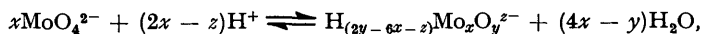


**375. Condensed Ions in Aqueous Solution. Part III.<sup>1</sup>  
Ion-exchange Behaviour of Molybdate Ions.**

By M. K. COOPER and J. E. SALMON.

Ion-exchange and pH-titration studies of the reaction,



indicate that it proceeds by two main stages for which the products correspond to ratios of  $x : z$  of 2 : 1 and 5 : 1, respectively. For the first stage the value of the ratio  $(2x - z) : x$  is 1.5 : 1. Studies of the selective sorption or selective exclusion (by an effect of the ionic-sieve type) of these two ions by resins of a wide range of porosities, coupled with a study of the effect of such sorption or exclusion on the equilibria in the external solutions, indicate that the two main products are  $\text{Mo}_4\text{O}_{13}^{2-}$  and  $\text{H}_2\text{Mo}_{10}\text{O}_{32}^{2-}$ .

In previous Parts <sup>1,2</sup> ion-exchange techniques have been used to study the formation of the isopolyacids <sup>2</sup> and of one heteropolyacid <sup>1</sup> of vanadium. The present paper is concerned with similar studies of the isopolymolybdates in which the method is developed to give further information.

Despite criticisms by Souchay <sup>3</sup> of the techniques which Jander <sup>4</sup> used, the sequence of condensation deduced by the latter for molybdate solutions of increasing acidity, namely, from ortho- to tri- to hexa-molybdate, has been supported by the studies of Brintzinger and Ratanarat <sup>5</sup> and to some extent by those of Byé and Schwing. <sup>6</sup> Doucet and Bugnon, <sup>7</sup> however, postulated the ion  $\text{Mo}_4\text{O}_{13}^{2-}$  as the first product of condensation and this view was supported by Carpeni, <sup>8</sup> by Britton, <sup>9</sup> and by Cannon. <sup>10</sup> Lindqvist, <sup>11</sup> who has reviewed earlier work, suggested, from his own X-ray studies of crystalline molybdates and from spectrophotometric and potentiometric studies of their solutions, that the pattern of condensation with increasing acidity is  $\text{MoO}_4^{2-} \rightarrow \text{Mo}_7\text{O}_{24}^{6-} \rightarrow \text{Mo}_8\text{O}_{26}^{4-}$ . Jenkins and Tyree <sup>12</sup> found this scheme to be in accord with their light-scattering and refractive-index measurements.

The general lack of accord between the various groups of workers suggested to us that the application of a technique hitherto untried in this system, namely, the determination by ion-exchange of the  $R$  values <sup>13</sup> (ratio of metal atoms present to units of charge) of the ions sorbed by resins of varying porosity, would be of value.

#### EXPERIMENTAL

*Preparation of Solutions.*—These were prepared from sodium molybdate or ammonium paramolybdate (both of analytical grade). Solutions of molybdic acid were obtained from solutions of either of these salts by passage through a column containing an excess of Zeo-Karb 225 resin in the hydrogen form. Stable solutions of the acid of concentrations up to 0.6 g.-atom of Mo per l. and of pH down to 1.4 (depending on concentration) were thus obtained. No precipitates were formed in these solutions, even on prolonged storage, but the products were

<sup>1</sup> Part II, Russell and Salmon, *J.*, 1961, 3211.

<sup>2</sup> Russell and Salmon, *J.*, 1958, 4708.

<sup>3</sup> Souchay *Bull. Soc. chim. France*, 1947, **14**, 914.

<sup>4</sup> Jander, *Metallbörse*, 1930, **20**, 1855.

<sup>5</sup> Brintzinger and Ratanarat, *Z. anorg. Chem.*, 1935, **224**, 97.

<sup>6</sup> Byé and Schwing, *Bull. Soc. chim. France*, 1957, 1023.

<sup>7</sup> Doucet and Bugnon, *J. Chim. phys.*, 1957, **54**, 155.

<sup>8</sup> Carpeni, *Compt. rend.*, 1948, **226**, 807.

<sup>9</sup> Britton, "Hydrogen Ions," Chapman and Hall, London, 1955, Vol. II, p. 245.

<sup>10</sup> Cannon, *J. Inorg. Nuclear Chem.*, 1959, **9**, 252.

<sup>11</sup> Lindqvist, *Nova Acta Reg. Soc. Sci. Uppsala*, 1950, IV, **15**, No. 1.

