

TABLE II  
EQUILIBRIUM FLAME TEMPERATURES AND RADICAL CONCENTRATIONS

$\frac{D_2O}{O_2 + A} \times 10^3$	Flame temp., °K.	Concentrations, atm. $\times 10^4$		
		D	OD	O
		11.11% C <sub>2</sub> N <sub>2</sub>		
11.4	2913	30.4	55.7	185.9
3.43	2938	14.17	24.6	203.0
		13% C <sub>2</sub> N <sub>2</sub>		
3.43	3023	19.30	21.54	218.7
		16% C <sub>2</sub> N <sub>2</sub>		
3.43	3143	28.7	14.27	193.1
1.15	3158	10.70	5.14	203.0
		19% C <sub>2</sub> N <sub>2</sub>		
3.43	3295	39.1	4.09	89.7
1.15	3323	13.81	1.294	92.3

mixtures with added heavy water. These figures are compared with corresponding values for OH concentrations to give the same burning velocity with ordinary water, read from Fig. 2. It is seen that the OH and OD appear to be about equally effective; in other words  $a_{OD} \cong a_{OH}$ . Apparently hydrogen and deuterium atoms do not make as great a contribution to the flame speeds; if they did we would not anticipate the agreement shown in Table III since H and D have different diffusion coefficients, such that  $a_H \cong 1.4 a_D$ . However, we

would like to emphasize again that the data on mixtures with heavy water are somewhat uncertain.

TABLE III

% C <sub>2</sub> N <sub>2</sub>	Burning velocity, cm./sec.	Calcd. OD concn., atm. $\times 10^4$	OH concn. for same burning velocity (from fig. 2) (atm. $\times 10^4$ )
11.11	40.3	55.7	38.3
11.11	35.7	24.6	25.2
13	38.2	21.5	19.8
16	41.2	14.3	12.4
16	37.2	5.1	5.7
19	(43.5)	4.1	4.1
19	38.9	1.3	1.8

That the hydroxyl radical is present in moist cyanogen flames is shown by the spectroscopic studies of Pannetier and Gaydon,<sup>13</sup> who demonstrated that while the dry cyanogen flame shows only the spectra of C<sub>2</sub> and CN radicals, with water present OH, NH and CH are observed. Possibly non-equilibrium concentrations of NH and CH could also serve as active particles; it would seem likely that their concentrations would be related to the initial water concentrations in a manner similar to the hydroxyl radical.

(13) G. Pannetier and A. G. Gaydon, *Compt. rend.*, **225**, 1300 (1947); G. Pannetier, *Rev. inst. Franc. petrole*, **4**, 418 (1949).

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[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY CHEMISTRY DIVISION]

## Anion Exchange Studies. V. Adsorption of Hydrochloric Acid by a Strong Base Anion Exchanger<sup>1,2</sup>

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The adsorption of HCl by the "strong base" anion exchange resin Dowex-1 was determined in the concentration range 0.002 to 16 molal HCl for the aqueous phase. From these data and measurements of the water content of the resin, the activity coefficients ( $\gamma_{\pm HCl}$ ) of HCl in the resin phase were calculated, and it was found that  $\log \gamma_{\pm HCl}$  increases linearly with the hydrochloric acid molality of the resin phase.

It has been demonstrated in a series of earlier papers that a number of metals can be strongly adsorbed by anion exchange resins from relatively concentrated hydrochloric acid solutions. These observations focused attention on the behavior of the resin in concentrated electrolytes. Of particular interest is the extent of electrolyte uptake by the resin since it, together with the capacity of the resin, determines the concentration of chloride ions in the resin phase, a variable which appears in the expressions for the adsorption equilibria.

