cm⁻¹ at pH 7.80 becomes a strong peak of 900 cm⁻¹ at pH 6.11, and at pH 3.26 splits into a strong peak at 900-923 cm⁻¹ and a weaker peak at 886 cm⁻¹.

3. A weak absorption at 940 cm⁻¹ develops in the solutions of pH 4.22 as a shoulder in the strong peak 920-30 cm⁻¹ and gradually increase in intensity with the decrease in pH so that at pH 1.47 it is stronger than 930 cm⁻¹ peak.

4. A weak absorption at 980 cm⁻¹ is observed in the solutions of pH 5.31, 2.26, and 1.47.

5. Absorptions near 1100 cm⁻¹ are due to sulphate ion.
**TABLE XX**

**Infrared Spectra of Molybdate Species in D$_2$O (cm$^{-1}$)**

<table>
<thead>
<tr>
<th>pH of the molybdate solutions</th>
<th>844 (vs)</th>
<th>915 (vw)</th>
<th>858 (w)</th>
<th>900-920 (s)</th>
<th>940 (w)</th>
<th>1100-1120 (vs, b)</th>
<th>923 (s)</th>
<th>953 (m)</th>
<th>1106 (s)</th>
<th>926 (s)</th>
<th>946 (w)</th>
<th>980 (w)</th>
<th>1105 (vs)</th>
<th>890 (w)</th>
<th>930 (m)</th>
<th>946 (s)</th>
<th>980 (w)</th>
<th>1057 (vs)</th>
<th>1110 (vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
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<tr>
<td>6.11</td>
<td>844 (s)</td>
<td>900 (s)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.31</td>
<td>846 (m)</td>
<td>900 (s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.22</td>
<td>858 (w)</td>
<td>900-920 (s)</td>
<td>940 (w)</td>
<td>1100-1120 (vs, b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>3.26</td>
<td>853 (w)</td>
<td>Intensity &gt; 100%</td>
<td>923 (s)</td>
<td>953 (m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2.26</td>
<td>853 (w)</td>
<td>886 (w)</td>
<td>926 (s)</td>
<td>946 (s)</td>
<td>980 (w)</td>
<td>1105 (vs)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>1.47</td>
<td>890 (w)</td>
<td></td>
<td>930 (m)</td>
<td>946 (s)</td>
<td>980 (w)</td>
<td>1057 (vs)</td>
<td>1110 (vs)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
II.11. INVESTIGATIONS OF TOA COMPOUNDS OF MOLYBDATES

It was found that the compounds of isopolymolybdate ions with TOA are insoluble in aliphatic hydrocarbons and therefore provide a method to obtain these compounds in solid state. The solvents used for this purpose were kerosene (b.pt. 170-190°C), and n-hexane. The general procedure for preparing these solids is as follows:

An organic solution of TOAH·Cl was prepared by dissolving a measured quantity of TOA in kerosene. A small amount of n-heptyl alcohol (about 4%) was added in order to increase the solubility of TOAH·Cl. TOA was then converted into TOAH·Cl by shaking the amine solution with 2M hydrochloric acid in a ratio of 2:1 by volume. The organic layer was separated and added to solutions of molybdic acid of various pH (prepared as described in section II.2.).

The two layers were shaken vigorously and a solid precipitated immediately in the organic layer. When the shaking was complete (3-4 hours), the organic layer containing solid was separated from the aqueous layer and filtered through
a Buchner funnel and washed repeatedly with kerosene to remove unreacted TOAH.Cl. When the solid was freed from solvent it was dried for several days in vacuo.

The solid obtained from the molybdic acid solution of pH 1.04 was greenish yellow in colour, whereas the solids which were precipitated from molybdic acid solutions of pH \(> 1.04\) were bright yellow in colour and had a soapy appearance. It was found that on using n-hexane as the solvent same solids may be obtained.

The elemental analyses of these solids is given in Table XXI. The solids precipitating at pH 1.96 and 4.02 were also sent for microanalysis for carbon, hydrogen, and nitrogen. It may be seen that both of these solids correspond to R value = 2.0, which was calculated as the \% mole ratio of molybdenum and 24 carbon atoms. In order to arrive at the degree of aggregation of molybdenum in these solids, their molecular weights were determined by means of the Vapour Pressure Osmometer. The results are given in Tables XXII and XXIII. A peculiar behaviour may be noticed in that these solids have low number-average molecular weight \(M_n\) at low concentrations. This indicates a dissociation of the
compound in dilute solutions, and though the values of $M_n$ are nearly constant at high concentration, an idea of real molecular weight of the compound is difficult to obtain.
TABLE XXI

Analysis of TOA-Molybdates

<table>
<thead>
<tr>
<th>pH of aq. phase at precipitation</th>
<th>Mo %</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
<th>R %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.04</td>
<td></td>
<td>31.84</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.96</td>
<td>29.71</td>
<td>42.81</td>
<td>7.36</td>
<td>2.20</td>
<td>2.07</td>
</tr>
<tr>
<td>3.00</td>
<td>27.92</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.02</td>
<td>28.68</td>
<td>43.39</td>
<td>7.67</td>
<td>2.47</td>
<td>2.02</td>
</tr>
</tbody>
</table>

TABLE XXII

Number-average Molecular Weight of Solid Precipitating at pH = 1.96

<table>
<thead>
<tr>
<th>Concentration in g/l C</th>
<th>ΔT (4 mins.)</th>
<th>Concentration (Mole/l) from graph</th>
<th>$M_n = C/m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.97</td>
<td>1.48</td>
<td>0.0035</td>
<td>1.134</td>
</tr>
<tr>
<td>8.82</td>
<td>2.64</td>
<td>0.007</td>
<td>1.260</td>
</tr>
<tr>
<td>19.82</td>
<td>5.26</td>
<td>0.014</td>
<td>1.415</td>
</tr>
<tr>
<td>36.80</td>
<td>8.84</td>
<td>0.024</td>
<td>1.533</td>
</tr>
<tr>
<td>58.90</td>
<td>14.63</td>
<td>0.039</td>
<td>1.510</td>
</tr>
<tr>
<td>61.30</td>
<td>16.30</td>
<td>0.043</td>
<td>1.409</td>
</tr>
<tr>
<td>70.75</td>
<td>18.29</td>
<td>0.049</td>
<td>1.443</td>
</tr>
</tbody>
</table>
TABLE XXIII