<sup>12</sup> Jenkins and Tyree, Symposium on Structure and Properties of Heteropoly Anions, Amer. Chem. Soc., 1956.

<sup>13</sup> Everest and Salmon, *J.*, 1954, 2438; 1955, 1444.

reduced to molybdenum blue if exposed to direct sunlight. Intermediate pH values were obtained by blending a solution of the acid with one of either the sodium or the ammonium salt of the same molybdenum concentration. The solutions of lowest pH values were obtained by adding hydrochloric acid to the molybdic acid solutions, and those of highest pH by adding sodium hydroxide or ammonia solutions to those of the corresponding salt. Solutions of 12-molybdophosphoric acid were prepared from those of the sodium salt by ion exchange.

*Anion-exchange Resins.*—In the preliminary experiments a sample of De-Acidite FF of relatively low porosity (water-regain value 0.7) was used. After tests had shown that this did not permit entry of the larger molybdate ions, a series of resins of the strong-base, monofunctional type with quaternary ammonium ( $R \cdot NMe_3$ ) active groups were prepared as in the method of Pepper, Paisley, and Young.<sup>14</sup> Before use these resins were converted completely into the chloride form by prolonged treatment in a column with an excess of 3*N*-hydrochloric acid, washed with deionised water, and dried at 100°.

Russell and Salmon,<sup>2</sup> who used mostly resins of water-regain values up to 1.3, together with a few of values 1.3—3.0, found that the pore size of anion-exchange resins was in direct relation to the water-regain (weight-swelling) values regardless of the method of preparation. In the present studies, however, it has been found that differences in method of preparation can lead to differences in porosity for resins of the same water-regain value, particularly for the higher values. Hence, for the present work, all resins used for the studies of the ionic-sieve effect were prepared in the laboratory by the one method<sup>14</sup> under carefully standardised conditions.

*Determination of R Values.*<sup>13</sup>—(a) *Batch experiments.* A known weight of chloride-form resin (0.5—1 g. except where otherwise specified) was left in contact with a known volume of solution (usually 50—100 ml.) until equilibrium had been reached; the most acid solutions were kept out of direct sunlight. For solutions of pH 6 or higher, five days were sufficient for attainment of equilibrium between solution and resin, but for the more acid solutions fourteen days were required. Resin and solution were then separated by filtration through a small column. The value of *R* was obtained from the analysis of the filtrate:

$$R = \frac{(\text{g.-atom of Mo in soln. initially}) - (\text{g.-atom of Mo in soln. finally})}{\text{g.-equiv. of Cl in soln. finally}}$$

A check on this was obtained by washing the resin rapidly, then displacing the species sorbed on it with the special eluent for molybdenum, and using aliquot parts of the eluate for analysis; then

$$R = \frac{\text{g.-atoms of Mo in eluate}}{(\text{g.-equiv. of resin capacity}) - (\text{g.-equiv. of Cl in eluate})}$$

where the resin capacity (chloride-form) was determined by a standard method.

(b) *Column experiments.* A solution of molybdic acid was passed slowly through a column (10 × 1 cm.) containing a weighed sample of chloride-form resin until no chloride was detected in the effluent. The solution was drained from the column, the resin washed quickly under suction with a small volume of water, the column refilled with water by reverse flow, the molybdate species displaced by the special eluent (see below), and the molybdenum content of the eluate determined. *R* was then given by

$$R = \frac{\text{g.-atom of Mo sorbed}}{\text{capacity of resin (g.-equiv.)}}$$

(c) *Studies of the hydrolysis of large molybdate ions sorbed on an anion-exchanger.* Small columns of resin were saturated with molybdenum by the passage through them of an excess of molybdic acid solution (0.15 g.-atom of Mo per l.) during 620 hr. The molybdenum sorbed was displaced from one of these as described under (b) above as a check on the *R* value of the species sorbed. The molybdic acid was then displaced rapidly from the remaining columns by the passage of 5—10 ml. of water; the columns were washed with various volumes of water at a steady flow rate of 0.33 ml./min. In each case the effluent was analysed to determine the

<sup>14</sup> Pepper, Paisley, and Young, *J.*, 1953, 4097.

quantity of molybdenum displaced on washing. The molybdenum remaining was then displaced with the special eluent and the  $R$  value of the species remaining was given by

$$R = \frac{\text{g.-atom of Mo sorbed (after washing)}}{\text{capacity of resin (g.-equiv.)}}$$

and that of the species sorbed initially by

$$R = \frac{(\text{g.-atom of Mo displaced by washing}) + (\text{g.-atom of Mo displaced by eluent})}{\text{capacity of resin (g.-equiv.)}}$$

*Special Eluent Used to Displace Molybdenum Anions from Resin.*—This was an alkaline solution (N in NaOH) of sodium nitrate (2–3M).

