

# Ion-Exchange Properties of Microporous Monovalent Salts of 12-Tungstophosphoric Acid and 12-Molybdophosphoric Acid Catalysts

G. B. MCGARVEY AND J. B. MOFFAT\*

*Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry,  
University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

Received September 12, 1990; revised August 30, 1990

Ion exchange of the ammonium, potassium, and cesium salts of 12-tungstophosphoric and 12-molybdophosphoric acids has been studied at 298 K. Residual protons contained in the nonstoichiometric salts are exchanged as well as the original cations. The completeness of the ion-exchange process varied from approximately 5 to 70%, depending on both the solid phase and liquid phase cations. The maximum exchange capacities are shown to decrease significantly as the size of the cation leaving the solid becomes larger than that of the cation entering the solid. © 1991 Academic Press, Inc.

## INTRODUCTION

The importance of ion exchange in modifying the structures of heterogeneous catalysts is well known (1-8). Of particular interest are the many studies reported on zeolites of various structures (see, for example, 1-6) in which ion exchange has been shown to modify the pore structure and/or alter the response of the solid to elevated temperatures. The resulting changes in both sorption and catalytic properties of the exchanged zeolites have both fundamental and practical implications (1-6). In the present work a study of ion exchange in the heteropoly oxometalate catalysts is reported.

Heteropoly oxometalates are inorganic cage compounds which form a unique family of materials (9). Of the several possible types of heteropoly anions, the 12-heteropoly or Keggin anions have attracted considerable interest. The anion is constructed of a tetrahedron of oxygen atoms which surround a central atom such as phosphorus, silicon, or arsenic. This central tetrahedron is in turn surrounded by 12 octahedra of oxygen atoms which have peripheral metal atoms (usually W, Mo, or V) at their centres. These octahedra share corners and edges

with one another and can be considered to form four  $M_3O_{13}$  trimetalate units which have oxygen atoms that are bonded to only one peripheral metal atom and therefore protrude from the surface of the anion.

Several applications have been found for heteropoly compounds that contain the Keggin anion. 12-Tungstophosphoric acid ( $H_3PW_{12}O_{40}$ ) and several metal salts and the ammonium salt have proven to be effective catalysts for the methanol to hydrocarbon process (10-14). The selective oxidation of unsaturated aldehydes such as acrolein and methacrolein to the corresponding acids is catalyzed by the 12-molybdophosphate ( $PMo_{12}O_{40}^{-3}$ ) anion and vanadium substituted Keggin anions (15-19). Molybdenum containing Keggin anions have also proven to be effective catalysts for the partial oxidation of methane (20-22).

Heteropoly oxometalates have also been studied for application as ion-exchange resins. The ammonium and heavy alkali metal salts of 12-molybdophosphoric acid and 12-tungstophosphoric acid possess very low solubilities in aqueous solutions and hence can be used as inorganic ion exchangers. Much of the work on heteropoly ion exchangers has dealt with ammonium molybdophosphate ( $(NH_4)_3PMo_{12}O_{40}$ ) (23-27) although some 12-tungstophosphate (28-34)

\*To whom correspondence should be addressed.

and 12-tungstoarsenate salts (35) have also been utilized in ion-exchange reactions.

Investigations concerning the bulk and surface properties of heteropoly oxometalate solids indicate that the ammonium, potassium, rubidium, and cesium salts of 12-tungstophosphoric acid, 12-molybdophosphoric acid (36), 12-tungstosilicic acid (37), and 12-tungstoarsenic acid (38) possess a microporous structure. The micropore distributions and micropore volumes of these catalysts were found to be dependent upon the size of the alkali metal cation. Previous ion-exchange studies have found that approximately one-half to two-thirds of the ammonium ions in  $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$  are exchangeable for the heavy alkali metals (26, 39) suggesting that exchange occurs in the bulk structure and not only on the external surface.

This study was initiated to investigate the nature of the formation of the microporous heteropoly salts and the ion-exchange processes which occur in several heteropoly oxometalate salts of 12-tungstophosphoric acid and 12-molybdophosphoric acid. Previous investigations of 12-heteropoly oxometalate salts used both as heterogeneous catalysts (40) and as ion exchangers (28, 30, 31) indicate that residual protons exist in the structure when stoichiometric quantities of heteropoly acid and monovalent cation are reacted with one another. Specifically, the ammonium, potassium, and cesium salts of the aforementioned heteropoly acids were prepared and subsequently were contacted with solutions containing ammonium, potassium, or cesium ions using a batch ion-exchange reactor. Solid and liquid phase analyses using ion chromatography have been made to determine stoichiometries, solubilities, and the extent of ion-exchange reaction.

#### EXPERIMENTAL

Ammonium tungstophosphate ( $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{NH}_4\text{PW}$ ), ammonium molybdophosphate ( $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ ,  $\text{NH}_4\text{PMo}$ ),

potassium tungstophosphate ( $\text{K}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{KPW}$ ), potassium molybdophosphate ( $\text{K}_3\text{PMo}_{12}\text{O}_{40}$ ,  $\text{KPMo}$ ), cesium tungstophosphate ( $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{CsPW}$ ), and cesium molybdophosphate ( $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$ ,  $\text{CsPMo}$ ) were employed as the solids in this study. 12-Tungstophosphoric acid (HPW) and 12-molybdophosphoric acid (HPMo) (both BDH, AnalaR Grade), were recrystallized prior to use. The required heteropoly salts were precipitated by slowly adding stoichiometric quantities of the required carbonate, ( $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ), dissolved in a minimum volume of water to a stirred solution of the appropriate heteropoly acid (also dissolved in a minimum volume of water). The mixtures were heated to drive off carbon dioxide and taken to dryness on a hot water bath. Anhydrous salts were obtained by heating at 523 K for 3 h in air followed by cooling in a desiccator. All of the possible combinations of cations ( $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ) were exchanged with each of the starting ion-exchange materials. Lithium and sodium 12-heteropoly salts were not studied because the high solubility of these materials in aqueous solutions precluded their usefulness as ion-exchange materials. The exchange of  $\text{Li}^+$  and  $\text{Na}^+$  into the  $\text{NH}_4^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$  salts was not attempted because these ions have been shown to exchange into salts containing the large cations to only a small extent (39), and in addition, these materials have been shown to be nonporous (36).