Number-average Molecular Weight of the Solid Precipitated at pH = 4.02

<table>
<thead>
<tr>
<th>Concentration (g/l)</th>
<th>δT (4 mins.)</th>
<th>Concentration (Mole/l)</th>
<th>Mₙ = C/ₙm</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.97</td>
<td>1.75</td>
<td>0.0045</td>
<td>1,993</td>
</tr>
<tr>
<td>14.66</td>
<td>2.89</td>
<td>0.0075</td>
<td>1,954</td>
</tr>
<tr>
<td>29.20</td>
<td>5.14</td>
<td>0.014</td>
<td>2,085</td>
</tr>
<tr>
<td>40.50</td>
<td>6.78</td>
<td>0.018</td>
<td>2,250</td>
</tr>
<tr>
<td>44.50</td>
<td>7.42</td>
<td>0.020</td>
<td>2,225</td>
</tr>
<tr>
<td>60.70</td>
<td>9.78</td>
<td>0.026</td>
<td>2,334</td>
</tr>
<tr>
<td>83.50</td>
<td>13.04</td>
<td>0.035</td>
<td>2,385</td>
</tr>
</tbody>
</table>
SECTION III

DISCUSSION
The results of the extraction of molybdic acid by TOA\textsubscript{HCl} give a strong indication that two isopolymolybdate ions prevail in solutions of pH below 5.0. These ions are characterised by the ratio of the number of molybdenum atoms per unit charge (R value) and their abundance is shown by the constant R value plateaux. Figure 3 indicates that there are two such plateaux, one of R = 2.0, and the other of R = 2.5. Confirmation of the R value = 2.0 ions was obtained by precipitating a compound of TOA molybdate using kerosene (section II.11). In solutions of pH higher than 5.0, hydrolysis of the amine hydrochloride, TOA\textsubscript{HCl}, takes place, and for this reason this pH region cannot be investigated by this method.

**IV.1. R = 2.0 ION**

The plateau representing R = 2.0 extends from pH 3.5 to 4.8. That the R value is constant for such a wide pH range indicates that all the molybdenum is probably in one particular ionic form over this range. The affinity of this ion for amine is evident from the very high percentage of the chloride of the organic phase which is replaced during the
extraction, with the result that the organic layer, after extraction, consists almost entirely of a solution of the amine salt of this particular ionic species. It may be noted that an \( R = 2.0 \) ion has also been observed in the ion exchange experiments of Cooper and Salmon[48].

Though it is quite obvious that the ion of \( R = 2.0 \) prevails in these solutions of isopolymolybdates, the determination of its formula is still a problem, since the \( R \) value gives only the metal to charge ratio of this ion. Therefore, an independent determination of number of metal atoms in an ion or the charge carried by this ion is needed. This aim was achieved in the present work by carrying out measurements of vapour pressure lowering by means of a Vapour Pressure Osmometer. The degree of aggregation \((n)\) and the charge \(z\) of the ion of \( R = 2.0 \) were then calculated as described in section II.9.g. Reference to Tables XIV to XVIII confirms the constancy of \( R = 2.0 \) in the range of pH 3.8 to 4.8, but similar constancy was not observed in the values of \( n \) and \( z \), however. The \( n \) and \( z \) values became fairly constant for a particular value of the pH of the aqueous layer at equilibrium but a slight increase in these values was observed at the lower pH end of the plateau.
The accuracy of the instrument is reported by the manufacturers to be better than 5% for solutes of molecular weight less than \(10^4\). However, the method of calculating the \(n\) values in the present work involves a correction for the unexchanged TOAH Cl, and, when account is also taken of the mixed nature of the solvent, the accuracy of the results may be much poorer. Moreover, it should be emphasised that in the present series of experiments a high accuracy in the values of \(n\) and \(z\) is not required since it is reasonable that these values should be integers for single species and since the \(n\) values have to be a multiple of 2.0. When these facts are borne in mind a survey of the results in Table XIV to XVIII reveals that the closest values meeting these requirements are \(n = 6\) and \(z = 3\). Isopolymolybdate ions containing 6 molybdenum atoms have been reported frequently in the literature and are listed in Table I. Obviously, a selection of the ion is not possible until some rules are formulated to eliminate some of the possibilities. Clearly, the structural characteristics of these ions must be an important factor in deciding their stability. It was realised that this was not the usual approach adopted in most of the early
work which was carried out on molybdates. Indeed several ions have been postulated without any evidence in support of one formulation as opposed to another. The determination of structure by means of X-ray crystallography is generally possible only in the case of solids. Although it is not justified to assume that a structure present in the solid state need necessarily be present in solution, a consideration of the known structures of similar types of compounds may provide a basis to decide the probable nature of ions in solution. Therefore, a survey of the known polyions, related to isopolymolybdates, is described below. In fact, in the present work, a solid precipitated from the organic phase by kerosene did not show, on dissolution in chloroform, exactly the same vapour pressure lowering characteristics as the organic layers themselves, although the solid had $R = 2.0$ (section 11.11). The constancy of the $R$ value, however, indicates that the complex polyanion itself is similar in both cases, whereas lattice and solvation energies may materially affect the respective colligative properties of an ionic salt on the one hand and a species formed in solution on the other.

In the case of isopolymolybdates, the crystal structures of the salts of two ions, \( \text{Mo}_7\text{O}_{24}^{6-} \) and \( \text{Mo}_8\text{O}_{26}^{4-} \) (Figure 6.1, 6.2) have been described by Lindqvist\(^97\). They are composed of units of \( \text{MoO}_6 \) octahedra which are joined together by sharing of edges.

Sharing of octahedra is a common feature of all the polyacid structures. In the case of the isopolytungstate series, it is the \( \text{WO}_6 \) octahedra which form the polymeric framework. One structure in this group is that of the paratungstate ion, \( W_{12}\text{O}_{46}^{20-} \), which was first reported by Lindquist\(^143\), after determining the positions of tungsten atoms only and deducing the position of oxygen atoms from symmetry considerations. On the basis of arguments set out below, Lipscomb\(^144\) has proposed a revision of this structure and has given a new formulation represented by \( W_{12}\text{O}_{42}^{12-} \) (Figure 6.3).