Until relatively recently it was generally assumed that when "strong base" (or "strong acid") ion exchange resins are immersed in electrolyte solutions, little adsorption of the electrolyte as a whole takes place. Thus one expected, for example, that a cation exchanger immersed in sodium chloride solutions would contain few chloride ions and a "strong

base" anion exchanger immersed in hydrochloric acid solutions would contain few hydrogen ions. In recent years, however, it was shown that both cation and anion exchangers<sup>3-7</sup> can adsorb considerable quantities of electrolyte if immersed in moderately concentrated solutions and that this adsorption increases with the concentration of electrolyte in the aqueous phase. In most of this work, it was assumed that this electrolyte uptake is closely related to a Donnan equilibrium.

A series of experiments has been carried out which was designed to determine this electrolyte uptake with hydrochloric acid (0.002 to 12 M HCl) for the resin used in the earlier anion exchange studies

(3) W. C. Bauman and J. Eichhorn, *ibid.*, **69**, 2830 (1947).

(4) W. J. Argersinger, Jr., and A. W. Davidson, *J. Phys. Chem.*, **56**, 92 (1952).

(5) J. T. Clarke, J. A. Marinsky, W. Juda, N. W. Rosenberg and S. Alexander, *ibid.*, **56**, 100 (1952).

(6) K. W. Pepper, D. Reichenberg and D. K. Hale, unpublished results reported by K. W. Pepper at the 1951 Gordon Research Conference on Ion Exchange.

(7) H. P. Gregor, *THIS JOURNAL*, **73**, 642 (1951).

(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous paper, G. E. Moore and K. A. Kraus, *THIS JOURNAL*, **74**, 843 (1952).

of metal complexes. This resin was a relatively highly cross-linked quaternary amine polystyrene-divinylbenzene resin (Dowex-1). In order to relate this acid uptake with the water content of the resin, the latter was also determined as well as volume changes accompanying changes in composition of the aqueous phase.

### Experimental

1. **Technique.**—The technique of measuring adsorption of hydrochloric acid by the resin was very similar to that used by Pepper<sup>8</sup> for cation exchangers. A known weight (*ca.* 1 g.) of resin (spherical particles, mesh size -200 + 230 wet-screened) was placed in a small sintered glass funnel. Hydrochloric acid was passed through this resin until the effluent concentration was equal to the initial concentration. The funnel was then centrifuged to constant weight in a "clinical" centrifuge at 2700 r.p.m. (*ca.* 300 g.). The resin was washed with water and the acid in the wash titrated with sodium hydroxide (standardized against potassium hydrogen phthalate). In some experiments, the amount of HCl "adsorbed" was determined by comparing the total number of moles of HCl passed into the resin with those appearing in the centrifugate. The two methods yielded approximately equal results.

The resin was purified by thoroughly washing with HCl, followed by washing with ethyl alcohol and water and further washing with concentrated HCl, dilute HCl and water. Some experiments were also carried out with resin washed only with HCl and water and not treated with ethyl alcohol.

Using essentially the same technique, the adsorption of HCl by spherical glass beads (-200 + 230 mesh, Minnesota Mining and Manufacturing Company) and of the empty filter funnel was determined.

All experiments were carried out at room temperature ( $26 \pm 2^\circ$ ).

2. **Determination of Water Content of Resin.**—For the determination of the water content the resin was dried to constant weight at room temperature in a vacuum desiccator over Anhydron. Approximately 100-200 hours appeared necessary.<sup>9</sup> Resins dried in this manner show negligible water content with Karl Fisher reagent<sup>10</sup> and hence this method appears adequate for the operational definition of "dry" resin. The usual technique of drying in an oven apparently did not yield the same degree of dryness as determined by weight ratios, resin dried at  $94^\circ$  being consistently 3% and at  $110^\circ$  1.9% heavier than resin dried over Anhydron.