*Analysis.*—Molybdenum was determined by reduction to molybdenum(III) in a Jones reductor from which the sample was run directly into an excess of standard ferric ammonium sulphate solution; the iron(II) and molybdenum(V) so produced were then oxidised by standard potassium permanganate to iron(III) and molybdenum(VI). Chloride was determined by Volhard's method.

*pH Titrations.*—Sodium molybdate solution (0.193 g.-atom of Mo per l.; pH 6.74) was titrated with molybdic acid (0.193 g.-atom of Mo per l.; pH 1.41), and the changes in pH were followed by a glass electrode-saturated calomel electrode system in conjunction with a pH meter. By this method changes in the total molybdenum concentration during the titration were avoided.

#### RESULTS AND DISCUSSION

The variations in  $R$  value and in the proportion of resin sites occupied by molybdenum-containing species over the pH range 1–9.2 found with a sample of De-Acidite FF (water-

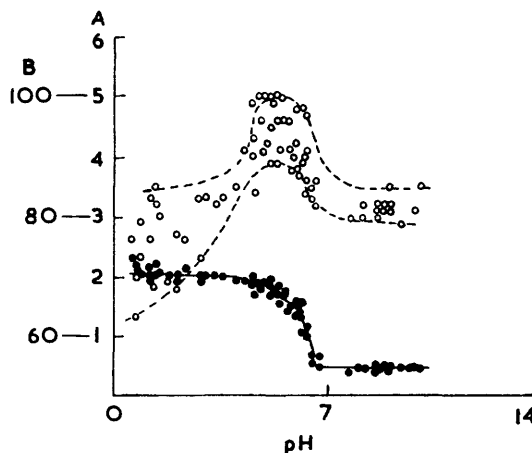


FIG. 1. Change of  $R$  value and proportion of resin sites occupied by Mo species with equilibrium pH value using De-Acidite FF of water regain 0.7.

● (Scale A)  $R$  value. ○ (Scale B). Resin sites (%) occupied by molybdate species as given by

$$\frac{[\text{Capacity of resin (g.-equiv.)}] - (\text{g.-equiv. of Cl on resin finally})}{\text{Capacity of resin (g.-equiv.)}} \times 100.$$

regain value 0.7) are shown in Fig. 1. The molybdenum concentration initially present in the solutions used was varied from 0.001 to 0.285 g.-atom of Mo per l. without discernible effect on the  $R$  values recorded (Fig. 1). For the solutions of pH greater than 7 the constant value of 0.5 for  $R$ , which corresponds to the presence and sorption of the simple molybdate ions ( $\text{MoO}_4^{2-}$ ), is in accord with the results of all previous workers. The value of  $R$  rises sharply with decrease in pH below 7, passes the value of 1.0 (corresponding to  $\text{HMoO}_4^-$ ) without break or inflection, and reaches a steady value of

2.0 between pH 4 and 2. The sharp rise in the proportion of resin sites occupied by molybdate species between pH 6.5 and pH 4.5 (Fig. 1) indicates that the species sorbed in this range has a higher relative affinity for the resin with respect to chloride than that of the simple molybdate ion. The fall in the proportion of resin sites occupied by molybdate species below pH 4.5 could correspond either to a further stage of condensation leading to species too large to penetrate the exchanger used or to the breakdown of the condensed species to give molybdenyl cations. Of these alternatives the former is in better accord with the reports of earlier investigations and is in some degree supported by the tendency for the  $R$  values to rise a little above 2.0 for the most acid solutions (Fig. 1).