The heteropolyacids are characterised by the presence of a foreign atom which usually occupies a central position around which octahedra of \( \text{MoO}_6 \) or \( \text{WO}_6 \) are arranged. They are
Fig. 6

(1) $\text{Mo}_7\text{O}_{24}^{-6}$

(2) $\text{Mo}_8\text{O}_{26}^{-4}$

(3) $\text{W}_{12}\text{O}_{42}^{-12}$
classified according to the number of octahedral groups
associated with the central hetero group and termed 6-poly, 
9-poly, and 12-poly acids. The structure of these acids 
reveals similarities in one group[145]. It has been found 
that 9-poly and 12-poly acids have a central group containing 
the hetero atom, XO₄, in a tetrahedral environment which, 
in turn, is surrounded by an appropriate number of MoO₆ or 
WO₆ octahedra. A typical 12-polyacid ion is PW₄₀⁴⁺⁻ which 
was found to consist of a central PO₄ tetrahedron surrounded 
by four tritungstate groups consisting of WO₆ octahedra 
joined by sharing of adjacent edges with each of two 
neighbours (Keggin structure, Figure 7.1). The metatungstate ion 
H₂W₄₀⁴⁻⁺⁻, is of similar structure but without any 
hetero atom, and is isomorphous with PW₄₀⁴⁺⁻⁻. The 
central hetero atoms usually found in 9-poly and 12-polyacids 
are P, As, Si, Ti, Ge, B, Sn, and Zr.

The structure of a 6-polyacid is found to be composed 
of a central XO₆ octahedron which shares oxygen atoms with 
six MoO₆ or WO₆ octahedra. A typical example is the 
telluromolybdate, TeMo₆O₂₄⁶⁻⁻ (Figure 7.2 ). The hetero atoms 
generally found in 6-polyacids are Te, I, Fe, Cr, Al, Co, Rl, 
and Mn.
Fig. 7

(1) PMo$_{12}$O$_{40}^3$-

(2) TeMo$_6$O$_{24}^6$-
III.2.a. Common Structural Groups

The survey of known structures of polyacids provides the possibility of looking into some similarities on the basis of common structural groups. These were found to be groups of 3 octahedra joined together in various ways giving rise to the following types (Figure 8):

1. The three octahedra may join linearly (Mo$_3$O$_{14}$$^{10-}$).

2. Two octahedra may join linearly while the third occupies the edges on the either side of the shared edge (Keggin structure) (Mo$_3$O$_{13}$$^{8-}$).

3. Two octahedra may join linearly while the third occupies one of the far edges of an octahedron. This arrangement exists in d- and l- forms (Mo$_3$O$_{14}$$^{10-}$).

4. Two octahedra may be placed on top of each other while the third occupies adjacent edges (Mo$_3$O$_{14}$$^{10-}$).

These groups of 3 octahedra are found invariably in the known structures as most of the structures may be constructed by joining together different combinations of these trimeric units. The polyionic aggregates with a number of metal atoms not divisible by 3, may be regarded as build up of groups of three plus one or two octahedra which are presumably always present albeit in small concentration in equilibrium.
Fig. 8

(1)  

(2)  

(3)  

(4)
with the trimers and higher polymers. A surprisingly high proportion of the known iso- and heteropolyacid species can be built up of units of types (2) and (3) above, occasionally involving type (4) as well. It seems possible, therefore, that these may be fundamental units of the iso- and heteropoly anion structures.

III.3. STRUCTURE OF THE Mo_6_ ION

It was decided to build models of the structures of 6-aggregated ions of molybdenum, evidence for which was obtained by vapour pressure lowering measurements. A limitation on deciding the possible structure is imposed by the R value of this ion which should be 2.0. For this reason, the non-protonated ion Mo_6^2^- is not possible. The ions with higher oxygen content will have to be protonated to get the correct R value and formulae like HMo_6^3^- , H_3Mo_6^3^- , and H_5Mo_6^3^- are possible. The higher protonated species than these are excluded from the scheme as being less likely to occur near pH 4.0.
Model building was carried out bearing in mind that the ultimate structure must be composed of groups of 3 octahedra described above. It was found, for example, that the structure $\text{HMo}_6\text{O}_{20}^{3-}$ cannot be constructed in this way. Two structures represented by $\text{Mo}_6\text{O}_{21}^6$- (or $\text{H}_3\text{Mo}_6\text{O}_{21}^3$-) and 15 structures represented by $\text{Mo}_6\text{O}_{22}^8$- (or $\text{H}_5\text{Mo}_6\text{O}_{22}^3$-), were made and are listed in Table XXIV. The positions of the six octahedra in a structure are described in the second column of Table XXIV by means of the notation of Lipscomb\textsuperscript{[146]}, which may be explained in the following way:

(i) $00$ indicates two octahedra joined linearly. The sign $\frac{1}{2}$ indicates a third octahedron in between the two; $+\frac{1}{2}$ indicates that this octahedron is in front of the plane of linear octahedra whilst $-\frac{1}{2}$ indicates that the third octahedron is behind the plane of two linear octahedra.

(ii) $0\phi$ indicates that a third octahedron is joined to the front edge of one of the linear octahedra. These notations become clearer on inspection of Figure 8, where the notations have been written by the side of the structural diagrams.

Selection rules were formulated in order to eliminate certain structure and to arrive at the best possible structures.
for Mo₆ ions. The following two points were taken into consideration:

(i) The structure should have an ability to form the known Mo₇O₂₄⁶⁻ and Mo₈O₂₆⁴⁻ structures by simple addition of one or two octahedra without any rearrangement of the basic Mo₆ unit.

(ii) From an inspection of the known structures of isopoly- and heteropoly- acid structures, Lipscomb[146] found that the sum of the formal negative charge on the oxygen atoms in an octahedron does not exceed to 7.5. (The formal negative charge of oxygen atoms is calculated by assuming that if the oxygen atom is held by only one molybdenum atom, the formal charge will be ²/₁ = 2.0, if it is shared by two molybdenum atoms the formal charge will be ²/₂ = 1.0, etc.) On almost the same basis, Lipscomb found that all the known isopoly- and heteropoly- acid structures have no octahedra containing more than two unshared oxygen atoms on any one octahedron. It was on this basis that he proposed the revision of the formula of the paratungstate mentioned above.