All ion-exchange reactions were performed in a batch-type reactor equipped with a temperature-regulated water jacket and an overhead stirrer assembly. Unless otherwise stated all exchanges were carried out at  $298 \pm 0.5$  K. A modified progressive batch technique was employed (41) which permitted significant quantities of the solid exchanger to be recovered following each exchange experiment for analysis and subsequent investigations. Six data points were obtained in each experiment in which a cation different from that initially present in the solid phase was exchanged into the solid

phase (i.e.,  $K^+$  initially present in the solid phase and  $Cs^+$  to be exchanged into the solid phase). For cases where the same cation was present in both the solid and liquid phase (i.e.,  $NH_4^+$ ) five data points were obtained. The procedure was carried out as follows. Each of six samples of the solid phase were contacted with an equimolar solution of the exchanging cation for 30 min. The solid and liquid phases were separated by centrifugation and each sample of solid material was dispersed and separated from distilled water twice before drying in air at  $115^\circ C$ . Five of the samples were taken and the identical procedure was repeated. Following this set of exchanges four samples were exposed to the ion-exchange procedure. This was repeated until the one remaining sample had been exchanged six times. Therefore a total of 21 ion-exchange reactions were required in order to construct a six-point exchange isotherm.

The cation content ( $NH_4^+$ ,  $K^+$ ,  $Cs^+$ ) of the solid was determined using ion chromatography (IC). Analyses were made using either a Dionex model 2010i or a Dionex series 4500i ion chromatograph equipped with a conductivity detector. Analyses made on the former system were performed using a Dionex HPIC-CG3 guard column and an HPIC-CS3 separator with the following eluant system: 15 mM HCl, 0.625 mM  $ZnCl_2$ , and 1 mM 2,3-diaminopropionic acid monohydrochloride (DAP). The eluant background conductivity was suppressed using a Dionex cation micromembrane suppressor column which was constantly regenerated using a 50 mM  $Ba(OH)_2$  solution. Chromatograms were recorded on a Sargent model SR recorder. Analyses on the latter system used the Dionex Fastcation separation columns and an eluant consisting of 20 mM HCl and 0.3 mM DAP. Background conductivity suppression was again achieved using a cation micromembrane suppressor column and the closed loop Autoregen system which used 0.1 M tetrabutylammonium hydroxide as the regenerant.

Chromatograms were recorded on a Spectra-Physics ChromJet integrator. All reported results are the mean of at least two measurements.

Prior to analysis, the samples were heated at 533 K for 2 h to remove any remaining adsorbed water. Known amounts of sample were then decomposed with a minimum volume of 1 M LiOH and the solution was subsequently diluted to the appropriate volume.

The proton contents of the solid samples and liquid phases were estimated using aqueous titration methods. Solid samples were suspended in water and titrated with dilute sodium hydroxide ( $\sim 0.002 M$ ) using bromocresol purple indicator. Known volumes of the liquid phases were titrated using the same titrant and indicator.

Cations present in the liquid phase were also analyzed using ion chromatography. Appropriate dilutions were made and the samples were analyzed using the same eluant systems as for the analysis of the solids.

X-ray powder diffraction patterns were recorded on a Phillips Model PW 1011/60 diffractometer using  $CuK\alpha$  radiation filtered through nickel. The cubic Pn3m diffraction pattern was observed for samples that had been exchanged as well as for the starting salts indicating that the exchange procedure did not alter the secondary structure of the salts.

Anion ion chromatography was used to determine the amounts of preparative anions which were retained on the heteropoly oxometalate salts. A Dionex AG5 guard column and AS5 separator column were used with a 5 mM  $Na_2CO_3/1 mM NaOH$  eluant. Background conductivity was reduced using an anion micromembrane suppressor with 30 mN  $H_2SO_4$  regenerant. The solid heteropoly salts were suspended in distilled water for 30 min followed by centrifugation to separate the two phases. Lithium hydroxide was added to an aliquot of the solution phase to decompose any of the heteropoly salt that was soluble in the water. The resulting solution was diluted

TABLE 1

Molecular Formulae for Monovalent 12-Heteropoly Oxometalate Salts as Prepared by the Precipitation Reaction of the Anions with the Appropriate Cation

Cation	Anion	
	PW <sub>12</sub> O <sub>40</sub> <sup>-3</sup>	PMo <sub>12</sub> O <sub>40</sub> <sup>-3</sup>
NH <sub>4</sub> <sup>+</sup>	2.69	2.08
	2.69	2.17
K <sup>+</sup>	2.80	2.02
	2.84	2.73
Cs <sup>+</sup>	2.91	2.78

Note. Quoted values are number of cations per Keggin Unit (3 for stoichiometric compound).

to the appropriate volume after which the analyses were performed. For 12-tungstophosphate and 12-molybdophosphate salts the WO<sub>4</sub><sup>-2</sup> and MoO<sub>4</sub><sup>-2</sup> peaks were detected using a conductivity detector and estimates of the solubility of the heteropoly salts were made.

## RESULTS

The precipitation reaction of the 12-heteropoly acids with alkali metal salts (and the ammonium ion) leads to the formation of incomplete or acid salts when stoichiometric quantities of the two reactants were used. This phenomenon has been reported previously (27, 28, 40) and was observed again in this investigation in the precipitation reaction for both of the anions and the three cations that were studied (Table 1). The cesium salts formed compounds which most closely approximated those expected for a stoichiometric material. The ammonium salts of both anions consistently deviated from stoichiometry to the greatest extent. Of the salts prepared by precipitation, those containing the 12-tungstophosphate anion most closely approximate the composition expected from a stoichiometric process which has proceeded to completion. The discrepancies between the measured number of cations and the expected three cations per Keggin anion are accounted for,

at least in part, by the number of protons which remain in the solid salt after its preparation from stoichiometric quantities of the preparative reagents. Anion chromatographic investigations of these starting salts indicate that there are negligible quantities of impurity anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, etc.) associated with the heteropoly salts.

Tables 2 and 3 show the experimentally measured quantities of the cations present in the various heteropoly ion exchanges following each exchange reaction. The concentrations of the entering and exiting cations in the solid phase are shown for each of the exchanges. The largest degree of exchange can be seen to occur in the first exchange, following which the quantity of ions exchanged in a given exchange generally decreases and approaches zero. It should be noted that, whereas in the original heteropoly salt, which has not been subjected to exchange, the predominant cation is accompanied by protons, in the solids which have experienced one or more exchanges, the entering and exiting cations are both present, together with reduced amounts of protons. The results in Table 2 show that, within experimental error, the total number of cations in the solid generally approximates the stoichiometric number of 3 at all steps in the six exchange experiments. This suggests that the protons are largely eliminated from the solid in the first exchange. In the exchange of Cs<sup>+</sup> into NH<sub>4</sub>PW, however, the total number of cations remains approximately 10% less than expected, for all exchanges.