The water content of the resin ideally would be given by the difference in weight of dry resin and resin equilibrated with water, after some correction is made for water held interstitially between the resin particles. In an attempt to obtain "wet" weights, resin was vapor-phase equilibrated in a vacuum desiccator with solution whose relative humidity (activity of water) varied from 81 to 99.2%. The resin weight was found to vary approximately linearly with humidity from 81 to 93%. However, serious deviation from a straight line occurred at higher humidity in disagreement with earlier assumptions by Gregor and co-workers.<sup>8b</sup> These deviations at least in part result from condensation of water between the resin particles since the resin began to cake excessively. Similar, though considerably smaller, water uptake also occurred with glass beads. Since the extent of condensation between the particles could not be estimated accurately, the "wet" weight of the resin was ascertained by shaking it with distilled water, weighing

(8) (a) K. W. Pepper, *J. Applied Chem. (London)*, **1**, 124 (1951).

(b) Some techniques for measuring resin volumes have been described by H. P. Gregor, K. M. Held and J. Bellin, *Anal. Chem.*, **23**, 620 (1951).

(9) Since this work was completed resins have been dried in the same manner at elevated temperature ( $60^\circ$ ) when equilibrium is reached in less than ten hours.

(10) (a) Karl Fisher, *Angew. Chem.*, **48**, 304 (1935); (b) E. G. Almy, W. C. Griffin and C. S. Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **12**, 392 (1940). We are indebted to Helen Cutcher of the ORNL Analytical Division for the Karl Fisher titrations. It should be pointed out that with this method erroneous results can be obtained, since the iodine liberated in the titration is readily adsorbed by the resin.

after centrifugation and correcting for the residual interstitial water by assuming that its volume was the same for the resin and for glass beads (0.033 l. per l. of bed.) It is of interest that these "wet" weights were 3.2% higher than the weights indicated from extrapolation of the straight line portion of the vapor-phase equilibrations.

The "wet" weight of the resin was found to be  $1.592 \pm 0.007$  g. per g. "dry" resin yielding a water content of the "wet" resin of 37.2%.

3. **Volume of Resin Bed.**—The volume of the resin bed was measured in water and 0.1, 0.4, 1.4, 2.1, 3.1, 4.2, 6.2 and 12.0 *M* HCl by determining with a cathetometer the height of the centrifuged bed in a calibrated tube with sintered glass bottom. It was found that, within experimental error, the volume of the bed remained constant throughout this hydrochloric acid concentration range. It averaged  $2.18 \pm 0.05$  l./kg. "Anhydron-dry" resin.

4. **Capacity of the Resin.**—The resin capacity for chloride ions was found to be  $3.563 \pm 0.005$  moles/kg. dry resin<sup>11</sup> by treating a known weight of "Anhydron-dry" resin in the chloride form with 1 *M* NaClO<sub>4</sub>. The chloride concentration of the effluent was determined by Mohr titration. The results for various samples agreed to better than  $\pm 0.2\%$ .

### Results and Discussion

1.—The amount of hydrochloric acid  $A_r$  held by a liter of resin bed was determined from the volume of the bed and titration of the acid which could be washed from the centrifuged sample after correction for the acid held by the filter stick. As shown in Fig. 1,  $A_r$  increases slowly with HCl concentration ( $M_{HCl}$ ) at low  $M_{HCl}$ . Under these conditions  $A_r$  is dependent on the treatment the resin received, the resin washed with alcohol showing considerably smaller values of  $A_r$  than that treated with aqueous solutions only. In the range 0.1 to 4 *M* HCl,  $A_r$  increases rapidly and is independent of the treatment of the resin. Above  $M_{HCl} = 4$ ,  $\log A_r$  is approximately linear in  $\log M_{HCl}$ .

2.—The amount of HCl held by a liter of glass beads ( $A_b$ ) was found to be proportional to  $M_{HCl}$ , *i.e.*, as shown in Fig. 1, a straight line of unit slope is obtained when  $\log A_b$  is plotted *vs.*  $\log M_{HCl}$ . Such linear plot of unit slope is expected if a constant volume of HCl solution adheres to the particles. This residual interstitial volume was estimated from these data to be  $0.033 \pm 0.001$  l. per l. of bed.