The applicability of these two rules for the 17 postulated structures of Mo₆ ions is now discussed.
(i) Capability of forming known Mo\textsubscript{$7$}O\textsubscript{24}\textsuperscript{6-} and Mo\textsubscript{$8$}O\textsubscript{26}\textsuperscript{4-} structures

From the inspection of the known structures of Mo\textsubscript{$7$}O\textsubscript{24}\textsuperscript{6-} and Mo\textsubscript{$8$}O\textsubscript{26}\textsuperscript{4-} ions it was realised that there are certain Mo\textsubscript{$6$} structural units which will not form either both or one of these structures, for example,

(a) Structures containing the units, 00\Phi , 00\textsuperscript{+2}0 , and 0\Phi 0 cannot form either the Mo\textsubscript{$7$}O\textsubscript{24}\textsuperscript{6-} or the Mo\textsubscript{$8$}O\textsubscript{26}\textsuperscript{4-} structure.

(b) Structures containing the unit 000 cannot form the Mo\textsubscript{$8$}O\textsubscript{26}\textsuperscript{4-} structure, whereas the unit 0\Phi cannot form the Mo\textsubscript{$7$}O\textsubscript{24}\textsuperscript{6-} structure.

This is, however, not a complete list of the criteria used to determine whether a structure will give the Mo\textsubscript{$7$}O\textsubscript{24}\textsuperscript{6-} and Mo\textsubscript{$8$}O\textsubscript{26}\textsuperscript{4-} structures, and therefore all the 17 postulated Mo\textsubscript{$6$} structures were examined individually to see if they are able to form the known Mo\textsubscript{$7$}O\textsubscript{24}\textsuperscript{6-} and Mo\textsubscript{$8$}O\textsubscript{26}\textsuperscript{4-} structures by the simple addition of one or two octahedra. The result of such an examination is listed in Table XXIV, where it may be seen that only one structure, number 17, was found to form both Mo\textsubscript{$7$}O\textsubscript{24}\textsuperscript{6-} and Mo\textsubscript{$8$}O\textsubscript{26}\textsuperscript{4-} structures, whilst six other structures, Nos. 2, 4, 5, 12, 13, and 15 were found to be
capable of conversion into either one or the other of the known structures. Since all the remaining structures do not form either of the known Mo_7 or Mo_8 structures, they are eliminated from the list of possible structure for the Mo_6 ion. The seven remaining structures are now subjected to an examination of the number and arrangement of formal charges on the oxygen atoms.

(ii) Formal charge on oxygen atom:

The formal charge on oxygen atoms in each octahedron of the Mo_6 structures was calculated and the results given in Table XXV. These results are described in the order of oxygen atoms occupying the ±x, ±y, ±z axes of an octahedron. The sum of the formal charges, $\sum n_i$ for each octahedron is also given in Table XXV, as well as the charge symmetry whereby a structure is described in terms of the number of octahedra having equal values of $\sum n_i$. A similar treatment is given to some of the known isopoly- and heteropolyion structures in Table XXVI, wherein it may be seen that the value of the highest charge on any particular octahedron is never greater than 7.5, and this may be considered to be a criterion for the stability of an ion.
Another criterion of stability may be deduced from the symmetry of charge distribution which is displayed to a great extent by the known structures (Table XXV). This means that the known structures have large groups of octahedra having the same total formal charge on oxygen atoms. Subjecting the seven Mo₆ structures to these criteria, it is immediately realised that all of these structures have some values of Σn_i > 7.5 (Table XXV). However, it was thought that a value of Σn_i = 8.5 should be regarded as too high a formal charge on an octahedron because the resulting structure may become very unstable. On these grounds, structures Nos. 4, 5, 12, 13, 15, were eliminated from the scheme of possible Mo₆ structures. It has also to be noticed that amongst these, structure Nos. 5 and 12 have a very unsymmetrical charge distribution. The choice is now left between structures 2 and 17. Structure 2 has a maximum value of Σn_i = 8.0 on only one octahedron and has two groups of equal charges, but it can form only the Mo₈O₂₆⁴⁻ structure (Table XXIV). Structure 17 has a maximum value of Σn_i = 8.33 on two octahedra and has three groups of equal Σn_i. However, this structure can form both the known Mo₇O₂₄⁶⁻ and Mo₈O₂₆⁴⁻ structures. Obviously
it is difficult to choose between these two, and therefore in the present discussion both of these will be assumed to coexist in the solution of hexamolybdates. These structures are shown in Figures 9.1 and 9.2.

After arriving at the nature of the ion of $R = 2.0$, the next stage of condensation represented by $R = 2.5$ is now discussed.

III.4. $R = 2.50$ ION

In Figure 3, it may be seen that the ion of $R = 2.50$ is predominant in solutions of pH below 1.5. The length of the plateau is rather short and also the tendency to precipitation in the aqueous phase over most of this region inhibits extensive studies. The $R$ value of the highest aggregated ion in the case of the ion exchange studies was 5.0. This difference is readily explained if it is assumed that the ion $H_2\text{Mo}_{10\text{0}}^{2-}$ is sorbed by the resin while the ion $\text{Mo}_{10\text{0}}^{4-}$ is extracted by the amine. Because of the large size of the 10-aggregated ion, four amine molecules surrounding it seems to be necessary to make the resulting compound stable in the organic solvent. Some determinations of vapour pressure
Fig. 9