Similarly for the 12-molybdophosphate salts the largest uptake of cations from the liquid phase occurs in the first exchange (Table 3). As the number of exchange reactions increases the uptake of ions from the liquid phase decreases, and generally by the third exchange negligible further uptake was observed. The reverse behaviour is observed for the cations that are exchanging from the solids into the liquid phase with the release of cations decreasing as the number of exchanges increases. Figure 1 shows the ion-exchange isotherms for NH<sub>4</sub>PW and KPW

TABLE 2  
Concentration<sup>a</sup> of Cations in the Solid 12-Tungstophosphate Salts following Ion Exchange with Monovalent Cations

Number of exchange reactions	(NH <sub>4</sub> ) <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>						K <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>						Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>															
	K <sup>+</sup>			Cs <sup>+</sup>			NH <sub>4</sub> <sup>+</sup>			K <sup>+</sup>			NH <sub>4</sub> <sup>+</sup>			Cs <sup>+</sup>			NH <sub>4</sub> <sup>+</sup>			K <sup>+</sup>						
	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Cs <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Cs <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Cs <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Cs <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Cs <sup>+</sup>	Total	
Initial <sup>b</sup> :	2.69																											
1	2.27	0.79	3.06	1.41	1.14	2.55	1.60	2.84	2.92	1.32	2.92	1.86	2.80	2.92	1.86	0.39	2.25	2.73	2.91	2.73	2.91	0.19	2.92	2.86	0.30	2.86	0.30	3.16
2	1.82	1.10	2.92	1.31	1.27	2.58	1.54	2.84	2.91	1.37	2.91	1.29	2.80	2.92	1.86	1.53	2.82	3.02	2.91	3.02	2.91	0.27	3.27	2.62	0.36	2.62	0.36	2.98
3	1.13	1.75	2.88	1.26	1.46	2.72	1.47	2.84	2.91	1.46	2.91	1.98	2.80	2.92	1.86	1.86	2.84	2.23	2.91	2.23	2.91	0.31	2.54	2.69	0.39	2.69	0.39	3.08
4	1.28	1.52	2.80	1.21	1.47	2.68	1.48	2.84	2.96	1.48	2.96	0.89	2.80	2.92	1.88	1.88	2.77	2.67	2.96	2.67	2.96	0.34	3.01	2.69	0.42	2.69	0.42	3.11
5	1.17	1.63	2.80	1.19	1.50	2.69	1.50	2.80	2.93	1.43	2.93	0.76	2.80	2.92	2.03	2.03	2.79	2.56	2.91	2.56	2.91	0.35	2.91	2.58	0.43	2.58	0.43	3.01
6	1.45	1.35	2.80	1.18	1.44	2.62	1.40	2.80	2.87	1.47	2.87	0.67	2.80	2.92	2.01	2.01	2.68	2.49	2.87	2.49	2.87	0.38	2.87	2.58	0.43	2.58	0.43	3.01

<sup>a</sup> Cations/Keggin Unit.

<sup>b</sup> Number of cations per Keggin Unit in the solid before exchanging.

TABLE 3  
 Concentration<sup>a</sup> of Cations in the Solid 12-Molybophosphate Salts Following Ion Exchange with Monovalent Cations

Number of exchange reactions	(NH <sub>4</sub> ) <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>						K <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>						Cs <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>												
	K <sup>+</sup>		Cs <sup>+</sup>		NH <sub>4</sub> <sup>+</sup>		NH <sub>4</sub> <sup>+</sup>		Cs <sup>+</sup>		NH <sub>4</sub> <sup>+</sup>		NH <sub>4</sub> <sup>+</sup>		Cs <sup>+</sup>		K <sup>+</sup>		NH <sub>4</sub> <sup>+</sup>		Cs <sup>+</sup>		K <sup>+</sup>		
	NH <sub>4</sub> <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Total	
Initial <sup>b</sup> :	2.17		2.17		2.02		2.02		2.73		2.73		2.78		2.78		2.78		2.78		2.78		2.78		2.78
1	1.99	0.60	1.75	2.90	1.15	2.90	1.67	1.00	2.67	1.76	1.00	2.67	1.23	2.99	2.59	0.04	2.63	2.93	0.26	3.19					
2	1.79	0.82	1.57	2.86	1.29	2.86	1.38	1.33	2.71	1.58	1.33	2.71	1.40	2.98	2.59	0.08	2.67	2.92	0.29	3.21					
3	2.10	0.97	1.42	2.83	1.41	2.83	1.64	1.12	2.76	1.58	1.12	2.76	1.45	3.03	2.56	0.10	2.66	2.94	0.30	3.24					
4	1.55	1.08	1.36	2.83	1.47	2.83	1.50	1.19	2.69	1.52	1.19	2.69	1.49	3.01	2.46	0.12	2.58	2.84	0.29	3.13					
5	1.49	1.17	—	—	—	—	1.39	1.24	2.63	1.48	1.24	2.63	1.52	3.00	2.65	0.13	2.78	2.90	0.29	3.19					
6	1.44	1.23	1.30	2.83	1.53	2.83	1.36	1.37	2.73	1.53	1.37	2.73	1.56	3.09	2.44	0.14	2.58	—	—	—					

Note. (+) number of cations per Keggin Unit in the solid before exchanging.  
<sup>a</sup> Cations/Keggin Unit.

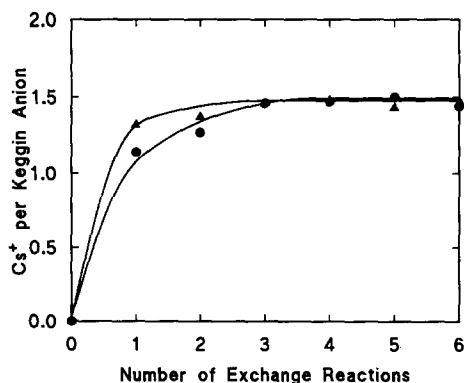


FIG. 1. Ion-exchange isotherm for Cs<sup>+</sup> exchanging into (NH<sub>4</sub>)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> ● and K<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> ▲.

with 0.1 M CsNO<sub>3</sub>. The behaviour of these two heteropoly salts in ion exchange reactions with Cs<sup>+</sup> is quite similar. In both cases the exchange of the original cation for Cs<sup>+</sup> appears to reach the maximum attainable value after two exchanges. Subsequent exchanges result in negligible additional exchange of Cs<sup>+</sup> into the solids.