3.—The extent of adsorption of HCl by the resin ( $A_r$ ) can be considered to be the sum of the HCl in the resin ( $A_r^*$ ) and that adhering interstitially. The latter was assumed to be equal to the residual interstitial volume  $A_b$  found for glass beads, *i.e.*, it was assumed that  $A_r^* = A_r - A_b$ . Values of  $A_r^*$  as a function of  $M_{HCl}$  have also been plotted in Fig. 1.

4.—The volume of the resin was found not to change when it was equilibrated with solutions ranging from pure water to 12 *M* HCl. It thus appears that the contribution of the aqueous part to the total volume of the resin is constant. From the values of  $A_r^*$ , the water content, and the assumption that the volume of the resin part does not change, one can thus directly calculate apparent molarities (moles per liter of aqueous fraction) of hydrogen ions (or hydrochloric acid) and chloride ions in the resin phase ( $M_{H^+}^r$ ,  $M_{HCl}^r$ ,  $M_{Cl^-}^r$ ). The values calculated for  $M_{HCl}^r$  are given in Table I. It appears of considerable interest that at high

(11) Capacity in other units:  $2.238 \pm 0.005$  equivalents/kg. wet resin (centrifuged, corrected for interstitial water); 1.63 equivalents/l. bed (centrifuged); 6.019 equivalents/kg. resin water (molality).

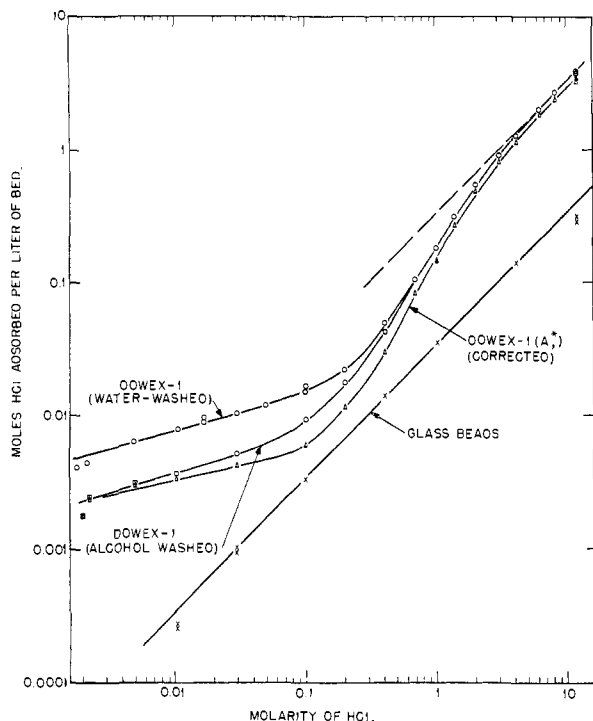


Fig. 1.—Adsorption of HCl by Dowex-1 and glass beads.

$M_{HCl}$ , the hydrochloric acid molarities of the two phases become approximately equal.

5.—The adsorption of hydrochloric acid by the resin can be treated as a two-phase equilibrium. The condition of such an equilibrium is that the chemical potentials of the hydrochloric acid in both phases are equal.<sup>12</sup> If the same standard states are used for the hydrochloric acid in the resin and aqueous phases, the activity of hydrochloric acid in the two phases must be equal, *i.e.*

$$a_H a_{Cl} = m_H m_{Cl} (\gamma_{\pm HCl})^2 = a_H^r a_{Cl}^r = m_H^r m_{Cl}^r (\gamma_{\pm HCl}^r)^2 \quad (1)$$

where  $a$  is the activity of the ions indicated as subscripts,  $m$  their molality and  $\gamma_{\pm HCl}$  the mean activity coefficient. Superscript  $r$  refers to the resin phase while lack of superscript indicates the aqueous phase. Since  $m_H m_{Cl} = (m_{HCl})^2$  it follows that

$$(m_{HCl})^2 / m_H^r m_{Cl}^r = (\gamma_{\pm HCl}^r)^2 / (\gamma_{\pm HCl})^2 \quad (2)$$