(1) $\text{Mo}_6\text{O}_{21}^{6-}$

(2) $\text{Mo}_6\text{O}_{22}^{8-}$

(3) $\text{Mo}_{10}\text{O}_{32}^{4-}$
lowering gave a value of the aggregation number between 9 and 11 (Table XIII). The fact that this value should be a multiple of 2.5 indicates an aggregate involving ten molybdenum atoms as the nearest value and confirms the $\text{Mo}_{10}^{0}32^{4-}$ formulation. The structure of $\text{Mo}_{10}^{0}32^{4-}$ is predicted by Lipscomb [146] as one of the ions which would follow his general rule for stable polyions, and the structure consists of 3 rows of octahedra, with the top and the bottom rows consisting of 3 octahedra whilst the remaining 4 octahedra form a middle row behind the other two. This structure is shown in Figure 9.3. It has a $C_{2v}$ symmetry and may be built up by the simple addition of a group of 3 octahedra (group (4) in section III.2.a.) to the structure of $\text{Mo}_7^{0}24^{6-}$. The structure of $\text{Mo}_8^{0}26^{4-}$, however, does not lead to this structure. Table XXVI gives the value of $\sum n_i$ and the charge symmetry of this structure, and from a consideration of the criteria used for a stable ion, which were discussed in section III.3., it seems that this is a very stable structure with a maximum value of $\sum n_i = 7.5$, whilst two groups, one consisting of 4 and the other consisting of 3 octahedra, each have equal values of $\sum n_i$. 
### TABLE XXIV

**Postulated Mo\textsubscript{6} Structures**

<table>
<thead>
<tr>
<th>Structure No.</th>
<th>Formula</th>
<th>Structural notation</th>
<th>Possibility of conversion into ( \text{Mo}<em>7^0 \text{O}</em>{24} ) or ( \text{Mo}<em>8^0 \text{O}</em>{26} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( \text{Mo}<em>6^0 \text{O}</em>{21} )</td>
<td>( 1/0 ) ( 1/0 )</td>
<td><strong>None</strong></td>
</tr>
<tr>
<td>2.</td>
<td>( \text{Mo}<em>6^0 \text{O}</em>{21} )</td>
<td>( 0^{+\frac{1}{2}} ) ( 0^{-\frac{1}{2}} )</td>
<td>( \text{Mo}_8 )</td>
</tr>
<tr>
<td>3.</td>
<td>( \text{Mo}<em>6^0 \text{O}</em>{22} )</td>
<td>( 0^{-\frac{1}{2}} ) ( \phi^\frac{1}{2} )</td>
<td><strong>Mo\textsubscript{8}</strong></td>
</tr>
<tr>
<td>4.</td>
<td>( \text{Mo}<em>6^0 \text{O}</em>{22} )</td>
<td>( -\phi^{+\frac{1}{2}} ) ( 0^\frac{1}{2} )</td>
<td><strong>Mo\textsubscript{8}</strong></td>
</tr>
<tr>
<td>5.</td>
<td>( \text{Mo}<em>6^0 \text{O}</em>{23} )</td>
<td>( 0^{+\frac{1}{2}} ) ( 0^\frac{1}{2} )</td>
<td><strong>Mo\textsubscript{8}</strong></td>
</tr>
<tr>
<td>6.</td>
<td>( \text{Mo}<em>6^0 \text{O}</em>{23} )</td>
<td>( 0^\frac{1}{2} ) ( 0^{-\frac{1}{2}} )</td>
<td><strong>None</strong></td>
</tr>
<tr>
<td>7.</td>
<td>( \text{Mo}<em>6^0 \text{O}</em>{24} )</td>
<td>( 0^{+\frac{1}{2}} ) ( \phi^{-\frac{1}{2}} )</td>
<td><strong>None</strong></td>
</tr>
<tr>
<td>8.</td>
<td>( \text{Mo}<em>6^0 \text{O}</em>{24} )</td>
<td>( 0^\frac{1}{2} ) ( 0^{+\frac{1}{2}} )</td>
<td><strong>None</strong></td>
</tr>
<tr>
<td>9.</td>
<td>( \text{Mo}<em>6^0 \text{O}</em>{25} )</td>
<td>( 0^\frac{1}{2} ) ( 0^{+\frac{1}{2}} ) ( 0^\frac{1}{2} )</td>
<td><strong>None</strong></td>
</tr>
<tr>
<td>10.</td>
<td>( \text{Mo}<em>6^0 \text{O}</em>{25} )</td>
<td>( 0^\frac{1}{2} ) ( 0^{-\frac{1}{2}} ) ( \phi^\frac{1}{2} )</td>
<td><strong>None</strong></td>
</tr>
<tr>
<td>11.</td>
<td>( \text{Mo}<em>6^0 \text{O}</em>{26} )</td>
<td>( 0^{+\frac{1}{2}} ) ( 0^{-\frac{1}{2}} ) ( 0^\frac{1}{2} )</td>
<td><strong>None</strong></td>
</tr>
<tr>
<td>12.</td>
<td>( \text{Mo}<em>6^0 \text{O}</em>{26} )</td>
<td>( 0^{+\frac{1}{2}} ) ( 0^{+\frac{1}{2}} ) ( 0^\frac{1}{2} )</td>
<td><strong>Mo\textsubscript{7}</strong></td>
</tr>
</tbody>
</table>
TABLE XXIV (Contd.)

<table>
<thead>
<tr>
<th>Structure No.</th>
<th>Formula</th>
<th>Structural notation</th>
<th>Possibility of conversion into $\text{Mo}<em>{7}^{6-}$ or $\text{Mo}</em>{8}^{4-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.</td>
<td>$\text{Mo}_{6}^{8-}$</td>
<td>$0\frac{1}{2} 0\frac{1}{2}$</td>
<td>None</td>
</tr>
<tr>
<td>14.</td>
<td>$\text{Mo}_{6}^{8-}$</td>
<td>$0\frac{1}{2} 0\frac{1}{2}$</td>
<td>None</td>
</tr>
<tr>
<td>15.</td>
<td>$\text{Mo}_{6}^{8-}$</td>
<td>$0\frac{1}{2} 0\frac{1}{2}$</td>
<td>$\text{Mo}_{8}$</td>
</tr>
<tr>
<td>16.</td>
<td>$\text{Mo}_{6}^{8-}$</td>
<td>$0\frac{1}{2} 0\frac{1}{2}$</td>
<td>None</td>
</tr>
<tr>
<td>17.</td>
<td>$\text{Mo}_{6}^{8-}$</td>
<td>$0\frac{1}{2} 0\frac{1}{2}$</td>
<td>$\text{Mo}<em>{7}$ and $\text{Mo}</em>{8}$</td>
</tr>
</tbody>
</table>
TABLE XXV