It is also interesting to note that for a given pair of cations, one entering and one leaving the solid, and a given anion, the nature of the exchange is found to depend on both the entering and exiting cation. The differences are largest when one of the cations involved in the exchange is cesium. The differences are exemplified by the K<sup>+</sup>/Cs<sup>+</sup>/PMo<sub>12</sub>O<sub>40</sub><sup>-3</sup> system by comparing the results for K<sub>3</sub>P Mo<sub>12</sub>O<sub>40</sub> exchanged with 0.1 M CsNO<sub>3</sub> and Cs<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> exchanged with 0.1 M KNO<sub>3</sub> in Table 3. The difference in the exchange behaviour is displayed in Fig. 2 where the ion-exchange isotherms for the two systems are shown. It can be seen that there is a greater tendency for the cesium ion to exchange from the liquid phase into the solid phase than to exchange from the solid phase into the liquid phase. Similar behaviour is observed for the NH<sub>4</sub><sup>+</sup>/Cs<sup>+</sup>/PMo<sub>12</sub>O<sub>40</sub><sup>-3</sup> system as well as for the K<sup>+</sup>/Cs<sup>+</sup>/PW<sub>12</sub>O<sub>40</sub><sup>-3</sup> and NH<sub>4</sub><sup>+</sup>/Cs<sup>+</sup>/PW<sub>12</sub>O<sub>40</sub><sup>-3</sup> systems (Tables 2 and 3).

Figure 3 shows the exchange isotherm for (NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> exchanged with 0.1 M

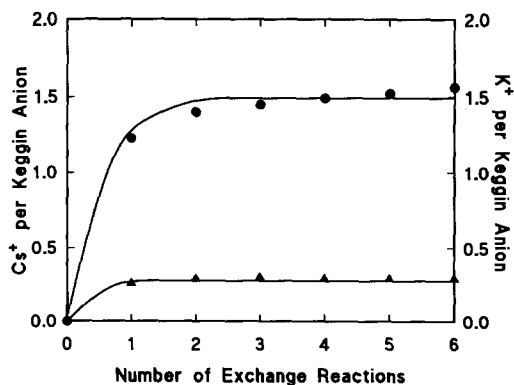


FIG. 2. Ion-exchange isotherms showing the effect of ions entering or exiting the solid ion exchanger: ● denotes Cs<sup>+</sup> exchanging from the liquid phase into the solid K<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> phase, ▲ denotes K<sup>+</sup> exchanging from the liquid phase into the solid Cs<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> phase.

KNO<sub>3</sub>. Both the increase in the number of ammonium ions and the decrease in the number of potassium ions in the solid phase can be observed as the number of ion exchanges increases. Tables 2 and 3 show that similar behaviour occurs for the other heteropoly ion exchangers.

The results of Tables 2 and 3 and Fig. 1–3 show that the maximum attainable exchange is appreciably less than the theoretical maximum exchange capacity for these materials.

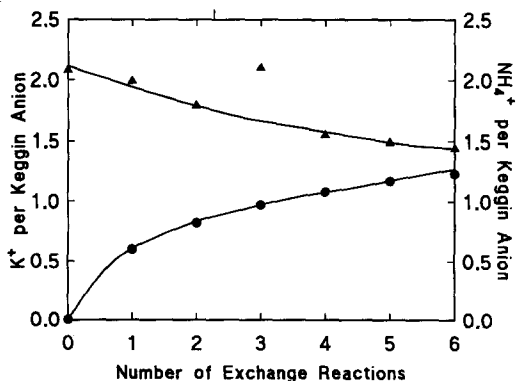


FIG. 3. Ion exchange isotherms showing the changes in concentration of the entering and exiting cations in the exchange of K<sup>+</sup> from the liquid phase into solid (NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, ● denotes K<sup>+</sup> and ▲ denotes NH<sub>4</sub><sup>+</sup>.

TABLE 4

Theoretical and Observed Maximum Exchange Capacities for Monovalent Heteropoly Oxometalate Ion Exchangers

Solid	Exchanging cation	mg Cation/ g solid (theoretical)	mg Cation/ g solid (observed)	Maximum exchange (%)
(NH <sub>4</sub> ) <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	K <sup>+</sup>	39.17	17.1	43.7
(NH <sub>4</sub> ) <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	Cs <sup>+</sup>	121.71	51.5	42.3
K <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	NH <sub>4</sub> <sup>+</sup>	18.46	13.1	67.2
K <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	Cs <sup>+</sup>	121.71	55.0	45.2
Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	NH <sub>4</sub> <sup>+</sup>	18.46	2.3	12.2
Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	K <sup>+</sup>	39.17	5.7	14.6
(NH <sub>4</sub> ) <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	K <sup>+</sup>	60.48	20.3	33.6
(NH <sub>4</sub> ) <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	Cs <sup>+</sup>	179.52	91.8	50.7
K <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	NH <sub>4</sub> <sup>+</sup>	29.41	13.5	45.9
K <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	Cs <sup>+</sup>	179.52	93.1	51.8
Cs <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	NH <sub>4</sub> <sup>+</sup>	29.41	1.4	4.8
Cs <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	K <sup>+</sup>	60.48	5.9	9.8

Table 4 lists the theoretical and observed maximum exchange capacities for the heteropoly salts that were investigated. For all of the systems that were investigated, the observed maximum exchange is less than that which would be expected if all three cations of the heteropoly salt were replaceable. The large differences that are observed for the exchanges involving cesium can be seen quite clearly. For the potassium–ammonium exchange systems with either anion the difference between the maximum exchange capacities is not as large.

Analyses for the cations which are released from the solid into the liquid phase indicate that the uptake of cations by the solid results from exchange of cations present originally in the solid as well as from replacement of residual protons (Tables 5–7). These tables show that the concentration of the cation being released from the solid exchanger phase into the liquid phase is, in most cases, highest following the first exchange reaction. Subsequent exchanges result in much lower concentrations of the cation released from the solid into the liquid phase. The results for Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and Cs<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> exchanged with 0.1 M KNO<sub>3</sub> or 0.1 M NH<sub>4</sub>NO<sub>3</sub> are quite similar (Table 5). The

release of cesium ions from the solid is greatest for the first exchange reaction for all four cases although the amount released is small. This follows from the low maximum exchange capacity that was obtained with these salts. On the other hand, for the exchange of Cs<sup>+</sup> ions into the (NH<sub>4</sub>)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, (NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, K<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, and K<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> solids, the initial release of cations from the solid is substantially higher (Tables 6 and 7). These materials were all found to have maximum exchange capacities of between 40 and 50%. As with the cesium salts the numbers of cations released into the liquid phase decreased rapidly as the number of exchange reactions increased. This behaviour agrees with the type of exchange isotherms obtained for these salts (Figs. 1 and 2), the uptake being initially high almost to the point of maximum exchange followed by a long plateau region. The (NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>/K<sup>+</sup> system showed a somewhat different type of dependence on the exchange number. The concentration of NH<sub>4</sub><sup>+</sup> ions in the liquid phase remained more or less constant over the six exchange reactions. This is consistent with the exchange isotherm for this system which does not possess a sharp knee following the first exchange but instead shows a more gradual increase in the amount exchanged.