Further support for the conclusion that there is a second stage of condensation is

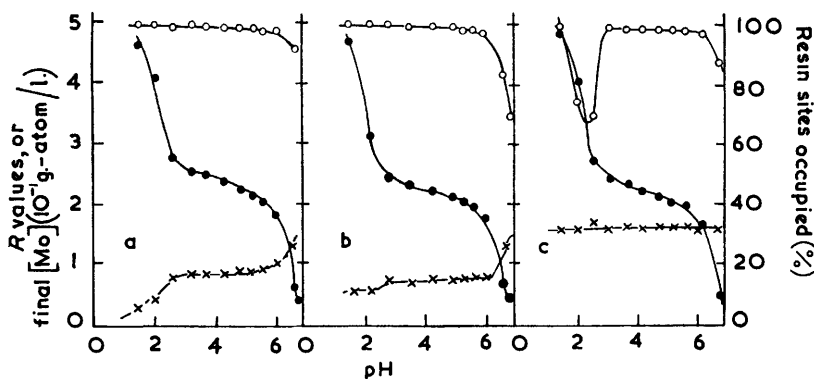


FIG. 2. Changes in  $R$  value and proportion of resin sites occupied by Mo species with equilibrium pH value; resin of water regain 22.5.

- $R$  value. ○ Resin sites (%) occupied by molybdate species (see legend to Fig. 1).
- × Final Mo concn. in solution (g.-atom/l.). (a) Soln. 100 ml. (0.150 g.-atom of Mo per l.), resin 0.650 g., 15 days. (b) Soln. 100 ml. (0.193 g.-atom of Mo per l.), resin 0.7—5.0 g., 20 days. (c) Soln. 150 ml. (0.193 g.-atom of Mo per l.), resin 0.25—2.0 g., 16 days.

provided by the results obtained with a molybdic acid solution and with laboratory-prepared resins of a wide range of water-regain values (Table 1). These show that there is present in the acid solutions a larger ion of  $R$  value 5.0 which cannot be sorbed by a resin of water-regain value of 1.0 or less.

The results of experiments with a resin of high porosity and with solutions of varying pH (Fig. 2) also indicate the occurrence of two stages of condensation. In two of these three series of experiments (Fig. 2b, c) the ratios of mass of resin to volume of solution

TABLE 1.

Sorption of molybdate ions with resins of increasing porosity.

0.500 g. of resin (Cl-form) left in contact with 100 ml. of molybdic acid solution (0.197 g.-atom of Mo per l.; pH 1.58) for 14 days.

Resin: water regain .....	0.69	1.12	1.50	1.92	2.0	2.8	3.3	5.4	
sites (%) occupied by Mo...	81	73	100	100	99	100	100	100	
$R$ value .....	2.1	2.1	3.5	3.4	4.0	4.3	4.5	4.7	
Resin: water regain .....	6.2	7.4	9.2	12.0	15.0	17.1	18.5	20.3	21.2
sites (%) occupied by Mo...	99	99	99	100	100	100	100	100	100
$R$ value .....	4.7	4.6	4.7	4.8	4.8	5.0	5.0	5.0	5.0

used were selected on the basis of the results of the first series with the intention that the final molybdenum concentration in solution in each series should be constant. Although this aim was not quite achieved (Fig. 2b, c) it is apparent that there is a first condensation stage at about pH 6 and a second one which begins below pH 4.5 but is fastest below

pH 2.5 and that these stages are not markedly sensitive to changes in the final molybdenum concentration. The drop in proportion of resin sites occupied with the solutions of highest final molybdenum concentration (Fig. 2c) in the pH range 2—3 is attributed to onset of precipitation in the resin pores which was occasionally observed with solutions of high molybdenum concentration containing small quantities of ammonium ion. It may be noted that the solutions of lowest pH, which are molybdic acid solutions free from the ammonium salt, are free from the complication and that with them the resin capacity is fully saturated by molybdate ions.

Addition of a strong acid to the molybdic acid causes no further increase in the value of  $R$  above 5.0, but eventually a fall (Table 2), which can be attributed to the decomposition of the species of  $R$  value 5.0 to form either molybdenyl cations<sup>15</sup> or molybdenum anions containing chloride as ligand.<sup>16</sup> The rise of the  $R$  value to 5.0 occurs only if the final concentration of molybdenum in solution is not less than 0.05 g.-atom/l. (Table 2).

Column experiments (Table 3) show that the sorption of the ion of  $R$  value of 5.0 also occurs in the absence of foreign anions such as chloride which is always present in the batch experiments, and that the hydrolysis of this on prolonged washing of the resin produces an effluent which contains molybdenum and leaves the ion of  $R$  value 2.0 as the species retained on the resin (Table 4).

TABLE 2.

Sorption of molybdate ions from molybdic acid–hydrochloric acid solutions (100 ml.) by a resin of high water-regain value (22.5).