Charge Distribution and Charge Symmetry of Postulated Mo6 Structures

<table>
<thead>
<tr>
<th>Structure No.</th>
<th>Charge Distribution</th>
<th>$\sum n_1$</th>
<th>Charge Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>$2 \frac{2}{3} 2 \frac{1}{2} \frac{2}{3} 2$</td>
<td>8.00</td>
<td>2 x 7.40</td>
</tr>
<tr>
<td></td>
<td>$\frac{2}{3} 1 \frac{2}{3} 1 \frac{2}{3} 2$</td>
<td>5.73</td>
<td>2 x 6.73</td>
</tr>
<tr>
<td></td>
<td>$\frac{2}{3} 1 2 \frac{2}{5} 2 \frac{2}{3}$</td>
<td>6.73</td>
<td>1 x 8.00</td>
</tr>
<tr>
<td></td>
<td>$\frac{2}{5} 2 1 1 2 1$</td>
<td>7.40</td>
<td>1 x 5.73</td>
</tr>
<tr>
<td>4.</td>
<td>$2 \frac{1}{2} 1 2 2 1$</td>
<td>8.50</td>
<td>2 x 8.5</td>
</tr>
<tr>
<td></td>
<td>$1 \frac{2}{3} 2 \frac{1}{2} \frac{2}{3} 2$</td>
<td>6.83</td>
<td>2 x 6.83</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{2} 1 \frac{2}{3} 2 \frac{1}{2} 2$</td>
<td>6.67</td>
<td>2 x 6.67</td>
</tr>
<tr>
<td></td>
<td>$1 \frac{1}{2} \frac{2}{3} 2 2 \frac{1}{2}$</td>
<td>6.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\frac{2}{3} 1 2 \frac{1}{2} 2 \frac{2}{3}$</td>
<td>6.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{2} 2 1 2 2 1$</td>
<td>8.50</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>$2 1 2 \frac{1}{2} 1 2$</td>
<td>8.50</td>
<td>2 x 8.5</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{2} 2 1 \frac{2}{3} \frac{1}{2} 2$</td>
<td>6.67</td>
<td>1 x 7.83</td>
</tr>
<tr>
<td></td>
<td>$2 \frac{1}{2} 1 \frac{2}{3} 1 \frac{1}{2}$</td>
<td>5.67</td>
<td>1 x 6.83</td>
</tr>
<tr>
<td></td>
<td>$\frac{2}{3} 2 \frac{1}{2} 2 1 \frac{2}{3}$</td>
<td>6.83</td>
<td>1 x 6.67</td>
</tr>
<tr>
<td></td>
<td>$1 2 2 1 2 \frac{1}{2}$</td>
<td>8.50</td>
<td>1 x 5.67</td>
</tr>
<tr>
<td></td>
<td>$2 \frac{2}{3} \frac{1}{2} 2 \frac{2}{3} 2$</td>
<td>7.83</td>
<td></td>
</tr>
</tbody>
</table>

contd.....
<table>
<thead>
<tr>
<th>Structure No.</th>
<th>Charge Distribution</th>
<th>$\sum n_1$</th>
<th>Charge Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>1 2 2 1 2 $\frac{1}{2}$</td>
<td>8.50</td>
<td>1 x 8.67</td>
</tr>
<tr>
<td></td>
<td>1 2 $\frac{2}{3}$ 2 2 1</td>
<td>8.67</td>
<td>1 x 8.50</td>
</tr>
<tr>
<td></td>
<td>1 $\frac{2}{3}$ $\frac{1}{2}$ 1 1 $\frac{2}{3}$</td>
<td>4.83</td>
<td>1 x 7.50</td>
</tr>
<tr>
<td></td>
<td>2 $\frac{1}{2}$ 2 1 1 1</td>
<td>7.50</td>
<td>1 x 7.33</td>
</tr>
<tr>
<td></td>
<td>$\frac{2}{3}$ 2 1 1 $\frac{2}{3}$ 2</td>
<td>7.33</td>
<td>1 x 7.17</td>
</tr>
<tr>
<td></td>
<td>1 1 2 $\frac{2}{3}$ $\frac{1}{2}$ 2</td>
<td>7.17</td>
<td>1 x 4.83</td>
</tr>
<tr>
<td>13</td>
<td>2 1 $\frac{1}{2}$ 2 2 1</td>
<td>8.50</td>
<td>2 x 8.5</td>
</tr>
<tr>
<td></td>
<td>1 1 2 $\frac{1}{2}$ 2 $\frac{1}{2}$</td>
<td>7.00</td>
<td>2 x 7.50</td>
</tr>
<tr>
<td></td>
<td>1 1 $\frac{1}{2}$ 1 $\frac{1}{2}$ 1</td>
<td>5.00</td>
<td>1 x 7.00</td>
</tr>
<tr>
<td></td>
<td>2 $\frac{1}{2}$ 2 1 1 1</td>
<td>7.50</td>
<td>1 x 5.00</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{2}$ 2 1 1 2 1</td>
<td>7.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 2 2 1 $\frac{1}{2}$ 2</td>
<td>8.50</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1 2 2 1 $\frac{1}{2}$ 2</td>
<td>8.50</td>
<td>2 x 8.50</td>
</tr>
<tr>
<td></td>
<td>2 $\frac{1}{2}$ 2 1 1 1</td>
<td>7.50</td>
<td>2 x 7.50</td>
</tr>
<tr>
<td></td>
<td>1 1 $\frac{1}{2}$ 2 $\frac{1}{2}$ 1</td>
<td>6.00</td>
<td>2 x 6.00</td>
</tr>
<tr>
<td></td>
<td>1 1 2 $\frac{1}{2}$ 1 $\frac{1}{2}$</td>
<td>6.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{2}$ 2 1 2 1 1</td>
<td>7.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 1 1 2 2 $\frac{1}{2}$</td>
<td>8.50</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>1 1 2 $\frac{2}{3}$ 2 $\frac{1}{2}$</td>
<td>7.17</td>
<td>2 x 8.33</td>
</tr>
<tr>
<td></td>
<td>$\frac{2}{3}$ 2 1 2 2 $\frac{2}{3}$</td>
<td>8.33</td>
<td>2 x 7.33</td>
</tr>
<tr>
<td></td>
<td>2 $\frac{1}{2}$ 2 1 1 1</td>
<td>7.50</td>
<td>1 x 7.50</td>
</tr>
<tr>
<td></td>
<td>1 $\frac{2}{3}$ $\frac{1}{2}$ 2 $\frac{2}{3}$ $\frac{2}{3}$</td>
<td>5.50</td>
<td>1 x 5.50</td>
</tr>
<tr>
<td></td>
<td>1 1 2 $\frac{2}{3}$ $\frac{1}{2}$ 2</td>
<td>7.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\frac{2}{3}$ 2 1 2 $\frac{2}{3}$ 2</td>
<td>8.33</td>
<td></td>
</tr>
</tbody>
</table>
## TABLE XXVI