Hence the ratio of the activity coefficients in the resin and aqueous phases can be determined from the concentration of hydrochloric acid in the aqueous phase and the concentrations of hydrogen and chloride ions in the resin phase. The latter is the sum of the concentrations of chloride ions resulting from the adsorbed hydrochloric acid and from the chloride capacity of the resin (number of resin sites).

In order to permit ready comparison of the activity coefficients in the resin phase with those in the aqueous phase, all concentrations will be expressed in moles per thousand grams of water (molality).

The molality of hydrogen and chloride ions of the

(12) The adsorption of hydrochloric acid has often been treated as a Donnan membrane equilibrium. The treatment used in this paper is formally the same. However, it should be pointed out that this treatment does not imply the applicability of any specific model, *e.g.*, the model that the resin behaves like a semi-permeable membrane.

resin phase were calculated from the molarities, discussed in section 4, by assuming that the conversion factors between molarity and molality are the same for the resin phase as for aqueous solutions of the same hydrochloric acid concentrations. The latter were obtained from the densities of Åkerlöf and Teare.<sup>13</sup> The results of the computations are listed in Table I.

TABLE I  
ACTIVITY COEFFICIENTS OF HCl IN THE RESIN PHASE

$m_{HCl}^a$	$M_{HCl}^r$	$m_H^r = m_{HCl}^r$	$m_{Cl}^r$	$m_{Cl}^{*r}$	$\gamma_{\pm HCl}^r$
0.00201	0.00635	0.00635	6.03	3.57	0.0098
.00220	.00859	.00859	6.03	3.57	.0092
.00500	.0108	.0108	6.03	3.57	.0182
.0104	.0121	.0121	6.03	3.57	.0348
.0302	.0150	.0150	6.04	3.57	.0891
.1008	.0215	.0215	6.04	3.58	.223
.1987	.0413	.0413	6.06	3.59	.305
.4077	.109	.109	6.14	3.63	.381
.703	.299	.301	6.36	3.74	.390
1.043	.539	.546	6.64	3.88	.448
1.463	.982	1.00	7.15	4.14	.488
2.141	1.75	1.82	8.07	4.60	.584
3.274	2.97	3.16	9.57	5.32	.843
4.56	4.17	4.56	11.15	6.03	1.33
7.16	6.85	7.98	14.99	7.62	2.99
10.00	8.98	11.06	18.48	8.88	7.36
16.27	12.33	16.8	25.0	10.86	35.3
16.27	12.45	17.0	25.2	10.93	34.9

<sup>a</sup>  $m_{HCl}$  = molality of HCl in the aqueous phase;  $m_H^r$ ,  $m_{HCl}^r$ ,  $m_{Cl}^r$  are molalities of H<sup>+</sup>, HCl and Cl<sup>-</sup> in the resin phase;  $M_{HCl}^r$  = molarity of HCl in the resin phase;  $m_{Cl}^{*r}$  = moles Cl<sup>-</sup> per kg. dry resin.

Using these molalities and equation (2) the activity coefficient ratio  $\gamma_{\pm HCl}^r / \gamma_{\pm HCl}$  was computed as