(a) 2 g. of resin; \* Mo concentration in solution 0.6 g.-atom/l. initially, ~0.2 g.-atom/l. finally; initial pH values of solution ranging from 1.20 to 0.81; time of contact 16 days.

HCl (g.-equiv./g.-atom of Mo) .....	0.00	0.05	0.10	0.19	0.29
$R$ value .....	5.0	5.0	5.0	5.0	5.0

(b) 0.5 g. of resin; † Mo concentration in solution 0.14—0.17 g.-atom/l. initially, 0.05—0.06 g.-atom/l. finally; time of contact 14—22 days.

HCl (g.-equiv./g. atom of Mo)	0.09	0.13	0.18	0.37	0.47	0.63	0.91	1.37	2.63
$R$ value .....	4.8	4.9	5.0	5.0	5.0	5.0	4.9	4.8	4.4

\* In a second series of experiments with 1 g. of resin, but other conditions unchanged,  $R$  values ranging from 5.0 to 5.1 were obtained.

† With 0.25 g. of resin (in contact for 8 weeks) similar results were obtained but with 0.80 g. of resin (in contact for 18 days), where the final Mo concentration was as low as 0.02 g.-atom Mo/l., lower  $R$  values (max. 4.7) were obtained.

TABLE 3.

Determination of  $R$  values by column experiments.

	Column 1	Column 2
Resin: mass (g.) .....	0.5	0.5
water regain .....	37	22.5
capacity (milliequiv./0.5 g.) .....	1.90	2.06
Molybdic acid soln.: Mo (g.-atom/l.) .....	0.150	0.151
pH .....	1.60	1.54
volume (ml.) .....	468	2300
time of passage (hr.) .....	312	120
Eluate: Mo (mg.-atoms) .....	9.63	9.97
Cl .....	Nil	Trace
$R$ value .....	5.1	4.9

In Fig. 3 the results of pH titrations and  $R$  value determinations for solutions containing 0.18 g.-atom of Mo per l. are both plotted as a function of pH. The calculation of g.-equiv. of hydrogen ion added per atom of molybdenum in the titration of sodium

<sup>15</sup> Babko and Nabivanets, *Zhur. neorg. Khim.*, 1957, **2**, 2085, 2096.

<sup>16</sup> Kraus, Nelson, and Moore, *J. Amer. Chem. Soc.*, 1957, **77**, 3972.

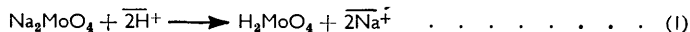
TABLE 4.

Hydrolysis of polymolybdate ions sorbed on an anion-exchanger.

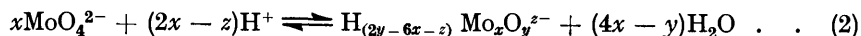
0.5 g. of resin (Cl form, water-regain value 22.5, capacity 2.06 milliequiv./0.5 g.) in each column loaded by passage of 14 l. of molybdic acid (0.151 g.-atom of Mo/l.; pH 1.54).

Column	1	2	3	4
Volume of wash water (ml.)	250	500	1000	2000
Effluent: pH	2.11	2.40	2.68	2.96
Mo (mg.-atom) (A)	5.40	5.49	5.79	6.14
Eluate: Mo (mg.-atom) (B)	4.49	4.34	4.05	4.01
$R$ { species sorbed after washing (B/2.06)	2.2	2.1	2.0	2.0
{ species sorbed initially [(A + B)/2.06]	4.8	4.8	4.8	4.9

molybdate with molybdic acid was based on the fact that in the preparation of the acid from the salt the solution obtained contains effectively two hydrogen ions per molybdenum atom:



where barred formulæ indicate ions in the resin phase. Although these hydrogen ions may in part be utilised in the formation of isopolymolybdate ions



they are readily available (like those of a weak acid) by the right-to-left reaction of expression (2), as can be shown by the titration of the molybdic acid solution by standard alkali.