Analysis of the cation which composed the liquid phase portion of the exchange pair showed that the smallest measured concentration of that cation was found following the first exchange. Measurement of the concentrations from subsequent exchanges yielded values which were greater than those measured following the first exchange. This behaviour agrees well with the previously mentioned behaviour in which the uptake of cations from the liquid phase was greatest for the first exchange reaction.

The proton content of the starting heteropoly ion-exchange materials and the exchanging systems were followed using titrations of the solid and liquid phases where it was possible. Measurement of the proton



TABLE 5  
Concentration (*M*) of Cationic Species Present in the Liquid Phase

Number of exchange reactions	Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>						Cs <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>					
	Cs <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Total	Cs <sup>+</sup>	K <sup>+</sup>	Total	Cs <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Total	Cs <sup>+</sup>	K <sup>+</sup>	Total
1	0.008	0.091	0.099	0.008	0.088	0.096	0.007	0.086	0.093	0.007	0.087	0.094
2	0.004	0.085	0.089	0.003	0.095	0.098	0.003	0.095	0.098	0.002	0.099	0.101
3	0.002	0.105	0.107	0.001	0.096	0.097	0.001	0.096	0.097	0.001	0.098	0.099
4	0.001	0.097	0.098	0.002	0.094	0.096	0.001	0.096	0.097	0.001	0.098	0.099
5	0.001	0.101	0.102	0.001	0.095	0.096	0.001	0.093	0.094	0.001	0.098	0.099
6	0.001	0.100	0.101	0.002	0.097	0.099	0.001	0.098	0.099	0.001	0.098	0.097

concentrations in the molybdophosphate salts was difficult to achieve directly using the titration method because the yellow colour of the suspensions obscured the end point. Therefore titrations of the protons released into the liquid phase following the ion-exchange reactions were performed. Results of the proton analyses for solid and liquid phases are shown in Tables 8 and 9. Table 8 shows the concentration of protons in NH<sub>4</sub>PW and KPW before exchange reactions have been performed and also following exchange with NH<sub>4</sub>NO<sub>3</sub> and CsNO<sub>3</sub>. A significant fraction of the protons are removed during the first exchange with a monovalent cation although small quantities of protons were detected following subsequent exchanges. The number of protons released into the liquid phase during the initial exchange reaction with the various cat-

ions is shown in Table 9. Subsequent exchanges resulted in very small numbers of protons being released into the liquid phase (<0.003) and therefore these are not listed.

Self-exchange studies of the various catalysts were carried out using the same procedure as for exchanges with different cations. The ion chromatographic results for the various self-exchange systems are presented in Table 10. The potassium and cesium salts of both the 12-tungstophosphate and 12-molybdophosphate anions are close to being stoichiometric. Both of the ammonium self-exchange series yielded salts that were substoichiometric in composition. Table 11 lists the liquid phase concentrations of the cations associated with the self-exchange reactions. The observation that the cation concentration is well below 0.1 *M* for the (NH<sub>4</sub>)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, (NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, and K<sub>3</sub>

TABLE 6  
Concentration (*M*) of Cationic Species Present in the Liquid Phase

Number of exchange reactions	K <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>						K <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>					
	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Total	K <sup>+</sup>	Cs <sup>+</sup>	Total	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Total	K <sup>+</sup>	Cs <sup>+</sup>	Total
1	0.033	0.066	0.099	0.035	0.056	0.091	0.061	0.002	0.063	0.032	0.063	0.095
2	0.005	0.091	0.096	0.002	0.093	0.095	—	—	—	0.004	0.097	0.101
3	0.001	0.091	0.092	0.001	0.096	0.097	0.003	0.094	0.097	0.002	0.093	0.095
4	0.001	0.096	0.097	0.001	0.097	0.098	0.001	0.096	0.097	0.001	0.098	0.099
5	0.002	0.097	0.099	0.001	0.098	0.099	0.001	0.099	0.100	0.001	0.102	0.103
6	0.002	0.096	0.098	0.001	0.099	0.100	0.001	0.096	0.099	0.001	0.101	0.102

TABLE 7  
Concentration (*M*) of Cationic Species Present in the Liquid Phase

Number of exchange reactions	(NH <sub>4</sub> ) <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>						(NH <sub>4</sub> ) <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>					
	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Cs <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Total	NH <sub>4</sub> <sup>+</sup>	Cs <sup>+</sup>	Total
1	0.011	0.075	0.086	0.019	0.055	0.074	0.003	0.077	0.080	0.013	0.066	0.079
2	0.010	0.086	0.096	0.002	0.089	0.091	0.005	0.088	0.093	0.003	0.072	0.075
3	0.007	0.098	0.105	0.001	0.092	0.093	0.004	0.091	0.095	0.002	0.081	0.083
4	0.004	0.103	0.107	0.001	0.090	0.091	0.003	0.091	0.094	0.001	0.087	0.088
5	0.004	0.103	0.107	0.001	0.090	0.091	0.003	0.093	0.096	0.001	0.095	0.096
6	0.002	0.108	0.110	0.001	0.093	0.094	0.002	0.091	0.093	0.001	0.087	0.088

PMo<sub>12</sub>O<sub>40</sub> systems for the first exchanges is consistent with the observation that there are larger numbers of protons in these solids that are exchanged for the cations. For the subsequent exchanges the cation concentration is close to the original 0.1 *M* of the liquid phase indicating that the uptake of additional cations is negligible.

The solubilities of the heteropoly ion exchangers were estimated by measuring the amount of tungstate (WO<sub>4</sub><sup>2-</sup>) or molybdate (MoO<sub>4</sub><sup>2-</sup>) ion in the solution following contact with distilled water and decomposition of the anion using lithium hydroxide. The solubility of the salts in distilled water was less than 10% except with one KPMo sample.