Charge Symmetry of Some Known Isopoly- and Heteropolyanion Structure

<table>
<thead>
<tr>
<th>No.</th>
<th>Formula</th>
<th>Structural notation</th>
<th>Charge Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.</td>
<td>Mo$<em>7$$O</em>{24}$</td>
<td>$0 \frac{1}{2} 0 \frac{1}{2} 0$</td>
<td>2 x 7.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4 x 7.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 x 4.33</td>
</tr>
<tr>
<td>19.</td>
<td>Mo$<em>8$$O</em>{26}$</td>
<td>$0 \frac{1}{2} \frac{1}{2} 1$</td>
<td>2 x 7.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4 x 6.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 x 5.10</td>
</tr>
<tr>
<td>20.</td>
<td>TeMo$<em>6$$O</em>{24}$</td>
<td>$0 \frac{1}{2} 0 \frac{1}{2} 0$</td>
<td>6 x 7.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 x 3.00</td>
</tr>
<tr>
<td>21.</td>
<td>MnMo$<em>9$$O</em>{32}$</td>
<td>$0 \frac{1}{2} \frac{1}{2} \frac{1}{2} 0$</td>
<td>3 x 7.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6 x 6.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 x 3.00</td>
</tr>
<tr>
<td>22.</td>
<td>Mo$<em>{10}$$O</em>{32}$</td>
<td>$0 \frac{1}{2} 0 \frac{1}{2} 0 \frac{1}{2} 0$</td>
<td>2 x 7.50</td>
</tr>
<tr>
<td></td>
<td>(postulated)</td>
<td></td>
<td>4 x 7.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 x 5.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 x 4.33</td>
</tr>
</tbody>
</table>
III.5. THEORY OF THE FORMATION OF ISOPOLYMOLYBDATE IONS IN AQUEOUS SOLUTION

III.5.a. SIMILARITIES IN THE SPECIES IN THE AQUEOUS AND ORGANIC PHASES

Before giving a scheme for the formation of isopolymolybdate ions in aqueous solution, it has to be emphasised that the species which are extracted by amine and were present in the organic phase are thought to prevail in the aqueous solution. Sufficient proof of this is available from a comparison of the sorption of molybdate species by ion exchange resins and the extraction by TOAH.CI from aqueous solutions. There are marked similarities in the two types of extractions despite the fact that in one, the solution is essentially an aqueous gel and in the other the extractant is essentially non-aqueous. Furthermore, from the infrared spectra of the organic layer and of sodium molybdate solutions in D₂O and sulphuric acid (described in section II.10), the following similarities are observed:

(i) The spectra of the less acid solutions (pH 6.58 for extractions into the organic layer, and pH 7.8 for D₂O solutions), contain few peaks, but as the pH of the solutions
decreases, the number of peaks in both the phases increases, so that at the lowest pH (which was 0.92 for extractions into the organic layer and 1.47 for D₂O solutions) the spectra are most complicated.

(ii) For the organic layer, a distinct peak at 840-850 cm⁻¹ is present in the solutions in equilibrium with an aqueous layer of pH 6.58, but this becomes weaker as the pH is lowered so that below pH 2.38 it is a weak shoulder on the broad peak of chloroform. For the aqueous layer, a strong peak at 844 cm⁻¹ is present in solutions of pH 7.80, and this becomes weaker as the pH is lowered and shifts slightly to 853 cm⁻¹ at pH 1.47.

(iii) For the organic layer, two distinct peaks, one at 920 cm⁻¹ and the other at 950-960 cm⁻¹ are observed throughout the pH region. The height of the 950-960 cm⁻¹ peak increases relative to the 920 cm⁻¹ peak as the pH decreases so that at pH 5.69, the higher frequency peak is of greater intensity than the lower.

For the aqueous layer, a weak peak at 940 cm⁻¹ develops near to the intense peak at 920-940 cm⁻¹ in solutions of pH = 4.22 and gradually increases in intensity so that at pH = 1.47 it is stronger than the lower frequency peak.
Apart from the peaks described above, there are some other peaks also in the spectra of the two phases. The general trend of the absorption on going from a higher pH to a lower pH remain somewhat similar though a slight shift in the absorbance in different phases is observed. Although the features described above do not arise at exactly the same pH for both aqueous and organic solutions, these differences may be explained as due to the difference in the nature of the two solvents systems, but there is a general similarity which suggests that the ions existing in both phases may be the same at any particular pH.