It can be seen (Fig. 3) that there is an inflection in the pH-titration curve after the addition of 1.5 g.-equiv. of  $\text{H}^+$  per g.-atom of Mo and that this corresponds to a pH ( $\sim 4.5$ )

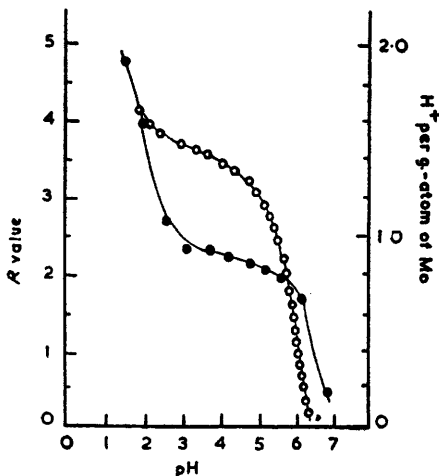


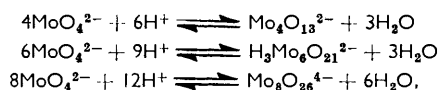
FIG. 3. Comparison of pH-titration data and  $R$  values for solutions containing 0.18 g.-atom of Mo per l.

●  $R$  value. ○ G.-equiv. of  $\text{H}^+$  per g.-atom of Mo.

at which the species sorbed by the ion-exchanger have an  $R$  value very close to 2.0. The fact that the  $R$  value is not constant in this region of pH shows that the ion of  $R$  value 2.0 is always present in admixture with either the simple molybdate ion or the larger one of  $R$  value 5.0.

Now the process of condensation of the molybdate ion is represented by expression (2) and hence for the product of the first stage of condensation the ratio of  $(2x - z) : x$  is 1.5 : 1 and the ratio of  $x : z (= R)$  is 2.0.

These requirements are all met by the three ions  $\text{Mo}_4\text{O}_{13}^{2-}$  (refs. 7—10),  $\text{H}_3\text{Mo}_6\text{O}_{21}^{3-}$  (refs. 4, 5), and  $\text{Mo}_8\text{O}_{26}^{4-}$  (refs. 11,12), *viz.*:



but not by  $\text{Mo}_7\text{O}_{24}^{6-}$ .<sup>17</sup> The absence of an inflexion or levelling off between pH 4.5 and 6.5 at  $R = 1.17$  corresponding to this last ion for solutions of molybdenum concentrations ranging from 0.01 to 0.285 g.-atom/l. (Figs. 1 and 2) is in striking contrast with the conclusions of Sasaki, Lindqvist, and Sillén.<sup>17</sup> For reasons which are given below an ion such as  $\text{Mo}_7\text{O}_{24}^{6-}$  should be very strongly sorbed by a resin of open structure if it is present in solution, yet neither column nor batch experiments have provided evidence of its presence. It is noteworthy too that the hydrolysis of the ion of  $R$  value 5.0, when sorbed on the resin, yields an ion of  $R$  value 2.0 and not  $\text{Mo}_7\text{O}_{24}^{6-}$  (Table 4). Our results are in better accord so far with those of earlier workers.<sup>4-12</sup> We can account for this difference only by assuming that the presence of 3M-sodium perchlorate as a supporting electrolyte in the experiments of Sasaki, Lindqvist, and Sillén<sup>17</sup> had a greater effect on the equilibrium of equation (2) than they realised or that their supposition that it is unlikely that as good agreement could be obtained by substituting any other mechanism for their proposed reactions is incorrect. On this basis it would appear that the product of the first stage of condensation is an octa-, hexa-, or tetra-molybdate of  $R$  value 2.0.

The structure deduced by Lindqvist from X-ray studies of solid octamolybdates, which he believed to apply to octamolybdates in solution as well,<sup>11,18,19</sup> and the structure which he derived<sup>11</sup> for the hexamolybdate ion of Jander<sup>4</sup> and Brintzinger<sup>5</sup> both contain 5 co-ordinate oxygen atoms, which, while possible in a crystalline lattice, seem unlikely to occur in ions in aqueous solution. We have been unable to devise alternative structures for either of these ions which avoid this difficulty yet retain the  $R$  value of 2.0.

The  $\text{Mo}_4\text{O}_{13}^{2-}$  ion can be represented most simply as a flexible chain of four linked  $\text{MoO}_4$  tetrahedra, which would have a low cross-sectional area and thus allow the ion to penetrate resins of low porosity. In fact it is found in experiments with resins of a range of water-regain values that the ion of  $R$  value 2.0 is admitted without restriction by resins of water-regain values of about 0.7 (Fig. 4, Table 1). This may be compared with the water-regain values of 0.65 and 4.0 at which the unrestricted sorption of tetravanadate<sup>2</sup> and 12-molybdophosphate ions (Fig. 4), respectively, occurs. The structure of the latter ion is well established<sup>20</sup> and it shows the expected  $R$  value of 4.0 for  $\text{PMo}_{12}\text{O}_{40}^{3-}$ .