#### DISCUSSION

Previous studies of the methanol to hydrocarbon process on heteropoly oxometalates have suggested that the presence of residual protons in the solid salts is an important factor in the activity and selectivity of the catalysts (12-14, 40). In the oxidative dehydrogenation of isobutyric acid to methacrylic acid over molybdovanadophosphoric acid (42) and mixed stoichiometry salts (43), the presence of acidic protons leads to decarboxylation and the formation of propene. The presence of residual protons also appears to be important in the partial oxidation of methane to formaldehyde and methanol (20) on the heteropoly oxometalates. It is believed that the protons are involved in a process in which oxygen atoms are stripped from the Keggin anion, leaving vacancies which are operative in the partial oxidation process.

Consistent with earlier work (40), residual protons have been found to exist in varying amounts in the K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and Cs<sup>+</sup> salts of

TABLE 8  
H<sup>+</sup> Concentration a in Solid 12-Tungstophosphate Ion Exchangers

Solid exchanger	Cation in liquid phase	Initial	Number of exchange reactions					
			1	2	3	4	5	6
(NH <sub>4</sub> ) <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	NH <sub>4</sub> <sup>+</sup>	0.51	0.06	0.06	0.05	0.05	0.06	
(NH <sub>4</sub> ) <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	Cs <sup>+</sup>	0.51	0.12	0.06	0.07	0.07	0.08	0.09
K <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	NH <sub>4</sub> <sup>+</sup>	0.10	0.04		0.02		0.02	
K <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	Cs <sup>+</sup>	0.10	0.07	0.04	0.06	0.05	0.08	0.04

<sup>a</sup> H<sup>+</sup>/Keggin Unit.

TABLE 9

H<sup>+</sup> Concentration<sup>a</sup> in the Liquid Phase following the Initial Ion-Exchange Reactions

Solid exchanger	Cation present in the liquid phase		
	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Cs <sup>+</sup>
(NH <sub>4</sub> ) <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0.013	0.015	0.020
K <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0.007	0.002	0.003
Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0.003	0.003	0.003
(NH <sub>4</sub> ) <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	0.022	0.029	0.017
K <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	0.036	0.038	0.045
Cs <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	0.002	0.002	0.003

<sup>a</sup> H<sup>+</sup>/Keggin Unit.

12-molybdophosphoric and 12-tungstophosphoric acid. In all cases the ion-exchange isotherms obtained with these materials showed smooth changes as the numbers of exchanges increased, indicating that nonstoichiometric compounds of mixed cation composition were formed. The monotonic nature of the isotherms also suggests that the exchange of the proton from the acid salts follows a mechanism similar to the heavy cation exchange. A large fraction of these residual protons are replaced during the first ion-exchange reaction with solutions of the heavy cation salts. It should

TABLE 10

Concentration<sup>a</sup> of Monovalent Cations in the Solids following the Self-Exchange Process<sup>b</sup>

Solid Exchanger	Number of Exchange Reactions				
	1	2	3	4	5
(NH <sub>4</sub> ) <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	2.66	2.61	2.66	2.65	2.80
K <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	3.04	3.00	2.96	3.02	2.99
Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	3.08	3.14	3.16	3.21	3.09
(NH <sub>4</sub> ) <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	2.50	2.66	2.47	2.51	2.51
K <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	3.03	3.03	3.03	3.00	2.90
Cs <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	2.82	3.09	2.50	3.09	3.08

<sup>a</sup> Cations/Keggin Unit.

<sup>b</sup> Liquid phase contains the same cation as the solid exchanger.

TABLE 11

Concentration (*M*) of Monovalent Cations in the Liquid Phases following the Self-Exchange Process<sup>a</sup>

Solid exchanger	Number of exchange reactions				
	1	2	3	4	5
(NH <sub>4</sub> ) <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0.082	0.100	0.100	0.102	0.102
K <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0.106	0.109	0.104	0.102	0.102
Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0.093	0.103	0.103	0.102	0.103
(NH <sub>4</sub> ) <sub>3</sub> Mo <sub>12</sub> O <sub>40</sub>	0.078	0.103	0.101	0.099	0.103
K <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	0.066	0.102	0.098	0.110	0.098
Cs <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	0.095	0.101	0.100	0.099	0.102

<sup>a</sup> Liquid phase contains the same cation as the solid exchanger.

be noted that the cations released from the exchanger are found in the liquid phase following the first exchange as well as protons indicating that ion exchange, not merely salt formation by proton displacement, is occurring. Analyses of the liquid phases of subsequent exchanges indicate that both protons and cations are exchanged into the liquid phase in these later exchanges (Tables 5–7). Therefore, although it appears that the proton exchange is the more labile process one cannot infer from the present results that a simple two-step mechanism in which the entering cation replaces the proton before there is any exchange with the exiting cation is valid. Instead it appears that, as the number of protons decreases from the number present in the original solids, exchange occurs with both the proton and the heavy cation that are present.

As mentioned earlier the maximum exchange capacities for the exchange systems studied varied greatly depending on (i) the specific pair of cations and (ii) which cation of the pair was initially present in the solid ion exchanger. Figure 4 is a plot of the maximum exchange capacity for a particular cation pair as a function of the ratio of the ionic radius (*r*) of the cation in the solid relative to that of the cation exchanging into the solid. The plot shows a decreasing trend in the maximum exchange capacity as the

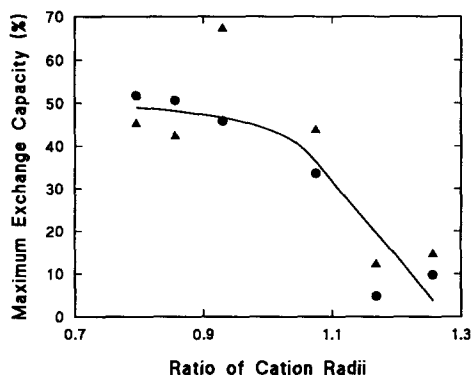


FIG. 4. Maximum exchange capacities of the heteropoly ion exchangers as a function of the ratio of the cation radius of the cation exiting the solid to that of the cation entering the solid, ● denotes  $\text{PMo}_{12}\text{O}_{40}^{-3}$  salts, ▲ denotes  $\text{PW}_{12}\text{O}_{40}^{-3}$  salts.

radius of the cation in the solid phase becomes larger. From this figure it can be seen that the exchange of the cesium ion from the solid to the liquid phase by the ammonium or potassium ion is relatively difficult whereas the potassium and ammonium ions can be exchanged from the solid by the cesium ion with relative ease. Further, the ammonium and potassium ions can be interchanged to approximately the same extent. This phenomenon may be related to the ionic radii of the cation species used in the study. The ionic radii of the ammonium and potassium differ by only 0.1 Å while that of cesium is 0.24 Å larger than ammonium and 0.34 Å larger than potassium. It seems possible that the differences in the observed exchange capacities may be related to the ability of the cation to diffuse in and out of the microporous network that is known to exist (36–38).