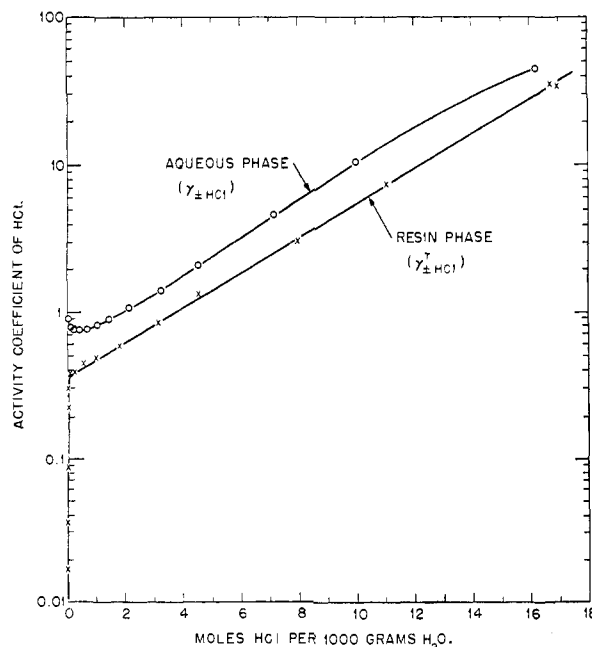


Fig. 2.—Activity coefficients of HCl in the resin and aqueous phases.

(13) G. Åkerlöf and J. W. Teare, THIS JOURNAL, 60, 1226 (1938).

well as  $\gamma_{\pm\text{HCl}}^r$ , using the activity coefficient  $\gamma_{\pm\text{HCl}}^r$  for the aqueous phase given in the literature.<sup>14</sup> Figure 2 gives a plot of  $\log \gamma_{\pm\text{HCl}}^r$  as a function of the molality  $m_{\text{H}}^r$  of hydrogen ions in the resin phase. A similar curve would have been obtained if  $\log \gamma_{\pm\text{HCl}}^r$  were plotted as a function of molality  $m_{\text{Cl}}^r$  of chloride ions in the resin phase.

It may be noticed that through most of the range of  $m_{\text{H}}^r$ ,  $\log \gamma_{\pm\text{HCl}}^r$  varies linearly with  $m_{\text{H}}^r$ , *i.e.*, it follows the equation

$$\log \gamma_{\pm\text{HCl}}^r = a + bm_{\text{H}}^r \quad (3)$$

where  $a = -0.43$  and  $b = 0.117$ . If equation 3 had been given in terms of  $m_{\text{Cl}}^r$ ,  $a$  would become  $-1.06$  while  $b$  would become  $0.104$ . At low concentration of hydrogen ions in the resin phase  $\gamma_{\pm\text{HCl}}^r$  drops rapidly with decreasing  $m_{\text{H}}^r$ . This is the region where, according to Fig. 1, the amount of HCl adsorbed changes only slowly with the HCl concentration of the aqueous phase and where adsorption is dependent on the purification of the resin. In this range, probably some of the adsorption is due to the reaction of HCl with an impurity in the resin, probably an acid-base reaction with

(14) (a) H. S. Harned and R. W. Ehlers, *THIS JOURNAL*, **55**, 2179 (1933); (b) M. Randall and L. E. Young, *ibid.*, **50**, 989 (1928); (c) G. Åkerlöf and J. W. Teare, *ibid.*, **59**, 1855 (1937).

tertiary and lower amines,<sup>15</sup> although the rapid decrease in the activity coefficients is not necessarily entirely due to such impurities. The amount of HCl held in this way is very small compared with the total capacity of the resin ( $<0.3\%$ ). This amount was estimated by assuming that  $\gamma_{\pm\text{HCl}}^r$  follows equation 3 to  $m_{\text{H}}^r = 0$ , calculating  $m_{\text{H}}^r$  according to equation 1 and comparing these values of  $m_{\text{H}}^r$  with those found experimentally.

For comparison Fig. 2 also contains the activity coefficients  $\gamma_{\pm\text{HCl}}$  as a function of  $m_{\text{HCl}}$  for the aqueous phase. It may be noticed that for  $m_{\text{HCl}} > 1$ , *i.e.*, at concentrations where the Debye-Hückel interaction becomes essentially constant, the activity coefficients of HCl in the aqueous and resin phases vary similarly with  $m_{\text{H}}$  although they are consistently smaller in the resin phase than in the aqueous phase. It thus appears that the resin phase has some properties in common with concentrated aqueous electrolytes and that to a considerable extent the hydrocarbon network of the resin appears to act as a relatively inert diluent in this concentrated electrolyte.