It is known that a resin of a given water-regain value will have a range of pore sizes. Indeed it can be seen from Fig. 4 (and from Table 1) that a resin of water-regain value 1.5 can admit a small proportion of the molybdate ion of  $R$  value 5.0 and must have some pores capable of admitting this ion, while a resin of water-regain value 2.8 sorbs that ion to a greater extent and must have a greater proportion of pores of this or greater size, whilst in one of water-regain value 5.0 all the pores appear able to accommodate such an ion. This last stage where the ion just has free access to all the sites in the resin is considered to provide a useful basis for the comparison of the relative orders of ionic sizes, provided that, as in the present experiments, the resins used are all prepared under the same carefully standardised conditions, that the solutions are of comparable ionic strength (the lower the water-regain value the less important small changes in ionic strength become), and that the ions compared are of similar type (*e.g.*, based on linked  $\text{MoO}_x$ ,  $\text{WO}_x$ , or  $\text{VO}_x$  polyhedra, so that polarisation effects are not markedly different). Earlier studies<sup>1,2</sup> and current ones

<sup>17</sup> Sasaki, Lindqvist, and Sillén, *J. Inorg. Nuclear Chem.*, 1959, **9**, 93.

<sup>18</sup> Lindqvist, *Acta Cryst.*, 1950, **3**, 159.

<sup>19</sup> Lindqvist, *Acta Chem. Scand.*, 1951, **5**, 568.

<sup>20</sup> Keggin, *Proc. Roy. Soc.*, 1934, *A*, **144**, 75.

on the tungstate<sup>21</sup> support this view and it is noteworthy that a differentiation between the penta- and hepta-germanate ions is possible on this basis.<sup>22</sup> Thus on the basis of the results presented the ion of  $R$  value 2.0 appears to be much closer in size to the tetra-vanadate ion than to the 12-molybdophosphate ion. It is more likely, therefore, to be a

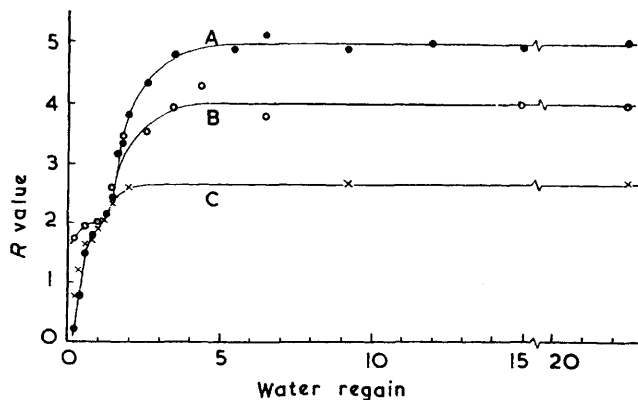


FIG. 4. Effect of ionic-sieve type with molybdate and 12-molybdophosphate solutions.

A (●) Molybdic acid (0.282 g.-atom of Mo per l.)-HCl soln. pH 1.1; B (○) 12-molybdophosphoric acid (0.121 g.-atom of Mo per l.), pH 1.6; C (×) molybdate solution (0.189 g.-atom of Mo per l.), pH 3.6.

tetramolybdate or a hexamolybdate ion than an octamolybdate and in view of the difficulties of assigning structures to either hexa- or octa-molybdates of  $R$  value 2.0 is most probably a tetramolybdate,  $\text{Mo}_4\text{O}_{13}^{2-}$ .

Whilst the ion of  $R$  value 5.0 could contain any number of molybdenum atoms that is a multiple of five, the evident similarity of its size to that of the 12-molybdophosphate ion (Fig. 4) leads us to infer that it is  $\text{H}_2\text{Mo}_{10}\text{O}_{32}^{2-}$ , a protonated form of  $\text{Mo}_{10}\text{O}_{32}^{4-}$  which can be represented by a structure (Fig. 5) closely related to that of molybdenum(VI) oxide,<sup>23</sup> the paramolybdate ion,<sup>24</sup> and the 6-molybdotellurate ion.<sup>25</sup> This ion is slightly larger than the 12-molybdophosphate ion in one dimension, which would account for the slightly

FIG. 5. Model of the decamolybdate ion,  $\text{Mo}_{10}\text{O}_{32}^{4-}$ .