The data in Fig. 4 clearly demonstrate that the largest maximum exchange capacities are obtained where the cations entering into and exiting from the solid have similar radii and where the cation present in the solid is smaller than the entering cation. Where the cation present in the solid is larger than that entering into the solid the maximum exchange capacity is considerably reduced.

Although the source of this difference is unclear, a qualitative rationalization may be tentatively proposed. Since the lattice constants found with the larger cations are, not surprisingly, larger than those found with the smaller cations it may be surmised that the binding energy of these larger cations is, in turn, larger than that which exists for the smaller cations. Consequently it may be anticipated that the smaller entering cations would have more difficulty in displacing a larger cation from the solid than the larger entering cation.

A previous investigation of the limited ion exchange of  $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$  postulated that during the course of ion exchange with potassium ions there was a reorientation of the ammonium ions in the lattice (27). This process involved the rupturing of existing hydrogen bonds along with the formation of new hydrogen bonds with exposed oxygen atoms at the external region of the 12-molybdophosphate anion. The breaking of the hydrogen bonds is compensated for through the strengthening of the anion bonds but once a certain point in the exchange is reached, no anion restructuring can proceed and the exchange is complete. It was further argued that the higher exchange capacity for  $\text{NH}_4^+$  on  $\text{K}_3\text{PMo}_{12}\text{O}_{40}$  was due to the fact that there were no hydrogen bonds to be broken in order to permit the entrance of the  $\text{NH}_4^+$  ion. A similar situation exists in the present study where the exchange capacity is greater for the ammonium ion exchanging into the potassium salt of both the 12-molybdophosphate and 12-tungstophosphate anions.

Unfortunately these postulations do not explain the low degree of exchange that was achieved on the two cesium heteropoly salts. The situation is analogous to the potassium case mentioned previously except for the size difference between the two cations. The experimental data suggests, however, that there is some barrier to the exchange of the cesium ions which is quite unlike that for potassium.

An apparent exchange quotient has been defined for the ion-exchange reaction

TABLE 12

Apparent Exchange Quotients for Monovalent Heteropoly Oxometalate Ion Exchangers

Solid	NH <sub>4</sub> <sup>+</sup>			K <sup>+</sup>			Cs <sup>+</sup>		
	1 <sup>a</sup>	3	6	1	3	6	1	3	6
(NH <sub>4</sub> ) <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	—	—	—	0.044	0.064	0.034	0.135	0.008	0.002
K <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0.069	0.016	0.005	—	—	—	0.286	0.009	0.005
Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0.006	0.002	0.001	0.021	0.004	0.001	—	—	—
(NH <sub>4</sub> ) <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	—	—	—	0.016	0.024	0.016	0.090	0.016	—
K <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	0.016	0.010	0.004	—	—	—	0.198	0.014	0.006
Cs <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	0.0014	0.0004	0.0002	0.0079	0.0004	0.0001	—	—	—

<sup>a</sup> Numbers refer to position in the sequence of six exchanges.

as

$$A = \frac{C_{M_2}(l) C_{M_1}(s)}{C_{M_1}(l) C_{M_2}(s)}, \quad (2)$$

where  $C_{M_1}(l)$  and  $C_{M_2}(l)$  are the concentration of cations 1 and 2 in the liquid phase ( $\text{mol cm}^{-3}$ ) and  $C_{M_1}(s)$  and  $C_{M_2}(s)$  are the concentrations of cations 1 and 2 in the solid phase ( $\text{mol g}^{-1}$ ). Thus one can obtain a dimensionless quantity based on cation concentrations for each exchange reaction performed.

The apparent exchange quotients are shown in Table 12 and Figs. 5 and 6. In Fig. 5 the quotients for  $\text{NH}_4\text{PMo}$  and  $\text{KPMo}$  exchanged with  $0.1 M \text{ CsNO}_3$  are shown. The behaviour of these systems is very similar in that a maximum value for the exchange quotient is obtained for the first exchange, followed by a sharp decrease for the second exchange reaction. The values for subsequent exchanges decrease slowly in magnitude for both systems. The exponential decay type of behaviour in the apparent exchange quotient was observed for all of the cation pairs which included  $\text{Cs}^+$ . A different type of trend was observed for the  $\text{K}^+$  and  $\text{NH}_4^+$  pair of cations. Figure 6 shows the apparent exchange quotients for the exchanges of  $\text{NH}_4\text{PW}$  with  $\text{K}^+$  as well as with

$\text{Cs}^+$ . Unlike the cases shown in Fig. 5 and the  $\text{NH}_4\text{PW}$  exchanged with  $\text{Cs}^+$  shown in Fig. 6, there is a maximum observed for the  $\text{NH}_4\text{PW}/\text{K}^+$  system. Similar results were obtained for  $\text{NH}_4\text{PMo}$  exchanged with  $\text{K}^+$  and  $\text{KPMo}$  exchanged with  $\text{NH}_4^+$ . Although the source of this difference in behaviour is not known it is interesting to note that it occurs for cases where the sizes of the exchanging cations are most comparable.

At the present time it is not yet possible to explain the limited conversion of the heteropoly ion exchangers. The low exchange capacities of the cesium molybdophosphate

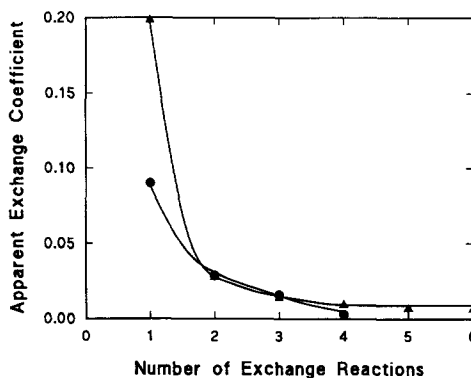


FIG. 5. Apparent exchange coefficient as a function of the number of exchange reactions showing the effect of exchanging  $\text{Cs}^+$  from the liquid phase into  $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$  ● and  $\text{K}_3\text{PMo}_{12}\text{O}_{40}$  ▲.