(15) It was found that in this region the adsorbed HCl is quite difficult to wash out, indicating that some reaction (*e.g.*, neutralization) had occurred. At higher HCl concentrations where the activity coefficients follow Equation 3, no such difficulty was observed.

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## Anion Exchange Studies. VI.<sup>1,2</sup> The Divalent Transition Elements Manganese to Zinc in Hydrochloric Acid

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The anion exchange behavior of the divalent transition elements manganese to zinc was studied in hydrochloric acid solutions. The adsorbabilities of the elements differ sufficiently as a function of hydrochloric acid concentration to permit their separation. The hydrochloric acid concentrations where noticeable adsorption occurs increase in the order Zn, Cu, Co, Fe and Mn with no noticeable adsorption for Ni, even in concentrated hydrochloric acid. It appears that the stability of the negatively charged chloride complexes of these divalent elements decreases in this order.

A survey of the anion exchange behavior of the first row transition elements of oxidation number two from Mn(II) to Zn(II) has been carried out in hydrochloric acid solutions. The results for Co(II) and Ni(II) have been given earlier.<sup>3</sup> In the case of these two elements, it was found that they differed greatly in their adsorbability, Ni(II) not being adsorbed from concentrated hydrochloric acid and Co(II) showing strong adsorption. This difference in anion exchange behavior suggested great differences in the stabilities of the negatively charged complexes of the transition elements, and a systematic study of these elements seemed indicated. In addition, there existed the possibility of establishing good separation procedures for these elements by use of anion exchange techniques.

### Experimental

The anion exchange behavior of these elements was studied with the quaternary amine polystyrene-divinylbenzene

resin Dowex-1 at room temperature, with a column technique.<sup>4</sup> From it the elution constant  $E = dA/V$  is obtained where  $d$  is the distance an adsorption maximum travels on passage of  $V$  cc. of eluent through a column of cross-sectional area  $A$  cm.<sup>2</sup>.

The columns, *ca.* 20 cm. long and of cross-sectional area *ca.* 0.03 sq. cm., were made of Pyrex tubing plugged with glass wool and filled with  $-200 + 230$  mesh wet-screened resin in the chloride form. The columns were pretreated with the acid of interest and a small volume (*ca.* 0.025 ml.) of the metal solution containing 1 to 3 mg. of metal in the same acid was placed on the column. After the solutions seeped into the columns, the eluent was added from a buret to permit ready determination of  $V$ .

The solutions were prepared from C.P. salts except for the Fe(II) solutions which were prepared by dissolving iron filings in hydrochloric acid. Since Fe(II) and Fe(III)<sup>5</sup> behave very differently on the column and since the two oxidation states can be identified readily analytically, there was no difficulty in the determination of the elution constants of Fe(II). Since copper was found to form a colored band (yellow up to 4 *M* HCl, brown to 9 *M* HCl and orange to 12 *M* HCl) and since the resin is light tan changing to light brown in 12 *M* HCl,  $d$  could be determined visually and  $E$  obtained from the slope of a straight line plot of  $d$  vs.  $V$ . The elution constants for the weakly colored and colorless ions Mn(II), Fe(II) and Zn(II) were determined by meas-

(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous paper, K. A. Kraus and G. E. Moore, *THIS JOURNAL*, **75**, 1457 (1953).

(3) G. E. Moore and K. A. Kraus, *ibid.*, **74**, 843 (1952).

(4) K. A. Kraus and G. E. Moore, *ibid.*, **73**, 9 (1951).

(5) G. E. Moore and K. A. Kraus, *ibid.*, **72**, 5792 (1950).