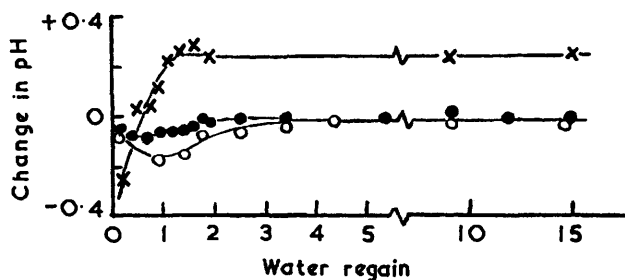
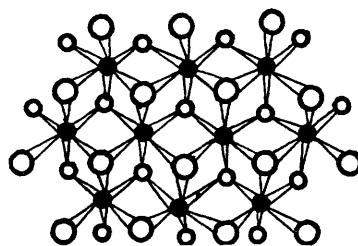


FIG. 6. Variation in pH change of solutions on coming to equilibrium with resin with changes in resin porosity. Key as in Fig. 4.

higher water-regain values in the resins which just permit its entry to all exchange sites ( $\sim 5$ ) as compared with those which permit the entry of the heteropoly-ion ( $\sim 4$ ).

It is evident from the results presented in Table 1 and in Figs. 2-4 that a larger molybdate ion is sorbed more strongly than a smaller one, and is preferentially

<sup>21</sup> McPartlin and Salmon, unpublished work.

<sup>22</sup> Everest and Harrison, *J.*, 1959, 2178.

<sup>23</sup> Wooster, *Z. Krist.*, 1931, 80, 504.

<sup>24</sup> Sturdivant, *J. Amer. Chem. Soc.*, 1937, 59, 630.

<sup>25</sup> Evans, *J. Amer. Chem. Soc.*, 1948, 70, 1291.



sorbed if both are present and if the resin is of sufficiently high porosity (similar results are found in the vanadate<sup>2</sup> and tungstate<sup>21</sup> systems). With resins of low porosity, however, the smaller ions are preferentially sorbed. In either case the balance of the equilibrium (2) is disturbed with a corresponding change in hydrogen-ion concentration as this is restored. Where the ion sorbed is the preponderant one in solution, then there is a negligible change in pH accompanying its sorption—the possibility that a similar result could arise by the simultaneous sorption of two or more ions by the resin in the same relative proportions as those in which they occur in solution can be discounted since

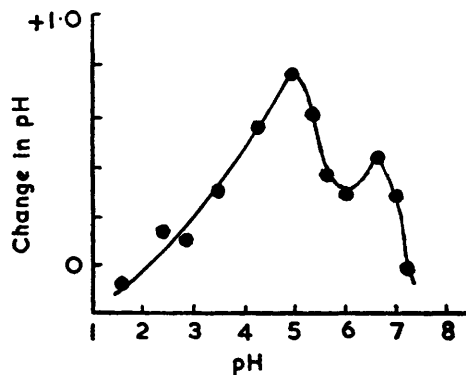


FIG. 7. Variation in pH change of solutions on coming to equilibrium with resin with changes in final pH of solution.

Molybdate solution (100 ml., 0.193 g.-atom of Mo per l. initially; 0.06—0.13 g.-atom/l. finally) and resin (water-regain value 22.5, 0.7—5.0 g.) in contact for 20 days.

this would require them to have the same relative affinities, which is not the case (see above).

The data given in Fig. 6 show that for both molybdic and 12-molybdophosphoric acid solutions there is no change of pH when the porosity of the resin permits free entry of the decamolybdate and 12-molybdophosphate anions to all resin sites. It is apparent that these ions are the predominant ones in the respective solutions. In both cases the sorption of the ion of  $R$  value 2.0 as a result of the partial or complete exclusion of the larger ions by resins of lower porosity is marked by a fall in pH, showing that it is accompanied by a decondensation and liberation of hydrogen ions [right-to-left reaction (2)]. Both the ion of  $R$  value 2.0 and those of  $R$  value 5.0 must be present in significant proportion in the solution of molybdate of pH 3.6, for with resins of low porosity there is a fall in pH which changes to a rise in pH with increasing porosity (Fig. 6).

A plot of change in pH against the initial pH for a range of solutions with a resin of high water-regain value (Fig. 7) shows peaks at pH 7 and 5 where it is known that the formation of the ions of  $R$  values 2.0 and 5.0 is commencing, but at no other places, indicating once again that these are the only two main stages in the condensation.

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