III.5.b. A Scheme for the Formation of Isopoly(molybdate) Ions in Solution

The scheme now proposed for the formation of isopoly- molybdate ions in solution is as follows:

\[
\begin{align*}
\text{MoO}_4^{2-} & \rightarrow [\text{MoO}_6^{6-}] \rightarrow \text{dimers} \rightarrow \text{trimers} \rightarrow \text{Hexamolybdate} \\
& \rightarrow H_3\text{MoO}_6^{21-} \\
& \rightarrow H_5\text{MoO}_6^{22-} \\
& \rightarrow A \rightarrow B \rightarrow \text{Mo}_7^{24-} \rightarrow \text{Mo}_8^{26-} \\
& \rightarrow \text{Mo}_{10}^{32-}
\end{align*}
\]
The first condensed ion to occur in any appreciable concentration is probably a hexamolybdate, from which, by different reaction routes, higher aggregates may be formed. It has to be mentioned that, although the basic groups of three linked octahedra which were discussed in section III.2.a., are important structural constituents, they are probably never present in a high concentration in solution possibly because they are highly reactive. It is noteworthy that all the possible trimolybdate ions contain a relatively high proportion of unshared oxygens per octahedron and thus deviate considerably from Lipscomb's rule. This becomes more apparent from Table XXVIII, where values of $\bar{N}_i$ for each octahedron are given. The first product of the reaction of trimolybdate could easily be hexamolybdate, the structure of which is given in the proposed scheme as either $\text{H}_j\text{Mo}_6^0\text{O}_{21}^{3-}$, or $\text{H}_5\text{Mo}_6^0\text{O}_{22}^{3-}$. These two different structures may possibly co-exist together in the solution and it certainly is not possible to eliminate one in preference to the other on the basis of the evidence available. Both of these structures violate Lipscomb's rules for a stable ion, but since they do not do so to a very marked extent it is possible that they may exist as such in solution, but will be very susceptible to change to a higher aggregate under conditions differing from those existing in
TABLE XXVII

Some of the Charge Distribution in Trimolybdate Units

<table>
<thead>
<tr>
<th>No.</th>
<th>Formula</th>
<th>Structural notation</th>
<th>$\Sigma n_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$\text{Mo}<em>3\text{O}</em>{14}^{10-}$</td>
<td>0 0 0</td>
<td>10.0, 8.0, 10.0</td>
</tr>
<tr>
<td>2.</td>
<td>$\text{Mo}<em>3\text{O}</em>{13}^{8-}$</td>
<td>$0 - \frac{1}{2} 0$</td>
<td>9.67, 8.67, 8.67</td>
</tr>
<tr>
<td>3.</td>
<td>$\text{Mo}<em>3\text{O}</em>{14}^{10-}$</td>
<td>$0 0 - \frac{1}{2}$</td>
<td>10.0, 8.0, 10.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(or $0 0 \frac{1}{2}$)</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>$\text{Mo}<em>3\text{O}</em>{14}^{10-}$</td>
<td>$0 \frac{1}{2}$</td>
<td>9.67, 9.67, 8.67</td>
</tr>
</tbody>
</table>
the solutions studied in the present work. Furthermore, whilst Lipscomb's rule does appear to apply to all known solid iso- and heteropolyacid species it is not clear whether it applies equally to species in solution which may be more heavily hydrated or protonated. On the structural basis, $\text{H}_5\text{Mo}_6\text{O}_{22}^3-$ gives rise to both hepta- and acta-molybdates (reactions A and B), whereas $\text{H}_3\text{Mo}_6\text{O}_{21}^3-$ could give rise to only the octamolybdate structure (reaction B). The hepta-molybdate ion has a $C_{2v}$ symmetry and can give rise to a decamolybdate ion $\text{Mo}_{10}\text{O}_{32}^4-$ of the same symmetry, but it is not possible to form this decamolybdate from the octamolybdate structure. These structural relationships will be helpful in describing the conditions favourable to either reaction A or B.

The results of the extraction of molybdic acid of pH 3.8 to 4.8 by TOAH.CI (Tables XIV to XVII) show a constant R value = 2.0, and a slight increase in the degree of aggregation, n, occurs near pH 3.8. This leads us to suggest the presence of an ion with a degree of aggregation = 6.0, but on R value = 2.0. Such an ion is $\text{Mo}_8\text{O}_{26}^4-$ and the presence of this ion in the lower pH end of R value = 2.0 plateau is not ruled out. The reaction A, however, leads to
Mo\(\text{V}^{0}\)\(\text{O}_{24}\)\(^{6-}\), the R value of which is 1.17. Since no lowering of R value (Figure 3) was observed it may be said that this reaction is very slow so that under normal conditions the concentration of Mo\(\text{V}^{0}\)\(\text{O}_{24}\)\(^{6-}\) is too low to be observed. The next stage of the A series reaction, i.e., the formation of Mo\(\text{V}^{0}\)\(\text{O}_{32}\)\(^{4-}\), is, however, comparatively fast so that the curve showing the variation of R value with pH (Figure 3) gradually rises from R = 2.0 to R = 2.5.

The equilibria discussed in the proposed scheme may shift if the conditions used in the present work are changed. In the present work, the isopolymolybdate solutions were 0.20-0.35M Mo and did not contain any foreign ions in large concentration. If, however, a high concentration of a foreign cation is added, there is sufficient evidence in the literature\(^{[21]}\) to show that this enhances the condensation reaction leading to heptamolybdate formation. Accordingly, the proposed scheme, under such conditions would lead to the formation of hepta-, and octamolybdates rather than the formation of hexamolybdates. This is presumably what has happened in the case of the work involving high ionic strength (1-3M) of a foreign electrolyte in molybdate solutions in order to keep the activity coefficients
effectively constant, since they have generally found evidence of the presence of hepta- and octamolybdates. It may also be pointed out that the conditions during precipitation may be regarded as similar to those in solutions which contain a high concentration of a foreign electrolyte and this would favour the formation of hepta- and octamolybdates.

The proposed scheme, therefore, shows the critical nature of the equilibrium involving hexamolybdate ions and this is because their structures, in some cases, could be metastable, particular if such ions are protonated. This equilibrium would, therefore, shift entirely towards higher aggregates when conditions favourable for enhanced condensation exist and would form hepta- and octamolybdate ions rather than hexamolybdate ions. A scheme was put forward by Lindquist[97] and is as follows:

\[
\begin{align*}
\text{MoO}_{4}^{2-} & \rightarrow \text{Mo}_{7}^{6-} \rightarrow \text{Mo}_{8}^{4-} \rightarrow \text{larger complexes}; \\
\text{and this was supported later on}^{[50]}, \text{but it is not generally acceptable on the grounds that a direct transition from} \\
\text{Mo}_{7}^{6-} \text{to Mo}_{8}^{4-} \text{is unlikely from structural considerations.}
\end{align*}
\]

The present scheme takes into account the structural basis as well as describing the conditions under which hepta- and octamolybdate ions are likely to be formed.
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