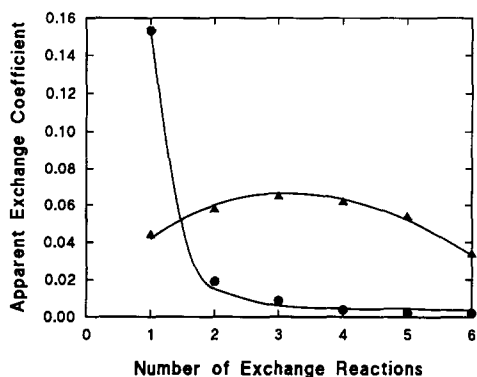


FIG. 6. Apparent exchange coefficient as a function of the number of exchange reactions showing the different behaviour observed for solid  $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$  exchanged with 0.1 M  $\text{CsNO}_3$  ● and 0.1 M  $\text{KNO}_3$  ▲.

and cesium tungstophosphate for the ammonium and the potassium ions relative to that for the potassium salts with the ammonium ion indicate that the previously proposed explanation based on hydrogen bonding (27) may not be sufficient to rationalize the behaviour of all heteropoly ion exchangers.

#### ACKNOWLEDGMENTS

The financial support of the Natural Sciences and Engineering Research Council is gratefully appreciated. G.B.M. acknowledges the financial support of NSERC provided in the form of a Postgraduate Scholarship. The authors thank Dr. J. J. Byerley for the use of his ion chromatograph in the initial stages of this work.

#### REFERENCES

- Scherzer, J., *Catal. Rev. Sci. Eng.* **31**, 215 (1989).
- Stephens, H. P., and Dosch, R. G., in "Preparation of Catalysts IV" (B. Delmon, P. Grange, P. A. Jacobs, and J. Poncelet, Eds.), p. 271. Elsevier, Amsterdam (1987).
- Chu, P., and Dwyer, F. G., in "Intrazeolite Chemistry" (G. D. Stucky and F. G. Dwyer, Eds.), ACS Symposium Series. ACS, Washington (1983).
- Kerr, G. T., *Catal. Rev.-Sci.* **23**, 281 (1981).
- Hathaway, P. E., and Davis, M. E., *J. Catal.* **119**, 497 (1989); and references therein.
- Engelhardt, J., Szanyi, J., and Valyon, J. *J. Catal.* **107**, 296 (1987).
- Stammach, M. R., Thomas, D. J., Trimm, D. L., and Wainwright, M. S., *Appl. Catal.* **58**, 209 (1990).
- Waller, F. J., *Catal. Rev.-Sci. Eng.* **28**, 1 (1986).
- Pope, M. T., "Heteropoly and Isopoly Oxometalates." Springer, Berlin (1983).
- Ono, Y., Mori, T., and Keii, T., in "Proc. 7th Int. Congr. Catal.", 1980, Tokyo, Kodansha (1982), p. 1414. Elsevier (1982).
- Ono, Y., Baba, T., Sakai, J., and Keii, T. *J. Chem. Soc. Chem. Comm.*, 400 (1981).
- Hayashi, H., and Moffat, J. B., *J. Catal.* **77**, 473 (1982).
- Hayashi, H., and Moffat, J. B., *J. Catal.* **81**, 61 (1983).
- Hayashi, H., and Moffat, J. B., *J. Catal.* **83**, 192 (1983).
- Black, J. B., Scott, J. D., Serwicka, E. M., and Goodenough, J. B., *J. Catal.* **106**, 16 (1987).
- Serwicka, E. M., Black, J. B., and Goodenough, J. B., *J. Catal.* **106**, 23 (1987).
- Misono, M., Komaya, T., Sekiguchi, H., and Yoneda, Y., *Chem. Lett.*, 53 (1982).
- Kim, J. J., Lee, W. H., and Rhee, H.-K., *Chem. Eng. Commun.* **34**, 49 (1985).
- Ai, M., *J. Catal.* **116**, 23 (1989).
- Kasztelan, S., and Moffat, J. B., *J. Catal.* **106**, 512 (1987).
- Ahmed, S., and Moffat, J. B., *Appl. Catal.* **40**, 101 (1988).
- Ahmed, S., and Moffat, J. B., *Catal. Lett.* **1**, 141 (1988).
- Van R. Smit, J., Robb, W., and Jacobs, J. J., *J. Inorg. Nucl. Chem.* **12**, 95 (1959).
- Van R. Smit, J., Robb, W., and Jacobs, J. J., *Nucleonics* **17**(9), 116 (1959).
- Van R. Smith, J., and Robb, W., *J. Inorg. Nucl. Chem.* **26**, 509 (1964).
- Coetzee, C. S., and Rohwer, E. F. C. H., *J. Inorg. Nucl. Chem.* **32**, 1711 (1970).
- Boeyens, J. C. A., McDougal, G. J., and Van R. Smit, J., *J. Solid State Chem.* **18**, 191 (1976).
- Krtil, J., and Kourim, V., *J. Inorg. Nucl. Chem.* **12**, 367 (1960).
- Krtil, J., *J. Inorg. Nucl. Chem.* **19**, 298 (1961).
- Krtil, J., *J. Inorg. Nucl. Chem.* **24**, 1139 (1962).
- Krtil, J., and Chavko, M., *J. Chromatogr.* **27**, 460 (1967).
- Choudhuri, D., and Mukherjee, S. K., *J. Inorg. Nucl. Chem.* **30**, 3091 (1968).
- Choudhuri, D., and Mukherjee, S. K., *J. Inorg. Nucl. Chem.* **32**, 1023 (1970).
- Choudhuri, D., and Mukherjee, S. K., *J. Inorg. Nucl. Chem.* **33**, 1933 (1971).
- Malik, W. U., Srivastava, S. K., and Kumar, S., *Talanta* **23**, 323 (1976).
- McMonagle, J. B., and Moffat, J. B., *J. Colloid Interface Sci.* **101**, 479 (1984).
- Taylor, D. B., McMonagle, J. B., and Moffat, J. B., *J. Colloid Interface Sci.* **108**, 278 (1985).
- McGarvey, G. B., and Moffat, J. B., *J. Colloid Interface Sci.* **125**, 51 (1988).

39. McDougal, G. J., *Diss. Abstr. Int. B* **37**(8), 3948 (1977).
40. Highfield, J. G., and Moffat, J. B., *J. Catal.* **88**, 177 (1984).
41. Helfferich, E., "Ion Exchange," p. 237. McGraw-Hill, New York (1962).
42. Akimoto, M., Ikeda, H., Okabe, A., and Echigoya, E., *J. Catal.* **89**, 196 (1984).
43. Haeberle, T., and Emig, G., *Chem. Eng. Technol.* **11**, 392 (1988).
44. "Handbook of Chemistry and Physics," 63rd ed. p. F 179. CRC Press, (1982/1983).